

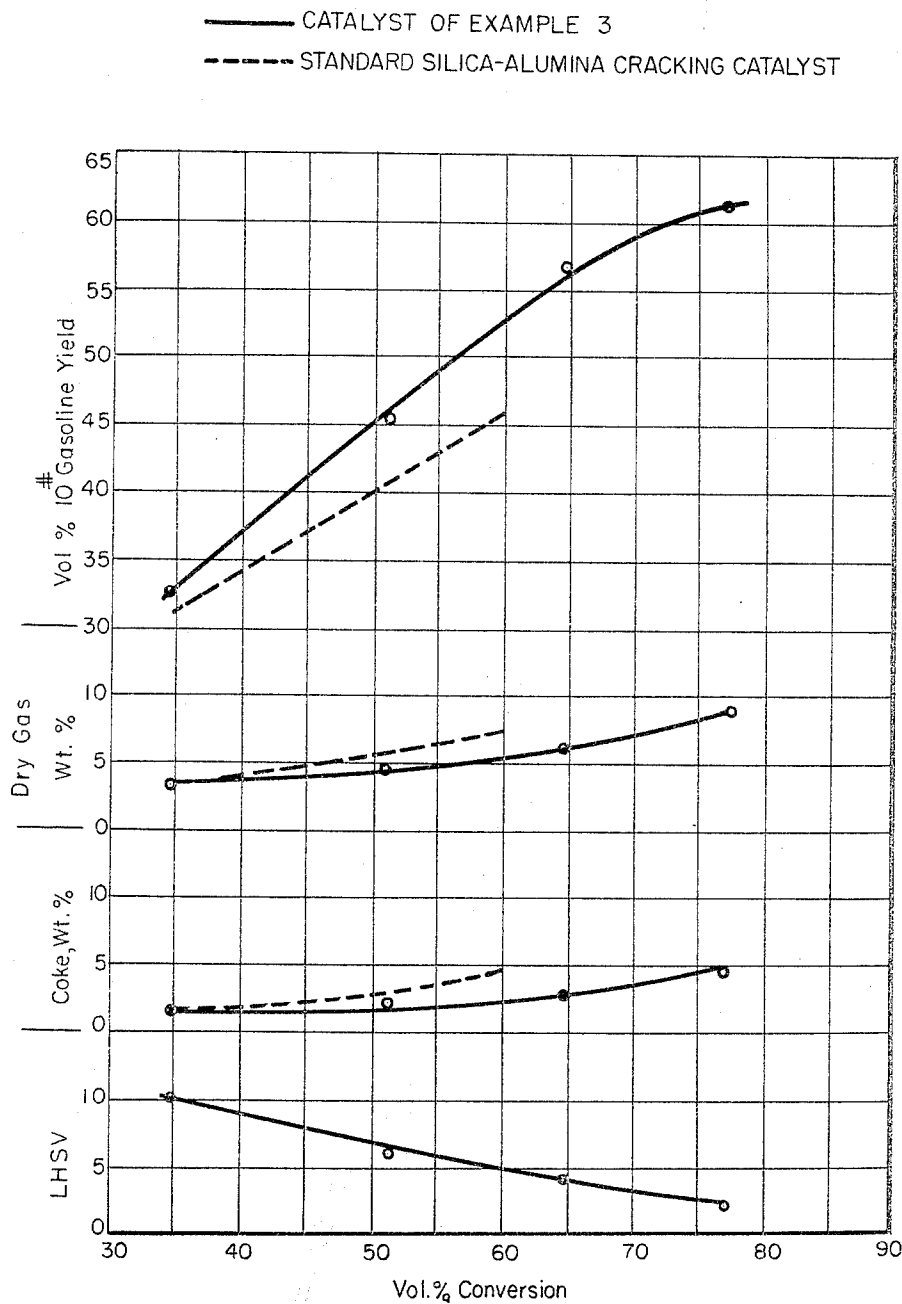
Sept. 6, 1966

C. J. PLANK ETAL

3,271,418

CATALYTIC CONVERSION OF HYDROCARBONS WITH A CRYSTALLINE
ALUMINO-SILICATE IN A SILICA-ALUMINA MATRIX

Filed June 22, 1965



Inventors
Charles J. Plank
Edward J. Rosinski
By *Raymond W. Barclay*
Attorney

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**CATALYTIC CONVERSION OF HYDROCARBONS
WITH A CRYSTALLINE ALUMINO-SILICATE IN
A SILICA-ALUMINA MATRIX**Charles J. Plank, Woodbury, and Edward J. Rosinski,
Deptford, N.J., assignors to Mobil Oil Corporation, a
corporation of New York

Filed June 22, 1965, Ser. No. 466,096

24 Claims. (Cl. 208—120)

This application is a continuation-in-part of one or
more of the following applications:

Serial No. 159,626¹—Filed December 15, 1961, now
abandoned.

