United States Patent Office
3,304,254
Patented Feb. 14, 1967

3,304,254

CATALYTIC HYDROCRACKING WITH A PHYSICAL MIXTURE OF A CRYSTALLINE ALUMINOSILICATE AND A POROUS SUPPORT CONTAINING A HYDROGENATION COMPONENT

Sylvander C. Eastwood, Woodbury, N.J., Richard J. Kelly, Morrisville, Pa., and Stephen J. Wantuck, Cherry Hill, N.J., assignors to Mobil Oil Corporation, a corporation of New York

No Drawing. Filed Jan. 21, 1965, Ser. No. 427,133

The portion of the term of the patent subsequent to Mar. 16, 1982, has been disclaimed

35 Claims. (Cl. 208—111)

This application is a continuation-in-part of our copending application Serial No. 94,147, filed March 8, 1961, issued as U.S. 3,173,854 on March 16, 1965.

This invention relates to an improved hydrocarbon conversion catalyst composite characterized by a physical particle-form mixture of (1) a crystalline aluminosilicate component having a low sodium content, and (2) a hydrogenation component comprising a predominant proportion of a porous support and a minor proportion of at least one constituent exhibiting hydrogenation activity. The invention is further directed to a process wherein a high boiling hydrocarbon or hydrocarbon mixture, for example, a petroleum fraction, is subjected to cracking in the presence of hydrogen and the aforementioned catalyst.

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 catalyst 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° F. to 1100° F. Such high temperatures have been inefficient from an economics 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 products.

As is well known, charge stocks heretofore employed in catalytic cracking operations have been limited to selected petroleum stocks. Thus, heavy residual stocks, as well as cycle stocks obtained from the catalytic cracking of non-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 high pressure, e.g. hydrocracking, do not impose the aforesaid limitations on the type of utilizable charge stock. Thus, cycle stocks, heavy residuals, etc. can be cracked in hydrocracking operations. Conventional operations of this type, however, are not completely without 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 heretofore been necessary to employ excessively high hydrogen pressures of the order of at least about 3500 pounds per square inch and preferably much higher.

There is accordingly great interest in the petroleum industry in moderate pressure hydrocracking processes. This interest arises from the ability of hydrocracking to increase substantially 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 interest in developing a less expensive, moderate-pressure process which will retain many of the demonstrated advantages, but at an acceptable cost.

In accordance with copending application, Serial No. 94,147, filed March 8, 1961, now U.S. Patent 3,173,854, issued March 16, 1965, of which this application is a continuation-in-part, there was discovered a catalyst possessing unusual activity and selectivity in the hydrocracking of petroleum hydrocarbons. Such catalyst comprises a hydrogenation component, particularly one selected from the group consisting of oxides of metals, sulfides of metals and metals of Groups VI and VIII of the Periodic Table, in intimate combination with a rare earth metal aluminosilicate, resulting from base-exchange of a crystalline alkali metal aluminosilicate having uniform pore openings between 6 and 15 Angstrom units with rare earth metal ions, to replace at least about 75 percent of the original alkali metal content of said alkali metal aluminosilicate with said ions and to reduce effectively the alkali metal content of the resulting composite to below 4 percent by weight, washing the base-exchanged material free of soluble salts, drying and thereafter thermally activating the product by heating at a temperature in the approximate range of 500° F. to 1500° F. for a period of between about 1 and about 48 hours.

In accordance with copending application, Serial No. 760,646, filed September 12, 1958, now U.S. Patent 3,182,012, issued May 4, 1965 it was 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 was found that cracking of hydrocarbons can be effected in the presence of hydrogen and a catalyst consisting essentially of alumina, silica and the oxides of molybdenum and cobalt combined in such manner that the resulting composite is characterized by a silica content of about 15 to about 40 percent by weight, a molybdenum trioxide content of about 3 to about 20 percent by weight, a cobalt oxide content of about 1 to about 8 percent by weight and the remainder alumina. Preferably the catalyst has a composition of about 15 to about 25 weight percent silica, about 7 to about 16 weight percent molybdenum trioxide, about 2 to about 4.5 percent cobalt oxide and the remainder alumina. Such catalysts employed in the processes of the aforesaid copending applications have been found to afford a highly favorable distribution of products of high quality. The processes described therein each have the further advantage of being applicable for catalytically hydrocracking a wide variety of charge stocks, including heavy residual and refractory charge stocks.

In accordance with the present invention, it has been discovered that a superior hydrocracking catalyst composite is realized in a physical particle-form mixture of two components: (1) a crystalline aluminosilicate component, having a sodium content less than 4 percent by weight; and (2) a hydrogenation component comprising a predominant proportion of a porous support and a minor proportion of at least one hydrogenation constituent. The crystalline aluminosilicate component may be base-exchanged with a solution of ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions, and mixtures thereof with one another, to reduce the sodium content thereof to below 4 percent. Preferably the sodium content of the final hydrocracking composite is less than 1 percent. The hydrogenation component may comprise as the porous support alumina promoted with silica according to the method of application U. S. Patent 3,182,012. Thus, preferably, the hydrogenation component comprises about 15 to about 40 percent silica by weight, about 4 to about 30 percent of a hydrogenation constituent and the remainder alumina.

A particularly preferred composition is a physical particle-form mixture of two components: (1) a crystalline alumino-silicate component base-exchanged with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions, and mixtures thereof with one another, to reduce the sodium content thereof to below about 1 percent; and (2) a silica-promoted cobalt molybdena alumina component, hereinafter designated CMAS, which hydrogenation component consists essentially of 15 to 40 percent by weight silica, 1 to 8 percent cobalt oxide, 3 to 20 percent molybdenum trioxide and the remainder alumina.

In alternative or prefered embodiments, one or more hydrogenation constituent may be added to the crystalline aluminosilicate component of the present catalyst.

Accordingly, most preferred compositions are physical particle-form mixtures of two components: (1) a crystalline aluminosilicate component containing a hydrogenation constituent, which component consists essentially of a constituent exhibiting hydrogenation activity selected from the group consisting of oxides of metals, sulfides of metals and metals of Groups VI and VIII of the Periodic Table in intimate combination with a crystalline rare earth-, hydrogen- or hydrogen percursor-containing aluminosilicate resulting from base-exchange of a crystalline alkali metal aluminosilicate having uniform pore openings between 6 and 15 Angstrom units with rare earth metal, hydrogen or hydrogen precursor ions to replace at least about 75 percent of the original alkali metal and to reduce the sodium content of the final component to below 2 percent by weight; and (2) the CMAS component described above.

As employed herein, the terms "rare earth-containing," "hydrogen-containing," "hydrogen precursor-containing" and the like shall refer to crystalline aluminosilicates containing as cations a substantial portion or a complete portion of such named cations, although other cations, such as sodium, may also be present.

The essence of the present invention is the unexpected discovery that a hydrocracking catalyst of the physical particle-form mixture of two components, above described, exhibits a synergistic catalytic effect in hydrocracking operations. Thus, the activity and selectivity of the catalyst of the present invention are unexpectedly superior to that of either component alone or to that, which would be expected by those skilled in the art, of a combination of the components.

The present invention provides a process for hydrocracking hydrocarbons and particularly petroleum 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 point of at least 600° F., and boiling substantially continuously between said initial boiling point and said end point; by contacting said fractions with the above catalyst in the presence of hydrogen at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge, at a liquid hourly space velocity of between about 0.1 and about 10, at a temperature between about 600° F. and about 950° F., and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80.

It has heretofore been proposed to desulfurize hydrocarbon fractions in the presence of certain catalytic composites containing alumina, silica, cobalt oxide and molybdena. The hydrocracking process described herein is distinguishable from such desulfurizing process. Thus, there are at least five differences between the cracking process of this invention and the aforesaid desulfurizing operations. First, it may be noted that the processes are carried out for two different purposes. Cracking is used to convert high boiling hydrocarbon fractions into low boiling hydrocarbon fractions, while desulfurizing is carried out for the sole purpose of removing sulfur from the charge stock undergoing treatment. Secondly, the silica content of the above type catalysts useful in desulfurization is substantially lower than the silica content of the preferred catalysts employed in the present hydrocracking process.

A third difference relates to the chemical reactions involved in the processes. In desulfurizing, it is desired to remove sulfur from a hydrocarbon by reaction of the sulfur compounds with hydrogen with resulting formation of H_2S. Cracking, on the other hand, involves conversion of high boiling hydrocarbons to lower boiling hydrocarbons by selective breakage of carbon-to-carbon bonds. A still further distinction resides in the fact that the hydrocracking process of the present invention is generally carried out at pressures outside the range specified for desulfurization.