Serial No. 161,237¹—Filed December 21, 1961, now
abandoned.

Serial No. 195,430¹—Filed May 17, 1962.

Serial No. 210,215¹—Filed July 16, 1962, now aban-
doned.

Serial No. 242,594¹—Filed December 6, 1962, now
abandoned.

Serial No. 242,648¹—Filed December 6, 1962, now
abandoned.

Serial No. 380,015¹—Filed July 2, 1964, now abandoned.

Serial No. 348,318²—Filed February 6, 1964, now aban-
doned.

Serial No. 380,986³—Filed June 30, 1964.

Serial No. 380,665⁴—Filed July 6, 1964.

The invention described herein relates to a process for
transforming organic compounds catalytically convertible
in the presence of acidic catalyst sites. Such conversion
processes include, by way of example, cracking (in-
cluding hydrocracking), alkylation, isomerization, polym-
erization, aromatization and dealkylation.

In one embodiment, the invention is concerned with an
improved catalyst composition comprising a crystalline
aluminosilicate having a structure of rigid three-dimen-
sional networks characterized by a system of cavities
with interconnecting pore openings having minimum di-
ameters greater than 4 Angstroms and less than 15
Angstroms, the cavities being connected with each other
in three dimensions by said pore openings, and possessing
activity in catalytically promoting the aforesaid processes
intimately combined with a porous material of substantial
but lesser activity. In another embodiment, the in-
vention is directed to a method for preparing the afore-
mentioned catalyst composition. Finely divided particles
of the above crystalline aluminosilicate portion of the
catalyst composite may be admixed with the porous ma-
terial in a variety of ways, such as, by incorporation in
a porous matrix of the material, including mechanical ad-
mixture of the same with particles of the porous ma-
terial.

In a particular embodiment, the present invention re-
lates to the catalytic conversion of a hydrocarbon charge
into lower boiling normally liquid and normally gaseous
products and to an improved cracking catalyst charac-
terized by usual attrition resistance, activity, selectivity
and stability to deactivation by steam. While the de-
scription which follows is directed, for the most part
to cracking of hydrocarbon charge stocks, it is within
the purview of this invention to utilize the catalyst as
such or with suitable modification, as hereinafter de-
scribed, in other processes catalyzed by the presence of
acidic catalyst sites.

¹ Which in turn is a continuation-in-part of Serial No.
42,284, filed July 12, 1960, and issued as U.S. 3,140,249 on
July 7, 1964.

² Which in turn is a division of Serial No. 210,215, filed
July 16, 1962.

³ Which in turn is a continuation of Serial No. 42,284, filed
July 12, 1960, and issued as U.S. 3,140,249 on July 7, 1964.

⁴ Which in turn is a continuation of Serial No. 364,301, filed
May 1, 1964, and issued as U.S. 3,140,253 on July 7, 1964.

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As is well known, there are numerous materials, both
of natural and synthetic origin, which have the ability to
catalyze the cracking of hydrocarbons. However, the
mere ability to catalyze cracking is far from sufficient to
afford a catalyst of commercial significance. Of the
presently commercially available cracking catalysts, a
synthetic silica-alumina composite catalyst is by far the
most widely used. While such type catalyst is superior
in many ways to the earlier employed clay catalysts and
is fairly satisfactory, it is subject to improvement, par-
ticularly in regard to its ability to afford a high yield of
useful product with a concomitant small yield of un-
desired product.

Modern catalytic processes, moreover, require catalysts
which are not only specifically active in the chemical re-
actions which are to be catalyzed but also possess phys-
ical characteristics required for successful commercial
operation. One of the outstanding physical attributes of
a commercial catalyst is the ability to resist attrition. The
ability of a particle to hold its shape in withstanding the
mechanical handling to which it is subjected upon stor-
age, shipment and use is a primary requirement for a
successful catalyst and for modern catalytic processes.

Thus, commercial catalytic cracking has been carried
out by contacting a hydrocarbon charge in the vapor or
liquid state with a catalyst of the type indicated here-
inabove under conditions of temperature, pressure and
time to achieve substantial conversion of the charge to
lower boiling hydrocarbons. Such cracking processes
are generally advantageously carried out employing
methods wherein the catalyst is subjected to continuous
handling. In these operations, a continuously moving
stream of catalyst is provided for the accomplishment of
conversion and thereafter the catalyst is continuously
regenerated and returned to the conversion zone. This
continuous handling and regeneration of the catalyst
particles results in considerable breakage and constant
abrasion, consuming the catalyst and giving rise to an
excessive amount of fines which are a loss since they gen-
erally cannot be reused in the same catalytic equipment.
Furthermore, there is a tendency for the catalyst fines
suspended in the gas or vapor present to act as an
abrasive in a manner analogous to sand blasting. This
not only wears away the equipment but also causes the
catalyst to take up foreign matter detrimental to its
catalytic properties. A hard porous catalyst having
the ability to withstand abrasion during the necessary
handling involved during continual conversion and re-
generation is definitely to be desired.