A further distinction is that the catalyst of the present invention is a composite characterized by a physical particle-form mixture of two catalytic components exhibiting an unexpected synergistic catalystic effect in hydrocracking operations, a constituent of which composite is essentially a crystalline aluminosilicate having a sodium content of less than 4 percent by weight. It will accordingly be appreciated that the aforementioned desulfurizing processes utilizing catalysts containing alumina, silica, molybdena and cobalt oxide are distinct from the hydrocracking process of this invention.

Catalysts proposed for hydrocracking operations have, heretofore, consisted almost entirely, of active hydrogenating 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 deposits 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 intimately compositing a physical particle-form mixture of two components: (1) a crystalline aluminosilicate component having a low sodium content, and (2) a hydrogenation component comprising a predominant proportion of a porous support and a minor proportion of at least one constituent exhibiting hydrogenation activity. The catalysts of this invention have 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 3000 pounds per square inch.

Thus, briefly, the hydrocracking composite of the present invention comprises two essential components in a particle-form mixture: (1) a crystalline aluminosilicate component, and (2) a hydrogenation component, both above described. Both components may consist of one or more constituents. Essentially the crystalline aluminosilicate component comprises a crystalline aluminosilicate constituent having a sodium content below 4 percent by weight. Alternatively, the crystalline aluminosilicate component may comprise in addition a hydrogenation constituent. The hydrogenation component comprises essentially both a porous support constituent and a hydrogenation constituent.

THE CRYSTALLINE ALUMINOSILICATE COMPONENT

The crystalline aluminosilicate component employed in preparation of the instant catalyst may contain one or more natural or synthetic zeolite. Representative of particularly preferred zeolites are zeolite X, zeolite Y, zeolite L, faujasite and mordenite. Synthetic zeolites have been generally described by Barrier in several publications in U.S. Patent 2,306,610 and U.S. Patent 2,413,134. These materials are essentially the dehydrated forms of crystalline hydrous siliceous zeolites containing varying quantities of alkali metal and aluminum with or without other metals. The alkali metal atoms, silicon, aluminum and oxygen in the zeolites are arranged in the form of an aluminosilicate salt in a definite and consistent crystalline pattern. The structure contains a large number of small cavities, interconnected by a number of still smaller holes or channels. These cavities and channels are precisely uniform in size. The alkali metal aluminosilicate used in preparation of the present catalyst has a uniform pore structure comprising openings characterized by an effective pore diameter of between 6 and 15 Angstroms.

The crystalline aluminosilicate suitable for the present invention may be prepared according to well-known methods, such as those described in greater detail in patents directed to specific crystalline aluminosilicates; to wit: Zeolite X, U.S. Patent 2,882,244; and Zeolite Y, U.S. Patent 3,130,007, incorporated herein by reference.

The crystalline aluminosilicate component utilized in the present process may be prepared by base-exchanging a crystalline alkali metal aluminosilicate, such as described hereinabove and in the cited patent references, having a structure of rigid three-dimensional networks characterized by a uniform pore diameter between 6 and 15 Angstrom units, with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions, and mixtures thereof with one another, and thereafter washing the base-exchanged material free of soluble salts, drying the washed composite and subjecting the same to a thermal activating treatment.

The base-exchange solutions employed may be contacted with the crystalline aluminosilicate of uniform pore structure as formed, after washing free of soluble salts, or in the form of a fine powder, a compressed pellet, extruded pellet, or other suitable particle shape. When in the form of a pellet the crystalline aluminosilicate may be combined with a binder such as clay. It has been established that the desired base-exchange may be effected most readily if the alkali metal aluminosilicate zeolite undergoing treatment has not previously been subjected to a temperature above about 600° F.

Base-exchange required for introducing the aforementioned exchange ions may be accomplished by contacting the alkali metal aluminosilicate for a period of time and under appropriate temperature conditions sufficient to replace at least about 75 percent, and preferably at least about 90 percent, of the sodium contained in the aluminosilicate with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions, and mixtures thereof with one another, effectively to reduce the sodium content of the resulting crystalline aluminosilicate component to below 4 percent and preferably less than 1 percent by weight.

It is contemplated that any readily available compound of the exchange ions may be employed for the above purpose. Generally, compounds will be used wherein the exchange ion is present in the cationic state.

Representative rare earth metal compounds include nitrates, bromides, acetates, chlorides, iodides and sulfates of one or more of the rare earth metals including cerium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Naturally occurring rare earth minerals offer a convenient source for the rare earth metals. The natural rare earth metal-containing mineral may be extracted with an acid such as sulfuric, or rare earth oxides and related metal oxides in admixture from a natural earth may be dissolved in other solubilizing acids such as acetic. For example, monazite which contains cerium compounds as the principal rare earth metal compound present with lesser portions of thorium compounds and other rare earth compounds may be used as a suitable source of cerium. Mixtures of rare earth metal salts, for example, chlorides of lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium available commercially at a relatively low cost may be effectively employed.

Similarly, the calcium, manganese or magnesium salt may be a chloride, sulfate, nitrate and the like. The hydrogen ion may be added in the form of a mineral or organic acid such as hydrochloric, nitric, sulfuric or formic acid and the like, under conditions such that the structure of the crystalline aluminosilicate is not adversely affected. The hydrogen precursor may be an organic or inorganic ammonium compound, generally an inorganic ammonium salt, which upon heating undergoes thermal degradation to hydrogen. A particularly effective base-exchange solution for continuous exchange is one containing rare earth metal and ammonium ions in the ratio of 1/10 to 1/100 to effect replacement of the alkali metal ion with rare earth and ammonium ions. Another effective method of exchange is to replace more than 75 percent of the alkali metal ion by contact with a solution of rare earth metal ions or rare earth metal and ammonium ions, followed by completing the alkali metal exchange, to less than 3 percent exchangeable sodium content, with ammonium ion exchange. Additional particularly effective base exchange solutions contain about 1 to 5 percent aqueous solutions of calcium chloride, manganese chloride, magnesium chloride, ammonium chloride or mixtures thereof, such as a combined solution of manganese chloride and ammonium chloride, magnesium chloride and ammonium chloride, or calcium chloride and ammonium chloride.

While water will ordinarily be the solvent in the base-exchange solutions used, it is contemplated that other solvents, although generally less preferred, may be used; in which case, it will be realized that the above list of representative exchange compounds may be expanded. Thus, in addition to aqueous solutions, alcoholic solutions, etc., of the exchange compounds may be employed in producing the catalyst utilized in the present process. It will be understood that such exchange compounds employed undergo ionization in the particular solvent used.

The concentration of exchange compounds employed in the base-exchange solutions may vary depending on the alkali metal aluminosilicate undergoing treatment and on the conditions under which treatment is effected. The overall concentrations of replacing metal ions, however, is such as to reduce the sodium content of the original alkali metal aluminosilicate to less than 4, and preferably, less than 1 weight percent. In base-exchanging the alkali metal aluminosilicate with a solution of an exchange compound generally the concentration of such compound is within the range of 1 to 30 percent by weight. The pH of such exchange solution is generally within the approximate range of 3.5 to 6.5 and, preferably, between about 4 and about 5.5.

The temperature at which base-exchange is effected may vary widely, generally ranging from room temperature to an elevated temperature below the boiling point of the treating solution. The volume of base-exchange solution employed in any instance may vary widely. Generally, however, an excess is employed and such excess is removed from contact with the crystalline aluminosilicate zeolite after a suitable period. The time of contact between the base-exchange solution and crystalline zeolite in any instance is such as to effect substantial replacement of the alkali metal ions thereof with the exchange ions. It will be appreciated that such period of contact may vary widely depending on the temperature of the solution, the nature of the alkali metal aluminosilicate used and the particular exchange compounds employed. Thus, the time of contact may extend from a brief period of the order of a few hours for small particles to longer periods of the order of days for large pellets. The exchange may also be carried out with several batches of solution wherein contact time per batch may range from about ½ hour to 2 hours. Generally, the total time of contact will, depending on the various aforementioned factors, be within the range of ½ hour to 80 hours.

After the base-exchange treatment, the low sodium crystalline aluminosilicate product is removed from the treating solution. Anions introduced as a result of treating with the base-exchange solutions may be removed by water-washing the treated composite for such period of time until the same is free of said anions. The washed product is then dried, generally in air to remove substantially all of the water therefrom. While drying may be effected at ambient temperature, it is generally more satisfactory to facilitate the removal of moisture by maintaining the product at a temperature between about 150 and about 600° F. for 4 to 48 hours.