During catalytic conversion of high boiling hydrocar-
bons to lower boiling hydrocarbons, the reaction which
takes place is essentially a cracking to produce lighter
hydrocarbons but is accompanied by a number of com-
plex side reactions, such as aromatization, polymeriza-
tion, alkylation and the like. As a result of these com-
plex reactions, a hydrocarbonaceous deposit is laid down
on the catalyst commonly called "coke." The deposition
of coke tends to seriously impair the catalytic efficiency
of the catalyst for the principal reaction and the con-
version reaction is thereafter suspended after coke to the
extent of a few percent by weight has accumulated on the
catalyst. The catalytic surface is then regenerated by
burning the coke in a stream of oxidizing gas and the
catalyst is returned to the conversion stage of the cycle.

As will be realized, coke and other undesired products
are formed at the expense of useful products, such as
gasoline. It will also be evident that during the period
of regeneration, the catalyst is not being effectively em-
ployed for conversion purposes. It accordingly is high-
ly desirable not only to afford a large overall conversion
of the hydrocarbon charge, i.e. to provide a catalyst of
high activity, but also to afford an enhanced yield of

useful product, such as gasoline, while maintaining undesired product, such as coke, at a minimum. The ability of a cracking catalyst to so control and to direct the course of conversion is referred to as selectivity. Thus, an exceedingly useful and widely sought characteristic in a cracking catalyst is high selectivity.

Another important property desirable in a cracking catalyst is steam stability, i.e. the ability not to become deactivated in the presence of steam at an excessively high rate. As a result of coke formation, it has generally been necessary to regenerate the catalyst at frequent intervals, first by stripping out entrained oil by contacting with steam and then burning off the carbonaceous deposits by contacting with an oxygen-containing gas at an elevated temperature. However, it has been found that the cracking activity of the catalyst deteriorates upon repeated use and regeneration and the silica-alumina catalysts heretofore employed have been sensitive to steaming. Since steaming has been found to be the most effective way of removing entrained oil from the spent catalyst prior to thermal regeneration with air and since steam is encountered in the seals and kiln of a commercial catalytic cracking unit, it is apparent that a catalyst characterized by good steam stability is definitely to be desired.

Inorganic oxide amorphous gels heretofore employed as hydrocarbon conversion catalysts have generally been prepared by the formation of a sol of desired composition that sets to a hydrogel after lapse of a suitable period of time. The hydrogel is then dried to remove the liquid phase therefrom. It has heretofore been suggested that various finely divided water-insoluble solids be added to the sol before the same undergoes gelation for the purpose of increasing the porosity of the ultimate dried gel so that the regeneration characteristics thereof are enhanced upon use in catalytic hydrocarbon conversion operations. It has also been proposed that pulverized dried gel, clay and similar materials be incorporated in the hydrosol before gelation in order that the hydrogel resulting upon setting of such hydrosol may be subjected to rapid drying without undergoing substantial breakage. The improved regeneration characteristics and the improvement in drying obtained have been attributed to the fact that the finely divided solid contained in the hydrosol does not shrink to the extent that the hydrogel does during drying, thereby creating in the resulting dried gel a large number of macropores having diameters greater than about 1000 Angstrom units. While the gels so prepared containing pulverized material of appreciable particle size exhibit improvement in regeneration and during drying, the physical strength thereof has been weakened due to the presence of large pores in the gel structure.

Gel preparation has heretofore been carried out by drying hydrogel in a mass, which is subsequently broken up into pieces of desired size. Hydrogel has also been prepared and dried in the form of small pieces of predetermined shape such as obtained by extrusion, pelleting or other suitable means. In more recent years, gels have been produced in the form of spheroidal or microspheroidal shape which have been found to be less susceptible to attrition.

Prior to the present invention, a considerable number of materials have been proposed as catalysts for the conversion of hydrocarbons into one or more desired products. In the catalytic cracking of hydrocarbon oils, for example, wherein hydrocarbon oils of higher boiling range are converted into hydrocarbons of lower boiling range, notably hydrocarbons boiling in the motor fuel range, the catalysts most widely used are solid materials which behave in an acidic manner whereby hydrocarbons are cracked. Acidic catalysts of this type possess many desired characteristics, but have limited activity, selectivity, and stability. For example, synthetic silica-alumina gel composites, the most successful of such catalysts heretofore

used, provide limited yields of gasoline for a given yield of coke. Other such catalysts less widely used include those materials of an argillaceous nature, e.g. bentonite, halloysite, kaolin and montmorillonite, which generally have been subjected to prior acid treatment. Catalysts of this general type are relatively inexpensive, but are only moderately active, and exhibit a decline in activity over periods of many conversions and regeneration cycles. Some synthetic materials, such as silica-magnesia gels, are more active than conventional silica-alumina catalysts, but have the disadvantage of producing a gasoline product of low octane number. Materials of these same types have been used as the acid components, in conjunction with hydrogenation components, in hydrocracking catalysts.