The dried material may then be subjected to an activating treatment which entails heating the dried material generally in air to a temperature within the approximate range of 500° F. to 1500° F. for a period of between 1 and 48 hours. The resulting product has a surface area within an approximate range of 50 to 60 square meters per gram and generally contains between about 0.1 and about 30 weight percent of exchange metal or hydrogen, between about 0.1 and about 4 weight percent sodium, between about 25 and about 40 weight percent alumina and between about 40 and about 60 weight percent silica.

In preferred embodiments, the above crystalline aluminosilicate component may be intimately combined with a constituent exhibiting hydrogenation activity. Suitable hydrogenation constituents include one or more of the metals or Groups VI and VIII of the Periodic Table either in elemental form or in the form of the oxides or sulfides. Representative of these metals are molybdenum, chromium, tungsten, iron, cobalt, nickel, and metals of the platinum group, i.e. platinum, palladium, osmium, rhodium, ruthenium and iridium 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 intimately combined with the above-described crystalline aluminosilicate by impregnation.

Combination of one or more of the above-indicated hydrogenation constituents with the crystalline aluminosilicate may take place in any feasible manner, for example, by impregnating the aluminosilicate with solutions containing ions of the appropriate hydrogenation constituent. In this manner, a hydrogenation constituent can be introduced by deposition of the incoming metal on the exchanged crystalline aluminosilicate, after removal of the impregnating solution from the crystalline aluminosilicate carrier. Other means for combining the exchanged crystalline aluminosilicate with the hydrogenation constituent are feasible such as for example, the addition of the hydrogenation constituent to a slurry of the aluminosilicate.

In its broader aspects, the hydrocracking catalyst composite of the present invention comprises two components, a crystalline aluminosilicate component and a hydrogenation component. The essential hydrogenation constituent, broadly, is included as part of the hydrogenation component. However, it is within the purview to incorporate, as described above, an additional hydrogenation constituent on the crystalline aluminosilicate component.

Thus, in preferred embodiments, a hydrogenation constituent may be added to the crystalline aluminosilicate component of the present catalyst. The amount of hydrogenation constituent combined with the crystalline aluminosilicate may vary widely and will depend on the charge stock undergoing hydrocracking as well as on the particular nature of the hydrogenation constituent. Generally the amount of hydrogenation constituent on the crystalline aluminosilicate will be within the range of about 0 to 25 percent by weight of the final component. When a metal of the platinum series is employed, the amount thereof will generally range from about 0 to 5 weight percent. With other hydrogenation constituents such as the oxides or sulfides of molybdenum, cobalt, tungsten, chromium, iron and nickel, the amounts employed will generally be within the approximate range of 0 to 25 weight percent. Thus, when the hydrogenation constituent is a combination of cobalt oxide and molybdenum oxide, the cobalt oxide content is generally in the approximate range of 1 to 4 weight percent and the molybdenum oxide is within the range of 5 to 15 weight percent. It is not essential, however, that a hydrogenation constituent be part of the crystalline aluminosilicate component. Such hydrogenation constituent may be either totally incorporated with the hydrogenation component or divided between the two components. It will be understood that, in any instance, the amount of hydrogenation constituent present may be such as to afford a resulting composite in combination with the crystalline aluminosilicate of a hydrocracking catalyst characterized by unusual activity and selectivity.

It is again emphasized that the present hydrocracking catalyst composite is a physical particle-form mixture of (1) the crystalline aluminosilicate component above described in detail, and (2) the hydrogenation component described in detail immediately below.

THE HYDROGENATION COMPONENT

The hydrogenation component essentially comprises a predominant proportion of a porous support and a minor proportion of at least one constituent exhibiting hydrogenation activity. The hydrogenation constituent is suitably selected from the group consisting of oxides of metals, sulfides of metals and metals of Groups VI and VIII of the Periodic Table. Representative of these metals are molybdenum, cobalt, chromium, tungsten, iron, nickel, the platinum group metals, as well as combinations of these metals, their oxides or sulfides. Combination of the hydrogenation constituent with a porous support may take place in any feasible manner, for example by impregnation, deposition, mechanical admixture or cogelation. Preferred methods of combination are discussed below in greater detail.

The porous support may be one or more of a large number of materials having high porosity and a surface area of at least 100 square meters per gram, which materials include organic and inorganic compositions with which the hydrogenation constituent may be combined by impregnation, admixture or dispersion. The porous support may be catalytically active or inactive.

Representative porous supports which can be employed include metals and alloys thereof, sintered metals and sintered glass, asbestos, silicon carbide aggregates, pumice, firebrick, diatomaceous earths, activated charcoal, refractory oxides, organic resins, such as polyepoxides, polyamines, polyesters, vinyl resins, phenolics, amino resins, melamines, acrylics, alkyds, epoxy resins, etc., and inorganic oxide gels. Of these porous supports, the inorganic oxide gels are particularly preferred because of their superior porosity, attrition resistance, and stability under reaction conditions, especially those reaction conditions encountered in the hydrocracking of gas oil.

Preferred inorganic oxide porous supports include one or more of the metal oxides of Groups II–A, III–A and IV–B of the Periodic Table. As employed herein the

Periodic Table refers to the standard long form, Webster's Third New International Dictionary, G. & C. Merriam Co. (Springfield, Mass., 1961), p. 1680.

Preferably, however, the hydrogenation component comprises alumina promoted with silica according to the teaching of copending application, Serial No. 760,646, filed September 12, 1958, and contains as hydrogenation constituents a mixture of cobalt oxide and molybdenum trioxide. Such preferred hydrogenation component is described in detail below. Thus, the hydrogenation component may comprise several constituents, e.g. alumina, silica, cobalt oxide and molybdenum trioxide.

The preferred hydrogenation component comprising silica, alumina, cobalt oxide and molybdenum trioxide constituents may be combined in any suitable manner. It has been discovered, however, as will be evident from data set forth hereinbelow, that it is preferable to produce the preferred component by mechanical admixture of the silica and alumina-containing constituents, rather than by chemical compositing of these oxides such as, for example, by cogelation. Either the silica or alumina-containing constituent may, prior to admixture with the other, have deposited thereon one or more hydrogenation constituents, i.e. cobalt oxide or molybdenum trioxide. Thus, the hydrogenation component may be produced by mechanically admixing silica with alumina which has previously been impregnated with the oxides of molybdenum and cobalt. Alternatively, the component may result from mechanical admixture of alumina with silica which has previously been impregnated with the oxides of molybdenum and cobalt. Another method of combining the constituents involves admixture of silica impregnated with either molybdenum trioxide or cobalt oxide with alumina impregnated with the other of such metal oxides. It is also feasible, and in some aspects preferable, initially to admix intimately the silica and alumina constituents and thereafter to impregnate the resulting silica-alumina composite with the oxides of molybdenum and cobalt. The composite obtained, in accordance with any of the above techniques, is dried and calcined to obtain the finished hydrogenation component.

While alumina or another porous support is the predominating constituent of the hydrogenation component and may have, of itself, no catalytic activity, its careful preparation is essential to the production of the catalyst affording the desired activity in the contemplated conversion of the hydrocarbon charge. Alumina, however, the preferred porous support, when properly prepared exerts a synergistic effect with the other catalyst components and constituents.

The alumina constituent of the preferred hydrogenation component is a porous alumina not adversely affected by the temperature conditions of the instant process, having a surface area greater than 100 square meters per gram and which may extend up to 500 square meters per gram or more. Catalysts prepared from alumina having a surface area of 100 square meters per gram or less have a considerably higher aging rate when employed in the instant low pressure hydrocracking process in comparison to catalysts in which the alumina component initially is characterized by a surface area in substantial excess of 100 square meters per gram. As mentioned above, similar surface area limitations are desirable for less preferred porous support constituents, other than alumina. The term "surface area" as used herein designates the surface area as determined by the adsorption of nitrogen according to the method of Brunnauer et al. Journal American Chemical Society 60, 309 et seq. (1938). The alumina constituent itself is devoid of or exerts negligible catalytic activity under the reaction conditions at which the present hydrocracking process is carried out. The density of the preferred alumina constituent, i.e. the bulk density thereof, will usually be within the range of .2 to 2.0 grams/cc. and more particularly between about 0.4 and about 1.2 grams/cc.