It has previously been shown in our patents U.S. 3,140,249 and U.S. 3,140,253 that crystalline aluminosilicates having uniform pores in which a substantial proportion of original alkali metal content has been replaced with other metal cations and/or hydrogen ions constitute a new, highly efficacious class of catalysts for catalytic cracking of hydrocarbons.

The alkali metal crystalline aluminosilicate zeolites, e.g., sodium faujasite, although substantially as active as the conventional silica-alumina amorphous gel catalysts, give a product distribution which is very similar to that of thermal cracking and completely different from that obtained with silica-alumina gel. Stated differently, the selectivity of alkali metal zeolites is extremely poor compared even to silica-alumina. Additionally, certain alkali metal zeolites are quite unstable to steam treatment. For these reasons, the natural and synthetic alkali metal zeolites as found or produced are generally totally unsatisfactory for use as commercial cracking catalysts.

In accordance with the present invention, there are now provided novel catalytic compositions, methods for their manufacture and catalytic conversion in the presence thereof, which catalytic compositions are characterized by a low sodium content and comprise a crystalline aluminosilicate having a structure of rigid three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 4 Angstroms and less than 15 Angstroms, preferably between 6 and 15 Angstroms, the cavities being connected with each other in three dimensions by said pore openings, and possessing substantial catalytic activity intimately admixed with a porous material likewise characterized by substantial catalytic activity, but of an appreciably lower order than that of the crystalline aluminosilicate with which it is combined.

The present invention is based in part on the discovery that while crystalline aluminosilicates as above defined containing certain cations, and a lowered proportion of alkali metal cations (especially sodium) are highly active catalysts for hydrocarbon conversion, many unusual and unique effects and safeguards are obtained by admixing such crystalline aluminosilicate catalysts with certain types of material which themselves possess catalytic activities of a lower order, but which in admixture contribute effects to the combination, and thereby provide prospects for such combination or composite materials not possessed by either of the principal ingredients alone. Thus, while in the catalytic cracking of hydrocarbon oils into hydrocarbon products of lower molecular weight, for example, the reaction rates per unit volume of catalyst that are obtainable by such crystalline aluminosilicates above referred to, vary up to many thousand times the rates achieved with the best siliceous catalysts heretofore proposed, as a practical matter it is neither possible nor practical to utilize such high reaction rates when catalytic cracking is performed with methods currently in use or available.

Accordingly, one object of the present invention is to intermix such crystalline aluminosilicate catalysts with a material which will dilute and temper the activity there-

of so that currently available cracking equipment and methods may be employed, thereby avoiding great and sudden obsolescence thereof, while permitting the beneficial properties of such zeolite catalysts to be enjoyed commercially to the greatest extent practicable.

An additional object of the present invention is to utilize materials in the form of a matrix or in physical admixture which do more than perform a passive role in serving as a diluent, surface extender or control for the highly active zeolite catalyst component. Consonant therewith, the present invention comprises combining the highly active crystalline aluminosilicate zeolite catalysts referred to above with a major proportion of a catalytically active matrix material which, in such combination, will enhance the production of gasoline of higher octane values than are produced by cracking with such zeolitic catalysts alone, while concomitantly providing a composite catalyst composition which may be used at much higher space velocities than those suitable for the best prior catalysts, and which composite catalyst composition also has greatly superior properties of product selectivity and steam stability. Cracking may be effected in the presence of said composite catalyst composition utilizing well-known currently available techniques including, for example, those wherein the catalyst is employed as a fluidized mass or as a compact particle-form moving bed.

The crystalline aluminosilicates employed in preparation of the instant catalyst may be either natural or synthetic zeolites. Representative of particularly preferred zeolites are Zeolite X described in U.S. 2,882,244, Zeolite Y described in U.S. 3,130,007, as well as other crystalline aluminosilicate zeolites having pore openings of between 6 and 15 Angstroms. 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 these 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 essentially 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 greater than 4 Angstroms and less than 15 Angstroms, and preferably between 6 and 15 Angstroms, the ports being sufficiently large to admit the molecules of the hydrocarbon charge desired to be converted. The preferred crystalline aluminosilicate zeolites will have a rigid three-dimensional network characterized by a system of cavities and interconnecting ports or pore openings, the cavities being connected with each other in three dimensions by pore openings or ports which have minimum diameters of greater than 6 Angstrom units and less than 15 Angstrom units. A specific typical example of such a structure is that of the mineral faujasite.

The zeolite catalysts which comprise the high activity component of the composite catalyst composition of the invention are aluminosilicates which have been treated to replace all or at least a substantial proportion of the original alkali metal ions with other cations, as disclosed in U.S. Patent 3,140,249. Such other metal cations include calcium, magnesium, manganese, chromium, aluminum, zirconium, vanadium, nickel, cobalt, iron, rare earth metals, and mixtures of one or more of the foregoing. In a preferred embodiment, a major portion of the alkali metal cations of the zeolite are replaced by calcium, manganese, magnesium or rare earth metal cations.

Metal compounds and particularly metal salts broadly represent the source of the above noted metal cations. The product resulting from treatment with a fluid medium containing a metal salt contains activated crystalline aluminosilicate in which the structure thereof has been

modified primarily to the extent of having such metal cations chemisorbed or ionically bonded thereto.

The zeolite catalyst component may also be rendered highly acidic by having the fluid treating medium also contain a hydrogen ion or ion capable of conversion to a hydrogen ion. Inorganic and organic acids broadly represent the source of hydrogen ions and ammonium compounds or salts of organic nitrogen compounds, the source of cations capable of conversion upon thermal degradation to hydrogen ions.

In preparing the catalyst compositions of this invention, the initial crystalline alkali metal aluminosilicate zeolite can be contacted with a non-aqueous or preferably an aqueous fluid medium containing a compound capable of replacing by base exchange a substantial portion of the alkali metal content of the aluminosilicate with one or more of the aforementioned ions. Exchange of the aluminosilicate zeolite may be accomplished either before and/or after admixture with the matrix material. The concentration of replacing cation in the fluid exchange medium may vary within wide limits depending upon the precursor aluminosilicate, and its silica to alumina ratio. Where the aluminosilicate has a molar ratio of silica to alumina in excess of 6, the fluid exchange medium may have a pH of from 3 to 12; with a silica to alumina ratio between 5 and 6, the fluid medium may have a pH of from 3.5 to 12, and preferably 4.5 to 8.5; with a molar ratio of silica to alumina of less than 5, the fluid exchange medium has a permissible pH from 4.5 to 12, and preferably 4.5 to 8.5. Thus, depending on the silica to alumina ratio of the precursor aluminosilicate, the pH of the exchange medium varies within rather wide limits. Precursor aluminosilicates having a silica to alumina ratio of about 2.3 to 6.0 are preferred for use herein.

In carrying out the treatment with the fluid exchange medium, the procedure employed comprises contacting the aluminosilicate with the desired fluid medium until such time as the alkali metal cations present are substantially removed. Elevated temperatures tend to hasten the speed of treatment whereas the duration thereof varies inversely with the concentration of ions in the fluid medium. In general, the temperatures employed range from below ambient room temperature of about 24° C. up to temperatures below the decomposition temperatures of the aluminosilicate. Following the fluid treatment, the treated aluminosilicate may be washed with water, preferably distilled or deionized water, until the effluent wash water has a pH of between 5 and 8.

The actual procedure employed for carrying out the fluid treatment of the aluminosilicate may be accomplished in a batchwise or continuous method under atmospheric, sub-atmospheric or superatmospheric pressure. A solution of the ions to be introduced in the form of an aqueous or non-aqueous solution may be passed slowly through the fixed bed of an aluminosilicate. If desired, hydrothermal treatment or a corresponding non-aqueous treatment with polar solvents may be effected by introducing the aluminosilicate and fluid medium in a closed vessel maintained under autogenous pressure.

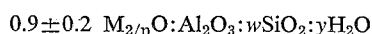
A wide variety of compounds of the metals noted hereinabove may be employed with facility as a source of replacing ions. Operable metal compounds generally include those which are sufficiently soluble in the fluid medium employed to afford the necessary ion transfer. Usually metal salts such as the chlorides, nitrates and sulfates are employed.

Of the aforementioned metals, particular preference is accorded the rare earth metals. Representative of the rare earth metals are cerium, lanthanum, praseodymium, neodymium, promethium (sometimes known as illinium), samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium and also closely related elements scandium and yttrium.

The rare earth metal salts employed can either be the salt of a single rare earth metal or mixtures of rare earth