The alumina constituent of the preferred hydrogenation component may be prepared by commingling a suitable basic compound including ammonium hydroxide, ammonium carbonate, etc. with an acidic compound of aluminum including the chloride, bromide, iodide, fluoride, sulfate, phosphate, nitrate, acetate, etc. or by the addition of a suitable acidic compound including hydrogen chloride, sulphuric acid, or phosphoric acid, etc., to an alkaline compound of the metal as for example, an alkali metal aluminate such as sodium aluminate. The resultant aluminum hydroxide is usually washed to remove soluble impurities and then is dried at a temperature of from 200° F. to about 600° F. for a period of from 1 to 24 hours or more. In one method the dried alumina constituent is formed into particles of definite size and shape in any suitable manner such as casting, pelleting extruding etc. and then is subjected to calcination at a temperature of from about 600° to about 1600° F. In another embodiment the alumina constituent may be formed into particles of spherical shape by dropping a suitable alumina sol into a suitable medium which may comprise air an inert atmosphere as for example nitrogen carbon monoxide etc. or into an oil or other suitable immiscible liquid. The resultant spheroids are then washed dried and calcined in the manner hereinbefore set forth. Alternatively the alumina constituent may be prepared in the form of a precipitate by controlled reaction of aluminm metal with water in the presence of a mercury compound whereby the aluminum undergoes amalgamation and the resulting amalgamated aluminum reacts with the water to form alumina.

The silica constituent contained in preferred hydrogenation components is initially prepared in the form of a hydrogel or gelatinous precipitate. Preferably the silica constituent is prepared in the form of a hydrogel by reaction between sodium silicate and an acid such as sulfuric acid while the pH of the reaction mixture generally is maintained below about 6 and preferably in the approximate range of 3.5 to 5. The initially-formed hydrosol of silica undergoes gelation after lapse of a suitable period of time to silica hydrogel. The gelation time can be controlled within desired limits by well-known means such as by adjustment of the temperature or solids concentration of the reaction mixture or hydrosol produced therefrom. The resulting hydrogel is thereafter water-washed base-exchanged to remove zeolitic sodium and dried. If it is desired to prepare silica initially free of alkali metal ions such may be accomplished by effecting hydrolysis of alkyl silicates i.e. ethyl silicate. The silica hydrogel constituent may be produced in the form of granules or in the form of a mass, which is thereafter broken up into pieces or particles of desired size. Alternatively, the silica hydrogel constituent may be produced in the form of spheroidal bead particles by methods such as those described by Marisic in U.S. 2,384,946, or in the form of uniformly shaped particles prepared by casting or extrusion methods. It is also feasible initially to produce silica in the form of finely divided particles of requisite particle size by employing techniques used in the preparation of fluid catalyst particles, for example, by spraying or rapid agitation of a hydrosol to form minute particles of hydrosol that set to particles of hydrogel, which, upon drying yield discrete particles of silica gel. Generally, it is preferred that the silica constituent, before admixture with the alumina and hydrogenation constituents, be in a finely divided state, generally of a particle size finer than 50 mesh (Tyler) and preferably of a particle size within the approximate range of 60 to 200 mesh (Tyler). The above indicated finely divided state of silica can be obtained either during initial formation of the silica or by grinding larger size pieces to the requisite particle size.

The alumina and silica constituents, prepared as above, may be composited by mechanical admixture and thereafter impregnated with hydrogenation constituents, such as cobalt oxide and molybdenum trioxide; or either of these constituents, prior to admixture with the other, may be impregnated with suitable compounds of molybdenum and cobalt to effect deposition thereon of cobalt oxide and molybdenum trioxide. The base material, i.e., alumina, silica, or composite resulting from admixture of silica and alumina, may be contacted with an impregnating solution of a cobalt compound, such as cobalt nitrate, and of a molybdenum compound, such as ammonium molybdate. In one method, the particle of base material are initially subjected to a vacuum to remove air from the pores thereof and while maintaining the vacuum, the above-described impregnating solution is brought into contact with the particles of base material. Alternatively, the base material, for example alumina, in the form of an aqueous slurry may be impregnated with the solution of molybdenum compound and cobalt compound. It is understood that any other suitable method of commingling the constituent particles of the base material with the impregnating solution may be employed.

In another preferred embodiment, separate impregnating solutions of the molybdenum compound and of the cobalt compound are prepared and are composited successively with the base material either with or without intervening heating of the support. In general, using this technique, it is preferred to composite the molybdenum constituent first and then the cobalt constituent, although the reverse procedure may be employed. After the impregnation, the base material is dried and then calcined to convert the metal compound to the oxides.

Other suitable cobalt compounds for effecting deposition of cobalt oxide on the base material may be employed including, for example, cobalt ammonium nitrate, cobalt ammonium chloride, cobalt ammonium sulfate, cobalt bromide, cobalt bromate, cobalt chloride, cobalt chlorate, cobalt fluoride and cobalt fluorate. In similar manner, other suitable compounds of molybdenum may be employed, including molybdenum tetrabromide, molybdenum oxydibromide, molybdenum tetrachloride, molybdenum oxydichloride, molybdenum oxypentachloride and molybdenum oxytetrafluoride.

The silica-containing constituent, preferably in finely divided form, is intimately mixed with the alumina-containing constituent which likewise is in a finely divided state preferably having a particle size within the approximate range of 60 to 200 mesh (Tyler). After thorough mixing of the constituents, the resulting mixture is formed by pelleting, casting, molding or other means into pieces of desired size and shape such as rods, spheres, pellets, etc. After forming into particles of desired size, the resulting particles are dried and thereafter calcined at an elevated temperature in the approximate range of 600° to 1200° F. It is understood that either the silica and alumina constituents may prior to admixture be impregnated with molybdenum trioxide and cobalt oxide or that the mixed composite of silica and alumina constituents may subsequently be impregnated with the oxides of molybdenum and cobalt to form the preferred hydrogenation component.

The impregnating solution for the preferred component ordinarily contains the cobalt and molybdenum compounds in the proportions preferred in the final component and the impregnation is controlled to produce a final component containing these constituents in the desired concentrations. The concentrations of the cobalt and molybdenum oxides in the hydrogenation component described herein may respectively range from about 1 to about 8 percent by weight and from about 3 to about 20 percent by weight of the final component. A more preferred hydrogenation component contains cobalt oxide (CoO) in a concentration of from about 2.0 to about 4.5 percent and molybdenum trioxide (MoO_3) in a concentration of from about 7 to 16 percent by weight of the final component. After impregnation the final component generally is dried at a temperature of from about 200° to about 600° F. for a period of from about 2 to 24 hours or more and thereafter calcined at a temperature of from about 600° to 1200° F. for a period of from about 1 to 12 hours or more.

It is highly preferred that the silica content of the hydrogenation component be at least about 15 percent by weight. Components containing amounts of silica less than about 15 percent by weight do not possess the superior hydrocracking activity observed in the case of the preferred component. The cobalt oxide content of the component, as noted hereinabove, is preferably between about 2 and about 4.5 percent by weight. A higher cobalt oxide content increased the saturation of the fuel oil and cycle stock, but decreased the combined naphtha and fuel oil yield and caused a slight increase in the aging rate of the catalyst. An increase in the molybdenum trioxide content of the catalyst was found to raise the heavy naphtha to fuel oil ratio and to increase the saturation of the fuel oil and cycle stock.

The hydrogenation component described hereinabove is the preferred CMAS component, silica promoted alumina containing cobalt oxide and molybdenum oxide as hydrogenation constituents. In its broadest aspects, of course, the hydrogenation component need not be silica-promoted and may contain one or more from a wide variety of hydrogenation constituents.

The crystalline aluminosilicate component and the hydrogenation component generally are combined as a mechanical admixture of particles in a weight ratio from about 1:10 to about 10:1, although useful composites may fall outside these ranges. Preferably the components are in a ratio from about 40:60 to about 60:40.

In the final particle-form mixture of the catalyst, the various components and constituents are present in the percentages, broadly and preferably, by weight, shown below in Table I:

TABLE I.—BROAD AND PREFERRED COMPOSITION RANGES OF CONSTITUENTS AND COMPONENTS

Component	Constituent	Percentages by weight			
		Broadly		Preferably	
		Component	Final catalyst	Component	Final catalyst
Crystalline aluminosilicate	Crystalline aluminosilicate	75-100	8-90	75-98	30-59
	Hydrogenation	0-25	0-22	2-25	1-10
Hydrogenation	Porous support (preferably alumina)	75-98	8-88	35-81	14-49
	Silica	0-40	0-36	15-40	6-24
	Hydrogenation	2-25	2-22	4-25	2-15

The hydrogenation constituent(s) may include one or more metal, metal sulfide or oxide as hereinabove described. In any case, the total weight of hydrogenation constituent(s) on the final particle form catalyst is within the approximate range of 2-25 percent. The sodium content of the crystalline aluminosilicate constituent is such that the sodium content of the crystalline aluminosilicate component (including preferably a hydrogenation constituent) is less than 4 percent by weight and preferably less than 1 percent.

The particle-form catalyst of this invention is prepared by mixing the crystalline aluminosilicate component and the hydrogenation component in the form of discrete particles, or the components may be admixed and pelleted, cast, molded or otherwise formed into pieces of desired size and shape such as rods, spheres, pellets or other configuration.

The particle size of the components may be very small, e.g. less than about 50 microns, as may result from ball-milling the components together. In an alternative embodiment of the invention, however, the particles of each of the two components will be sufficiently large and distinct as to permit ready separation thereof by mechanical means which, in turn, makes possible separate regeneration, reactivation and replacement of the two components. Accordingly, the particle size of the two components making up the particle-form catalyst composition will generally be within the approximate range of 2 to 50 mesh (Tyler).

However, it has been found necessary that the component particle size be consistently small when one or more hydrogenation constituent is added only to the hydrogenation component. Thus, for embodiments employing a crystalline aluminosilicate component without a hydrogenation constituent, the particle size of each component is specifically less than 100 microns, and preferably less than 15 microns, in diameter. In such cases superior hydrocracking activity and selectivity may be maintained.

The process of this invention may be carried out in any equipment suitable 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 operations using a fixed bed of catalyst. Additionally, 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 950° 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 700 and about 3000 pounds per square inch gauge and preferably about 1000 and 2000 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 to 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 hydrocarbons, mixtures of hydrocarbons, and particularly hydrocarbon fractions having an initial boiling point of at least about 400° F., a 50 percent point of at least 500° F. and an end boiling point of at least 600° F. and boiling substantially continuously between said initial boiling point and 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 (above 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 term "gas oil" as employed in the art includes a variety of petroleum stocks. As utilized herein, this term, unless further modified, includes any fraction distilled from petroleum which has 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 the initial boiling point and the end point. The exact boiling range of a gas oil accordingly will be determined by the initial boiling point, the 50 percent point, and by the end point. In practice, petroleum distillations have been effected under vacuum at temperatures as high as 1200° F. (corrected to atmospheric pressure). Accordingly, in the broad sense, a gas oil is a petroleum fraction which boils substantially continuously within an approximate range of 400° F. to 1200° F., the 50 percent point being at least about 500° F. Thus, a gas oil may boil over the entire approximate range of 400° F. to 1200° F. or over an intermediate range such as 500° F. to 900° F.

A residual stock is any fraction which is not distilled. Accordingly, any fraction, regardless of its initial boiling point, which includes heavy bottoms, such as tars, asphalts, etc., is a residual fraction. A residual stock may be the portion of the crude remaining undistilled at about 1200° F. or it may be made up of a gas oil fraction plus the portion undistilled at about 1200° F.

A whole topped crude is the entire portion of the crude remaining after the light ends; i.e., the portion boiling up to about 400° F. has been removed by distillation. Accordingly, such a fraction includes the entire gas oil fraction and the undistilled portion of the crude petroleum boiling above about 1200° F. If desired, the residual fractions and the whole topped crude may be deasphalted by any suitable well-known means. Such deasphalting treatment, however, is not considered necessary for charge stocks utilizable in the process of this invention.

The refractory cycle stocks are cuts of cracked stocks which boil above the gasoline boiling range usually between about 400° F. and about 850° F. The refractory cycle stocks can be charged to the process of this invention, together with a fresh petroleum charge stock or the refractory cycle stocks may be charged to the process alone.

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 fresh feed 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 for a specified charge stock.

The catalyst aging rate, as this term is utilized herein, is defined as the rate of temperature increase (° F./day) required to maintain constant conversion with all operating conditions except temperature held constant.

The following examples will serve to illustrate the process of the present invention without limiting the same. Examples 1–3 serve to illustrate the preparation of the low sodium crystalline aluminosilicate component of the present catalyst composition, which preferably may be combined with a constituent exhibiting hydrogenation activity.

Example 1

A crystalline sodium aluminosilicate having a uniform pore structure comprising openings characterized by an effective pore diameter in the range of 6 to 15 Angstroms was prepared by the addition of 199 parts by weight of an aqueous solution of sodium aluminate, containing the equivalent of 43.5 weight percent alumina (Al_2O_3) and 30.2 weight percent sodium oxide (Na_2O)

to 143 parts by weight of aqueous sodium silicate solution, containing the equivalent of 26.5 weight percent silica (SiO_2) and 8.8 weight percent sodium oxide (Na_2O). The gel which formed on mixing the two above solutions was broken by vigorous mixing. The entire mass was mixed thoroughly to a cream-like consistency and, thereafter, heated without agitation for 12 hours at 205° F. At the end of this period, a flocculant precipitate had formed beneath clear supernatant liquid. The precipitate was filtered and washed with water at room temperature until the pH of the filtrate was 11.0. The resulting crystalline aluminosilicate product contained 21.6 mol percent Na_2O, 22.6 mol percent Al_2O_3 and 55.08 mol percent SiO_2, based on the dried product.

The above crystalline sodium aluminosilicate was contacted at 150° F. with 1500 cc. of an aqueous solution having a pH of 4 and containing 1.0 pound of a rare earth metal chloride mixture consisting principally of cerium, lanthanum, praseodymium, neodymium, together with smaller amounts of other rare earth chlorides. The mixture was continuously agitated and after 24 hours, the solid was filtered, washed and contacted with fresh rare earth metal chloride solution as above. The above operation, during which sodium of the aluminosilicate solid was exchanged with rare earth metal, was repeated a number of times until the sodium content of the aluminosilicate had been reduced to 1.1 weight percent, corresponding to a replacement of 92 percent of the original sodium content of the crystalline aluminosilicate with rare earth metal ions. The exchanged aluminosilicate material had a rare earth metal content of 27 percent by weight, calculated as the oxides.

The product so obtained was washed, dried at 240° F., pelleted to ⅛ x ¹⁄₁₆ inch particles and calcined at 1000° F. in dry air. The calcined rare earth metal-exchanged aluminosilicate was then steam-treated for 10 hours at 1200° F. and a pressure of 15 p.s.i.g.

An 82 gram sample of the above pellets was then evacuated at a pressure of about 35 millimeters of mercury and contacted with 50 cc. of an aqueous solution of 11.5 grams of ammonium molybdate for ½ hour at room temperature. The impregnated pellets were then removed from their evacuated state, dried at 240° F. and calcined for 3 hours at 1000° F. with air flow through the pellets at 5 vol./vol. of pellets/minute. The calcined pellets were again evacuated to a pressure of about 35 millimeters of mercury and contacted with 30 cc. of an aqueous solution containing 9.0 grams of cobaltous chloride and 2.0 grams of ammonium chloride for 24 hours at room temperature. The impregnated pellets were then removed from their evacuated state, dried at 240° F., calcined for 3 hours at 1000° F. and then treated with a mixture of 50 volume percent hydrogen and 50 volume percent hydrogen sulfide at 800° F. The resulting product was found to contain 1.6 weight percent cobalt oxide (CoO) and 8.5 weight percent molybdenum oxide (MoO_3) before sulfiding, and contained 4.5 weight percent sulfur after sulfiding. The component exhibited a particle density of 1.17 g./cc., a surface area of 301 $m.^2/g.$, and a pore volume of 0.547 cc./g.

Example 2

Pellets of rare earth metal-exchanged aluminosilicate were prepared as described in Example 1. Eighty-four (84) grams of such pellets were then evacuated to a pressure of about 35 millimeters of mercury and contacted in two stages with a total of 62 cc. of an 11 percent by weight aqueous solution of ammonium tungstate, adjusted to 6.5 pH with citric acid, for ½ hour at room temperature, with drying at 240° F. for 16 hours after each stage. The impregnated pellets were then removed from their evacuated state and calcined in a nitrogen-air mixture up to 850° F. The calcined pellets were again evacuated to a pressure of about 35 millimeters of mercury and contacted with 47 cc. of an aqueous solution of 20.9 grams of nickel nitrate for 8 hours at room temperature. The impregnated pellets were then removed from their evacuated state, dried at 240° F. in air for 24 hours and calcined for 3 hours in dry air at 1000° F. The resulting composite was then sulfided at 800° F. for 5 hours with a mixture of 50 volume percent hydrogen and 50 volume percent hydrogen sulfide. The resulting product was found to contain 4.2 weight percent nickel and 7.9 weight percent tungsten before sulfiding, and 3.6 weight percent sulfur after sulfiding. The component exhibited a particle density of 1.3 g./cc., a surface area of 367 $m.^2/g.$, and a pore volume of 0.467 cc./g.

Example 3

Pellets of rare earth metal-exchanged aluminosilicate were prepared as described in Example 1. Seventy-four (74) grams of such pellets were then evacuated to a pressure of about 35 millimeters of mercury and contacted with 45 cc. of an aqueous solution of chloroplatinic acid containing 0.8 weight percent of platinum. The impregnated pellets were then removed from their evacuated state and maintained for 48–72 hours at 240° F. in their own vapor. The resulting composite was then calcined in hydrogen for 2 hours at 450° F. and, thereafter, for 2 hours at 950° F.