metals, such as rare earth chlorides or didymium chlorides. As hereinafter referred to, a rare earth chloride solution is a mixture of rare earth chlorides consisting essentially of the chlorides of lanthanum, cerium, neodymium and praseodymium with minor amounts of samarium, gadolinium and yttrium. Rare earth chloride solutions are commercially available and the ones specifically referred to in the examples contain the chlorides of rare earth mixture having the relative composition cerium (as CeO_2) 48% by weight, lanthanum (as La_2O_3) 24% by weight, praseodymium (as Pr_6O_{11}) 5% by weight, neodymium (as Nd_2O_3) 17% by weight, samarium (as Sm_2O_3) 3% by weight, gadolinium (as Gd_2O_3) 2% by weight, and other rare earth oxides 0.8% by weight. Didymium chloride is also a mixture of rare earth chlorides but having a lower cerium content. It consists of the following rare earths determined as oxides: lanthanum 45–65% by weight, cerium 1–2% by weight, praseodymium 9–10% by weight, neodymium 32–33% by weight, samarium 5–7% by weight, gadolinium 3–4% by weight, yttrium 0.4% by weight, and other rare earths 1–2% by weight. It is to be understood that other mixtures of rare earths are also applicable for the preparation of the novel compositions of this invention, although lanthanum, neodymium, praseodymium, samarium and gadolinium as well as mixtures of rare earth cations containing a predominant amount of one or more of the above cations are preferred since these metals provide optimum activity for hydrocarbon conversion, including catalytic cracking.

Aluminosilicates which are treated with a fluid medium or media in the manner above described include a wide variety of aluminosilicates both natural and synthetic which have a crystalline or combination of crystalline and amorphous structure. However, it has been found that exceptionally superior catalysts can be obtained when the starting aluminosilicate has either a crystalline or a combination of crystalline and amorphous structure and possesses at least 0.4 and preferably 0.6 to 1.0 equivalent of metal cations per gram atom of aluminum. The aluminosilicates can be described as a three-dimensional framework of SiO_4 and AlO_4 tetrahedra in which the tetrahedra are cross linked by the sharing of oxygen atoms whereby the ratio of total aluminum and silicon atoms to oxygen atoms is 1:2. In their hydrated form, the aluminosilicates may be represented by the formula:



wherein M represents at least one cation which balances the electrovalence of the tetrahedra, n represents the valence of the cation, w the moles of SiO_2 and y the moles of H_2O . The cation can be one or more of a number of metal ions, depending upon whether the aluminosilicate is synthesized or occurs naturally.

Typical cations of the starting aluminosilicates are, in general, the alkali metals and alkaline earth metals, although others may be used. Although the proportions of inorganic oxides in the silicates and their spatial arrangements may vary affecting distinct properties in the aluminosilicates, a main characteristic of these materials is their ability to undergo dehydration without substantially affecting the SiO_4 and AlO_4 framework.

Aluminosilicates falling within the above formula are well known and include synthesized aluminosilicates, natural aluminosilicates, and aluminosilicates derived from certain caustic treated clays. Since the primary object of this invention is to provide a novel and unusual cracking catalyst, the aluminosilicate zeolite should have a pore size sufficiently large to afford entry and egress of the desired reactant molecules. In this regard, the crystalline aluminosilicates having a pore size greater than 4 and less than 15 Angstrom units are desired. Particularly preferred aluminosilicates are the faujasites, both natural and the synthetic X and Y types. Such aluminosilicates can be derived from caustic treated clays. Of the clay materials, montmorillonite and kaolin families

are representative types which include the sub-bentonites, such as bentonite, and the kaolins commonly identified as Dixie, McNamee, Georgia, and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays may be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. One way to render the clays suitable for use is to treat them with sodium hydroxide or potassium hydroxide, preferably in admixture with a source of silica, such as sand, silica gel or sodium silicate, and calcine at temperatures ranging from 230° F. to 1600° F. Following calcination, the fused material is crushed, dispersed in water and digested in the resulting alkaline solution. During the digestion, materials with varying degrees of crystallinity are crystallized out of solution. The solid material is separated from the alkaline material and thereafter washed and dried. The treatment can be effected by reacting mixtures falling within the following weight ratios:

$\text{Na}_2\text{O}/\text{clay}$ (dry basis) -----	1.0–6.6 to 1
SiO_2/clay (dry basis) -----	0.01–3.7 to 1
$\text{H}_2\text{O}/\text{Na}_2\text{O}$ (mole ratio) -----	35–100 to 1

It is to be understood that mixtures of the various aluminosilicates previously set forth can be employed as well as individual aluminosilicates.

In accordance with the invention, the highly active base-exchanged zeolite or aluminosilicate component of the present catalyst prepared in the foregoing manner is combined, dispersed or otherwise intimately intermixed with a material which itself has cracking activity, but of a lower order than that of the zeolite component. The mixture is made in such proportions that the resulting product contains a minor proportion, up to about 25 percent by weight of the highly active zeolite catalyst component, preferably ranging from 1% to 25% by weight in the final composite, while the porous, catalytically active material constitutes the balance or the majority of the balance thereof. The incorporation of the zeolite into the catalytically less active material can be accomplished either before, after or during chemical base-exchange treatment of the type described above, as well as before, during, or after activation of any of the components. Thus, it is possible to treat an aluminosilicate zeolite with the fluid medium containing exchange ions and then disperse the base-exchanged zeolite throughout the catalytically less active component in any desired manner. Alternatively the zeolite may be chemically treated to replace the alkali metal ions either during or after admixture with the less active material. In a further embodiment, the zeolite, lower activity material, and a source of the replacement cation or cations may be intermixed and then suitably treated to accomplish the desired replacement of the original alkali metal ions of the zeolite. If it is desired to have the zeolite contain added hydrogen ions, hydrogen precursors or mixtures thereof, the resulting composition may be treated with another fluid medium containing such ions.