Examples 4–12 serve to illustrate the preparation of the hydrogenation component of the present composition. Particular emphasis is paid to the method of preparing the preferred hydrogenation component containing alumina and silica constituents.

Example 4

A composite of cobalt and molybdenum oxides on alumina in the form of ⅛″ x ⅛″ pellets and prepared by impregnation of alumina gel with approximately 3 percent by weight of CoO and approximately 9.5 percent by weight MoO_3, was crushed to a particle size of less than 100 mesh (Tyler). Approximately 85 parts by weight of the crushed material were mixed with approximately 43 parts by weight of silica hydrogel, containing about 35 weight percent SiO_2 and 65 weight percent water, and having a particle size of less than 60 mesh (Tyler). The resulting composite was intimately mixed by ball-milling the components for about 24 hours, at which time the particles were of 14 to 15 microns average size. The ball-milled material was then pelleted to ⅛″ diameter by ¹⁄₁₆″ thick pellets. The pellets, so obtained, were then tempered for 3 hours at 1000° F. in dry air. The resulting product contained, on a weight basis, about 2.5 percent CoO, about 8 percent MoO_3, about 15 percent SiO_2 and about 74.5 percent Al_2O_3 and possessed a surface area of approximately 220 square meters per gram.

Example 5

A alumina hydrogenation component was prepared following the procedure of Example 4 but by mixing approximately 95 parts by weight of the crushed constituents of cobalt and molybdenum oxides on alumina with approximately 14 parts by weight of the crushed silica hydrogel. The resulting product contained, on a weight basis, about 3 percent CoO, about 9 percent MoO_3, about 5 percent SiO_2 and about 83 percent Al_2O_3 and possessed a surface area of approximately 188 square meters per gram.

Example 6

A hydrogenation component was prepared following the procedure of Example 4 but by mixing approximately 75 parts by weight of the crushed constituents of cobalt and molybdenum oxides on alumina with approximately 72 parts by weight of the crushed silica hydrogel. The resulting product contained, on a weight basis, about 2 percent CoO, about 7 percent MoO_3, about 25 percent SiO_2 and about 66 percent Al_2O_3 and was characterized by a surface area of approximately 263 square meters per gram.

Example 7

In this example, no silica was combined with the composite of cobalt and molybdenum oxides on alumina but this material was ground, repelleted, and tempered under the conditions of Example 4. The resulting product contained, on a weight basis, about 3 percent CoO, about 9.5 percent MoO_3, and about 87.5 percent Al_2O_3 and had a surface area of approximately 185 square meters per gram.

Properties of the above four hydrogenation components are shown in Table II below:

TABLE II

Example	4	5	6	7
Component Composition, Wt. percent:				
CoO	2.5	3	2	3
MoO_3	8	9	7	9.5
Al_2O_3	74.5	83	66	87.5
SiO_2	15	5	25	0
Density, g./cc.:				
Packed	1.03	1.10	0.89	0.92
Particle	1.62	1.71	1.45	1.55
Real	3.38	3.54	3.16	3.72
Surface Area, m.²/g	220	188	263	185
Pore Volume, cc./g	0.320	0.301	0.374	0.373
Pore Diameter	58	64	57	81

It will be seen from the above table that an effect of increasing silica addition is to increase the surface area and to decrease the average pore diameter of the resulting hydrogenation component.

The following examples illustrate various methods for preparing the hydrogenation component of the catalyst composite of the invention:

Example 8

A hydrogenation component using the procedure of Example 4 was prepared. The resulting product contained, on a weight basis, 2.9 percent CoO, 8 percent MoO_3, 15.2 percent SiO_2 and 73.9 percent Al_2O_3 and was characterized by a surface area of approximately 238 square meters per gram.

Example 9

Alumina and silica hydrogel, containing about 35 weight percent SiO_2 and 65 weight percent water, were dried separately for 16 hours at 240° F. and were then crushed to a particle size of less than 60 mesh (Tyler). A composite containing about 82 parts by weight of alumina, and about 18 parts by weight of silica on a dry basis, was formed by mixing these crushed materials. The resulting composite was ball-milled dry for about 24 hours, at which time the particles were of 14 to 15 microns average size. The ball-milled material was then pelleted to ⅛" diameter by 1/16" thick pellets. The pellets, so obtained, were then calcined for 3 hours at 900° F. in dry air.

The pellets of silica and alumina were then pretreated with sufficient ammonium molybdate solution to yield a component containing about 10 weight percent MoO_3 on a dry basis. The impregnated pellets were dried for 8 hours at 240° F. and calcined for 3 hours at 900° F. in dry air.

The pellets were again pretreated with carbon dioxide and impregnated under vacuum with sufficient cobaltous nitrate solution to yield a final component containing about 3 weight percent CoO on a dry basis. The impregnated pellets were then dried for 8 hours at 240° F. and calcined for 3 hours at 900° F. in dry air, yielding the finished hydrogenation component.

Example 10

A cogel containing, on a dry basis, 79 weight percent of alumina and 21 weight percent of silica was prepared by mixing 1000 cc. of a sodium silicate solution containing 1.4 weight percent Na_2O, 4.5 weight percent SiO_2 and 94.1 weight percent water with 1000 cc. of 30.6 weight percent aqueous sodium aluminate solution in the presence of 800 cc. of a 34.2 weight percent aqueous solution of citric acid. The resulting cogel was aged for about 16 hours at room temperature and was then base-exchanged with 20 weight percent aqueous ammonium sulfate solution. The cogel was then washed with water until sulfate free. The washed cogel was dried for 24 hours at 240° F. to 250° F. in 100 percent steam and then ball-milled dry for 16 hours. The dried cogel was pelleted into ⅛" diameter by 1/16" thick pellets.

The resulting pellets were pretreated with carbon dioxide and impregnated under vacuum with sufficient ammonium molybdate solution to yield a component containing about 7.6 weight percent MoO_3 on a dry basis. The impregnated pellets were dried for 8 hours at 240° F. and calcined for 3 hours at 900° F. in dry air.

The pellets were again pretreated with carbon dioxide and impregnated under vacuum with sufficient cobaltous nitrate solution to yield a component containing about 3 weight percent CoO on a dry basis. The impregnated pellets were then dried for 8 hours at 240° F. and calcined for 3 hours at 900° F. in dry air, yielding the finished hydrogenation component.

Example 11

Alumina was extruded into ⅛" diameter particles. The extruded particles were dried at 230° F. and calcined for 3 hours at 1000° F. in dry air. The calcined particles were pretreated with carbon dioxide and impregnated under vacuum with a solution containing ammonium molybdate and cobaltous nitrate in amounts sufficient to yield a composite containing about 10 weight percent MoO_3 and about 3 weight percent CoO, on a dry basis. The alumina particles were soaked for about 16 hours in the impregnating solution. The impregnated alumina was then dried at 230° F. and calcined for 3 hours at 1000° F. in dry air.

The impregnated alumina was crushed to a particle size of less than 60 mesh (Tyler) and mixed with silica hydrogel, containing about 35 weight percent SiO_2 and about 65 weight percent water, having a particle size of less than 60 mesh (Tyler), in such proportions that the mixture contained about 85 weight percent impregnated alumina and about 15 weight percent silica, on a dry basis. The resulting component was intimately mixed by dry ball-milling for about 24 hours, at which time the particles were of 14 to 15 microns average size. The ball-milled material was then pelleted to ⅛" diameter, by 1/16" thick pellets. The pellets, so obtained were then tempered for 3 hours at 1000° F. in dry air.

Example 12

Alumina was mixed with water to form a slurry containing about 9 cc. of water per gram of dry alumina. Aqueous solutions of ammonium molybdate and cobaltous nitrate were added to this slurry in amounts sufficient to yield a component containing about 12 weight percent MoO_3 and 3 weight percent CoO, on a dry basis. The resulting component was aged for 16 hours at room temperature.

Silica hydrogel, containing about 35 weight percent SiO_2 and 65 weight percent water, and having a particle size of less than 60 mesh (Tyler), was added to the alumina-molybdena-cobalt oxide slurry in an amount sufficient to yield a component containing 15 weight percent SiO_2 on a dry basis. The resulting component was intimately mixed by wet ball-milling for about 24 hours, after which time the particles were of about 14 to 15 microns average size. The ball-milled material was then dried at 230° F., pelleted to ⅛" diameter by 1/16" thick pellets and calcined for 3 hours at 1000° F. in dry air.