The term "material of lower catalytic activity" or "porous matrix" material, as utilized herein, includes inorganic compositions with which the aluminosilicate can be combined, dispersed or otherwise intimately admixed wherein such material is itself catalytically active or is rendered active by interaction. It is to be understood that porosity of such material employed can either be inherent in the particular material or it can be introduced by mechanical or chemical means. As has been set forth, it is essential that such material be catalytically active in order to realize the fullest potential of the novel catalyst composition of this invention. The term "catalytically active" as used herein is intended to mean those materials which are capable of effecting at least 15 percent and preferably more than 20 percent conversion of a Mid-Continent gas oil having a boiling range of 450° to 950°

F. at a space velocity of 2 LHSV, a catalyst-to-oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure. Thermal conversion at these conditions is not more than about 5 percent. In other words, the matrix material utilized in the catalyst of this invention is sufficiently active to effect more than three times the conversion attributable solely to thermal conversion. Materials which do not meet the above standard are excluded from the scope of this invention since they do not provide the maximum benefit when composited with the active crystalline aluminosilicates previously described.

Representative active matrices which can be employed include preferably those silica-alumina catalysts known to have high octane number producing properties, e.g., silica-alumina gels, and certain raw clays, or raw clays which have been acid-treated. Other catalytically active matrix materials which may be used include inorganic oxides such as silica gel, alumina gel, and alumina-boria composites. Other gels suitable as matrices include those of silica-zirconia, silica-magnesia, silica-thoria, silica-rare earth oxide, silica-beryllia, silica-titania, as well as ternary combinations such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia. Of the foregoing gels, silica is generally present as the major component, and the other oxides of metals are present in minor proportion. Siliceous hydrogels utilized herein, and hydrogels obtained therefrom may be prepared by any method well known in the art, such as for example, hydrolysis of ethyl ortho silicate, acidification of an alkali metal silicate which may contain a compound of a metal, the oxide of which it is desired to cogel with silica, etc. The choice of porous matrix material will depend to some extent on the objectives sought. Thus, where a high yield of gasoline is desired, silica gel having sufficient inherent cracking activity to meet the above noted standard may be a preferred matrix. Where gasoline, in somewhat lower yield, but of high octane number is desired, silica-alumina is a preferred matrix.

Where the matrix material itself inherently possesses relatively high catalytic activity, it may be desirable to treat the matrix to render it catalytically less active. A notable example of matrix materials possessing high catalytic activity is silica-alumina gel. This material has itself been used as a conversion catalyst and has considerable catalytic activity by conventional standards. Such a matrix is preferably treated so that its activity is substantially decreased. Deactivation of a matrix, such as silica-alumina gel, may be carried out by severe heating or by steaming the material, or by exchanging with ions such as calcium or rare earths, or a combination of any of the foregoing treatments.

Typical catalytically active matrices and their characterizing activities under the above specified conditions after having been subjected to steam for 24 hours at a temperature of 1200° F. and a pressure of 15 p.s.i.g. are shown below:

	LHSV	Catalyst/Oil	Conversion
Halloysite Clay-----	2	3	32
McNamee Clay-----	2	3	25
Bentonite-----	2	3	17
Silica Gel-----	2	3	21
Silica-Alumina Gel (Conventional Cracking Catalyst Containing About 10 weight percent Al ₂ O ₃)-----	2	3	45

It will be understood that it is an essential feature of the catalyst of the present invention that the catalytically active crystalline aluminosilicate component thereof is mechanically intermixed, contained with or in, and distributed throughout a porous matrix material characterized by a substantial but lower catalytic activity than said crystalline aluminosilicate.

Catalytic compositions of the invention can be prepared by several methods wherein the aluminosilicate is reduced to a particle size less than 40 microns, preferably less than 10 microns, and intimately admixed with the matrix material. For example, when an inorganic oxide gel is used, the mixture may be made while the latter is in a hydrous state such as in the form of a hydrosol, hydrogel, wet gelatinous precipitate or mixtures thereof. Thus, finely divided active aluminosilicate can be mixed directly with a siliceous gel formed by hydrolyzing a basic solution of alkali metal silicate with an acid such as hydrochloric, sulfuric, etc. The mixing of the two components can be accomplished in any desired manner, such as in a ball mill or other types of mills. The aluminosilicate also may be dispersed in a hydrosol obtained by reacting an alkali metal silicate with an acid or alkaline coagulant. The hydrosol is then permitted to set in mass to a hydrogel which is thereafter dried and broken into pieces of desired shape or dried by conventional spray drying techniques or dispersed through a nozzle into a bath of oil or other water-immiscible suspending medium to obtain spheroidally shaped "bead" particles of catalyst such as described in U.S. Patent 2,384,946. The aluminosilicate-siliceous gel thus obtained is washed free of soluble salts, and thereafter dried and/or calcined as desired. The total alkali metal content of the resulting composite, including alkali metals which may be present in the aluminosilicate as an impurity, is less than about 4 percent and preferably less than about 1 percent by weight based on the total composition. If an inorganic oxide gel matrix is employed having too high an alkali metal content, the alkali metal content can be reduced by treatment with the fluid media previously set forth either before or after drying.