The following examples illustrate the synergistic effect realized by combination of a crystalline aluminosilicate component and hydrogenation component in a single hydrocracking catalyst composition:

Example 13

A cobalt molybdena on crystalline rare earth X aluminosilicate hydrocracking catalyst, i.e. CoMoREX, was prepared as in Example 1 for comparative purposes. The component composition is given below in Table III.

Example 14

A silica promoted cobalt molybdena on aliumina hydrocracking catalyst, i.e. CMAS, was prepared as in Example 4 for comparative purposes. The component composition is given below in Table III.

Example 15

A physical particle-form mixture of (1) the CoMoREX component of Example 13, and (2) the CMAS component of Example 14, was prepared as follows:

The CMAS component was sized to smaller than 100 mesh; the CoMoREX component was sized to smaller than 60 mesh. The two components were ball-milled as a physical mixture in equal weight ratio for 24 hours, pelleted to ⅛" x $\frac{1}{16}$" diameter pellets using stearic acid as a pelleting lubricant, and finally calcined up to 1000° F. for 3 hours. The catalyst composition is given below in Table III.

The components and catalyst of Examples 13 through 15 were evaluated for hydrocracking at 1500 p.s.i.g., 1 LHSV and 7500 s.c.f.h.$_2$/b., a pretreated 390° F.+gas oil fraction having the following properties:

Gravity, ° API	29.6
Nitrogen, p.p.m.	1
Sulfur, wt. percent	0.03
Hydrogen, wt. percent	12.67
Vac. assay, ° F.:	
IBP	411
5%	453
10%	464
20%	481
30%	508
40%	534
50%	579
60%	628
70%	686
80%	736
90%	796
95%	734

The results of the evaluation are presented below in Table III.

TABLE III.—HYDROCRACKING OVER A PHYSICAL PARTICLE-FORM MIXTURE CATALYST

	Catalyst		
	CoMoREX	CMAS	CoMoREX plus CMAS
Example	13	14	15
Temp. for 60% Conv. to <390° F., ° F	645	810	590
Product Yields, Percent of Chg.:			
Dry Gas, Wt	1.2	1.6	1.8
Butanes, Vol	10.1	12.1	12.0
Pentanes, Vol	9.7	10.6	10.2
Light Naphtha, Vol	7.1	8.1	8.3
Heavy Naphtha, Vol	49.0	43.8	47.2
Product> 390° F., Vol	40.0	40.0	40.0
Total C_4+ Product, Vol	115.9	114.6	117.7
Composition, Percent Wt.:			
CoO	3.0	2.6	2.8
MoO_3	10	7.9	9
Al_2O_3	----------	74.5	37
SiO_2	----------	15	7.5
Rare Earth Crystalline Aluminosilicate (REX) [1]	87	----------	43.5

[1] REX formula equals ⅓ RE_2O_3:Al_2O_3·2.5 SiO_2; (0.5% Na).

The temperature for 60 percent conversion for the catalyst of the present invention was 590° F. while the temperature for the 60 percent conversion for the CoMoREX component was 645° F., and the temperature for 60 percent conversion for the CMAS component was 810° F. Fresh catalyst selectivity of the composite catalyst was, in general, intermediate to that of the two components alone. The catalyst of the present invention had a low age rate after 17 days on stream of less than 1° F. per day.

Thus, a comparison of the catalyst of Example 15 with those of Examples 13 and 14 readily demonstrates the synergistic and unexpected effect realized from a physical particle-form mixture of (1) a crystalline aluminosilicate component of a low sodium content and having a hydrogenation constituent, and (2) a component comprising a predominant proportion of a porous support and a minor proportion of at least one component exhibiting hydrogenation activity.

The following examples further illustrate the superiority and synergism of the catalysts of the present invention, wherein a hydrogenation constituent is present only on the hydrogenation component.

Example 16

Cobalt molybdena on alumina (CMA) and a rare earth exchanged crystalline X aluminosilicate (REX), having a silica to alumina mole ratio of 2.5:1, after each component was ground to an average particle size of less than 5 microns, were intimately mixed in equal weight fractions as a particle-form mixture of the two components. The mixture was pelleted, calcined at 1000° F. for 3 hours, and sulfided at 700° F. with a 50:50 volume mixture of hydrogen and hydrogen sulfide. The final composite contained 1.9 percent by weight cobalt, 4.7 percent molybdenum, both based on the oxides, 43.4 percent alumina, and 3.5 percent sulfur. The catalyst exhibited a particle density of 1.72 g./cc., a surface area of 216 m.^{2}/g., and a pore volume of 0.276 cc./g.

Example 17

Crystalline sodium Y aluminosilicate, having a silica to alumina mole ratio of 4.9:1, was base exchanged with 3 normal ammonium sulfate solution at 180° F. until the sodium content thereof was reduced to 0.6 weight percent. The base-exchanged product was water washed to remove sulfate ions. The NH_4Y product was converted to a stable HY product by calcining in a 100 percent steam atmosphere, initially at 230° F., increased to 1000° F. in four hours and maintained at 1000° F. for 2 additional hours.

Cobalt molybdena on alumina (CMA), ground to an average weight particle size of less than 5 microns, and the above hydrogen-containing crystalline aluminosilicate (HY), having an average particle size of less than 5 microns, were intimately mixed in equal weight fractions as a particle-form mixture of the two components. The mixture was pelleted, calcined at 1000° F. for 3 hours and sulfided at 700° F. with a 50:50 volume mixture of hydrogen and hydrogen sulfide. The final composite contained 1.5 percent by weight cobalt, 7.5 percent molybdenum, both based on the oxides, and 41.0 percent alumina.

The hydrocracking composites of Examples 16 and 17 were evaluated for the hydrocracking of a West Texas 650°—Tar Gas Oil at 2000 p.s.i.g., 14,500 s.c.f.h.$_2$/b. and 1 LHSV. The results of the evaluation are presented below in Table IV.

TABLE IV.—HYDROCRACKING OVER PHYSICAL PARTICLE-FORM MIXTURE CATALYSTS

Catalyst Composite	CMA-REX	CMA-HY
Example	16	17
Hydrocracking Temp., ° F	818	754
Conv. to <650° F., Percent Vol	63.3	63.3
Product Yields, Percent Change:		
Methane, Wt	0.34	0.11
Ethane, Wt	2.53	0.50
Propane, Wt	4.32	2.34
Total Dry Gas, Wt	7.2	3.0
Iso-butane, Vol	10.8	4.4
Butenes, Vol	1.8	----
n-Butane, Vol	5.9	3.7
Total C_4, Vol	18.5	8.1
Iso-pentane, Vol	8.9	4.5
Pentenes, Vol	----	----
n-Pentane, Vol	2.2	2.2
Cyclo Pentane, Vol	----	0.6
Total C_5, Vol	11.1	7.3
Light Naphtha, Vol	9.0	9.7
Heavy Naphtha, Vol	30.5	36.5
Light Fuel Oil, Vol	13.0	16.9
Heavy Fuel Oil (>650° F.), Vol	36.7	36.7
Total C_4+Product, Vol	117.8	115.2
Hydrogen Consumption, s.c.f./b	1,880	1,450
Gravity, ° API:		
Light Fuel Oil	31	33
Heavy Fuel Oil	25	28
Diesel Index of L.F.O	34	----

The evaluation of the hydrocracking composites of Examples 16 and 17 in Table IV clearly shows a high hydrocracking activity and selectivity of the two-component particle-form catalyst composites of the present invention. The high selectivity and activity of the CMA-HY composite relative to the CMA-REX composite make the former composite most preferred.

It will be evident from the foregoing examples that the combination of the two catalytic components in a physical particle-form mixture comprising the hydrocracking catalyst composite of the present invention exhibits vastly improved catalytic activity. When used in conventional hydrocracking processes, the present catalyst composition exhibits activity and selectivity unexpectedly superior to that of both conventional hydrocracking catalysts and of the singular components. It will be understood that the above description is merely illustrative of preferred embodiments of the invention. Additional modifications and improvements utilizing the discoveries of the present invention can be readily anticipated by those skilled in the art from the present disclosure, and such modifications and improvements may fairly be presumed to be within the scope and purview of the invention as defined by the claims that follow.

We claim:

1. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight; and

(2) a hydrogenation component comprising a predominant proportion of a porous support, other than a crystalline aluminosilicate, and a minor proportion of at least one constituent exhibiting hydrogenation activity.

2. The hydrocracking catalyst composite of claim **1** wherein the crystalline aluminosilicate component is prepared by base-exchanging a crystalline aluminosilicate with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions and mixtures thereof with one another, to replace at least about 90 percent of the sodium content of the original aluminosilicate with said ions and effectively to reduce the sodium content of said crystalline aluminosilicate component to below about 2 percent by weight.

3. The hydrocracking catalyst composite of claim **2** wherein the base-exchanged crystalline aluminosilicate is impregnated with a hydrogenation constituent selected from the group consisting of oxides of metals, sulfides of metals and metals of Groups VI and VIII of the Periodic Table.

4. The hydrocracking catalyst composite of claim **1** wherein the crystalline aluminosilicate component is selected from the group consisting of a crystalline Y aluminosilicate and a crystalline X aluminosilicate, base-exchanged with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions and mixtures thereof with one another, and having a sodium content of less than about 2 percent by weight.

5. The hydrocracking catalyst composite of claim **4** wherein the hydrogenation component comprises between about 1 and 8 percent by weight cobalt oxide and between about 3 and 20 percent by weight molybdenum trioxide.

6. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 4 and 30 percent of at least one constituent exhibiting hydrogenation activity, and the remainder alumina.

7. The hydrocracking catalyst composite of claim **6** wherein the crystalline aluminosilicate component is prepared by base-exchanging a crystalline aluminosilicate with ions selected from the group consisting of rare earth, hydrogen, hydrogen percursor, calcium, magnesium and manganese ions and mixtures thereof with one another, to replace at least about 90 percent of the sodium content of the original aluminosilicate with said ions and effectively to reduce the sodium content of the final crystalline aluminosilicate component to below about 2 percent by weight.

8. The hydrocracking catalyst composite of claim **7** wherein the base-exchange crystalline aluminosilicate is impregnated with a hydrogenation constituent selected from the group consisting of oxides of metals, sulfides of metals and metals of Groups VI and VIII of the Periodic Table.

9. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight, and having impregnated thereon at least one constituent exhibiting hydrogenation activity; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 4 and 30 percent of at least one constituent exhibiting hydrogenation activity, and the remainder alumina.

10. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina.

11. The hydrocracking catalyst composite of claim 10 wherein in the crystalline aluminosilicate component is selected from the group consisting of a crystalline Y aluminosilicate and a crystalline X aluminosilicate, base-exchanged with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions and mixtures thereof with one another, and having a sodium content of less than about 2 percent by weight.

12. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight and having impregnated thereon at least one constituent exhibiting hydrogenation activity; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina.

13. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component comprising a hydrogenation constituent, selected from the group consisting of oxides of metals, sulfides of metals, and metals of Groups VI and VIII of the Periodic Table, impregnated thereon, said crystalline aluminosilicate having uniform pore openings between 6 and 15 Angstrom units, and having been prepared by base-exchanging a crystalline aluminosilicate with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions and mixtures thereof with one another, to replace at least about 90 percent of the sodium content of the original aluminosilicate with said ions and effectively to reduce the sodium content of the crystalline aluminosilicate component to below about 2 percent by weight; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina.

14. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component containing between about 1 and 4 percent by weight cobalt oxide and between about 5 and 15 percent molybdenum oxide impregnated upon a crystalline aluminosilicate resulting from base-exchange of a crystalline aluminosilicate, having uniform pore openings between 6 and 15 Angstrom units, with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions and mixtures thereof with one another, to replace at least about 90 percent of the original sodium content of the original aluminosilicate with said ions and effectively to reduce the sodium content of said crystalline aluminosilicate component to below about 2 percent by weight; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina.

15. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a rare earth-containing crystalline aluminosilicate component having impregnated thereon between about 1 and 4 percent by weight cobalt oxide and between about 5 and 15 percent molybdenum oxide, said rare earth-containing crystalline aluminosilicate component having a sodium content below about 2 percent; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina.

16. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, base-exchanged with ions selected from the group consisting of hydrogen and hydrogen precursor ions and mixtures thereof with one another, having impregnated thereon between about 1 and 4 percent by weight cobalt oxide and between about 5 and 15 percent molybdenum oxide, said hydrogen-, hydrogen precursor-containing crystalline aluminosilicate component having a sodium content below about 2 percent; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina.

17. A process for converting a hydrocarbon charge which comprises contacting the same in the presence of hydrogen with a hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight; and

(2) a hydrogenation component comprising a predominant proportion of a porous support, other than a crystalline aluminosilicate, and a minor proportion of at least one constituent exhibiting hydrogenation activity.

18. A process for converting a hydrocarbon charge which comprises contacting the same in the presence of hydrogen with a hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component having a sodium content of less than 4 percent by weight; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 4 and 30 percent of at least one constituent exhibiting hydrogenation activity and the remainder alumina.

19. A process for converting a hydrocarbon charge which comprises contacting the same in the presence of hydrogen with a hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component having a sodium content of less than 4 percent by weight, and having impregnated thereon at least one constituent exhibiting hydrogenation activity; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 4 and 30 percent of at least one constituent exhibiting hydrogenation activity and the remainder alumina.

20. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **1**.

21. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **4**.

22. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **6**.

23. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **9**.

24. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **10**.

25. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **12**.

26. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F., at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **13**.

27. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **14**.

28. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **15**.

29. A process for hydrocracking 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 point of at least about 600° F., boiling substantially continuously between said initial boiling point and said end point; at a temperature between about 600° F. and about 950° F.; at a liquid hourly space velocity between about 0.1 and about 10; at a hydrogen partial pressure between about 700 and about 3000 pounds per square inch gauge; and at a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80; which process comprises contacting said petroleum hydrocarbon fraction with the hydrocracking catalyst composite of claim **16**.

30. A method of preparing a hydrocracking composite consisting essentially of pellets of a physical particle-form mixture, which method comprises combining two components, each component having a particle size of less than about 100 microns in diameter:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight; and

(2) a hydrogenation component comprising a predominant proportion of a porous support, other than a crystalline aluminosilicate, and a minor proportion of at least one constituent exhibiting hydrogenation activity; with a suitable binder material, in the form of pellets, and heating said pellets in an oxygen-containing atmosphere to effect substantially complete combustion of said binder material, whereby pellets of a two-component, particle-form mixture are formed.

31. A method of preparing a hydrocracking composite consisting essentially of pellets of a physical particle-form mixture, which method comprises combining two components:

(1) a rare earth-containing crystalline aluminosilicate component having impregnated thereon between

about 1 and 4 percent by weight cobalt oxide and between about 5 and 15 percent molybdenum oxide, said rare earth-containing crystalline aluminosilicate component having a sodium content below about 2 percent; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina; with a suitable binder material, in the form of pellets and heating said pellets in an oxygen-containing atmosphere to effect substantially complete combustion of said binder material, whereby pellets of a two-component, particle-form mixture are formed.

32. A method of preparing a hydrocracking composite consisting essentially of pellets of a physical particle-form mixture, which method comprises combining two components:

(1) a crystalline aluminosilicate component base-exchanged with ions selected from the group consisting of hydrogen and hydrogen precursor ions and mixtures thereof with one another, having impregnated thereon between about 1 and 4 percent by weight cobalt oxide and between about 5 and 15 percent molybdenum oxide, said crystalline aluminosilicate component having a sodium content below about 2 percent; and

(2) a hydrogenation component comprising between about 15 and 40 percent by weight silica, 1 and 8 percent cobalt oxide, 3 and 20 percent molybdenum trioxide and the remainder alumina; with a suitable binder material, in the form of pellets and heating said pellets in an oxygen-containing atmosphere to effect substantially complete combustion of said binder material, whereby pellets of a two-component, particle-form mixture are formed.

33. A hydrocracking catalyst composite consisting essentially of a physical particle-form mixture of two components:

(1) a crystalline aluminosilicate component, having a sodium content of less than 4 percent by weight; and

(2) a hydrogenation component comprising a predominant proportion of alumina and a minor proportion of at least one constituent exhibiting hydrogenation activity.

34. The hydrocracking catalyst composite of claim **33** wherein the crystalline aluminosilicate component is selected from the group consisting of a crystalline Y aluminosilicate and a crystalline X aluminosilicate, base-exchanged with ions selected from the group consisting of rare earth, hydrogen, hydrogen precursor, calcium, magnesium and manganese ions and mixtures thereof with one another, and having a sodium content of less than about 2 percent by weight.

35. The hydrocracking catalyst composite of claim **33** wherein the hydrogenation component comprises between about 1 and 8 percent by weight cobalt oxide and between about 3 and 20 percent by weight molybdenum trioxide.

References Cited by the Examiner

UNITED STATES PATENTS

2,854,401	9/1958	Weisz	208—111
2,974,099	3/1961	Anderson	208—112
3,173,854	3/1965	Eastwood et al.	208—111

DELBERT E. GANTZ, *Primary Examiner.*

A. D. SULLIVAN, *Examiner.*

A. RIMENS, *Assistant Examiner.*