The catalytically active inorganic oxide matrix may also consist of a raw or natural clay, a calcined clay or a clay which has been chemically treated, e.g., with an acid medium or an alkali medium or both. The aluminosilicate can be incorporated in the clay simply by blending the two and fashioning the mixture into desired shapes. Suitable clays include attapulgite, kaolin, sepiolite, polygarskite, kaolinite, plastic ball clays, bentonite, montmorillonite, illite, chlorite and halloysite. Of the foregoing group, kaolinite, halloysite and montmorillonite are preferred.

The catalytic compositions contemplated herein may also comprise mechanical or physical mixtures of the crystalline aluminosilicate and porous material. Thus, particles of crystalline aluminosilicate or particles of high aluminosilicate content may be physically admixed with particles of the porous material under conditions such that each species of particle is free to move independently of each other. Such mixtures find particular application as fluid form catalysts wherein a dispersion of finely divided crystalline aluminosilicate is contained in a body of fluidized particles of the porous material.

In accordance with the invention, the use as matrices of materials having no or substantially no inherent catalytic activity of their own is to be avoided, or held to small proportions. Such materials include powdered metals, such as aluminum, and stainless steel, and powders of refractory oxides, such as zircon, barytes, etc., having very low internal pore volume. Minor amounts of such materials may occur adventitiously in the composite and may serve as diluents of catalytic activity. Also such materials may be deliberately introduced for such purposes as modifying specific heat, density, and similar properties of the composite. It will be understood, however, that the invention requires the presence in the composite of substantial quantity of matrix material which of itself has catalytic cracking activity, or is capable of acquiring catalytic cracking activity, albeit of a substantially lower order than that of the active zeolite component for which it serves both as a matrix and to supply some of the catalytic effects in which the zeolite

may be deficient or become deficient during extended use. In particular, the matrix material desirably should possess substantial ability to effect conversion to gasoline of relatively high octane number, and in this respect the silica-alumina gels and acid treated clays have been found superior, as will appear more particularly from the comparative examples hereinafter set forth.

It is generally preferred that there be a low content of alkali metal cations, e.g., Na, associated with the zeolite since the presence of alkali metal cations tends to suppress or limit catalytic properties, the activity of which as a general rule decreases with increasing content of alkali metal cations. Thus, for best results there should be a substantial reduction in the sodium content of the zeolite component of the composite catalyst. The overall amount of alkali metal which can be tolerated in the composite catalyst material will vary depending on the particular aluminosilicate and the catalytic use involved. The total amount of alkali metal is less than 4 percent by weight of the composite catalyst, and preferably less than 3 percent. In use, the amount of exchangeable alkali metal should be less than 1 percent by weight of the composite. Exchangeable alkali metal, such as sodium, is the alkali metal, for example sodium, removed when 5 grams of catalyst is contacted with 20 grams of 25 weight percent NH_4Cl solution at 180°F . for 24 hours and then washed until free of chloride ion. For cracking operations the total amount of exchangeable sodium in the composite of zeolite and matrix should be less than about 1 percent when aluminosilicates are used which have a silica to alumina ratio less than about 3. For aluminosilicates having a silica to alumina ratio greater than 3, the total alkali metal content should be less than 4 percent by weight, preferably less than 3 percent by weight based on the final composite. Thus when the matrix material itself is sodium free, a greater amount of sodium or alkali metal may be tolerated in the zeolite ingredient.

The catalyst product either separately before introduction into the catalytic cracking unit or during its residence in such unit is subjected to thermal treatment. Such treatment, which results in increased production, entails heating the composition in an atmosphere which does not adversely affect the catalyst such as air, nitrogen, hydrogen, flue gas, helium or other inert gas. Generally, the catalyst undergoing such treatment is heated in air to a temperature in the approximate range of 500°F . to 1500°F . for a period of at least 1 hour, and usually between 1 and 48 hours.

The catalytic selectivity of the composite increases upon exposure to steam. Exposure of the catalyst to steam is, as will appear from data set forth hereinafter, a highly desirable step in obtaining a product capable of affording an enhanced yield of gasoline. Steam treatment may be carried out either before or after introduction of the catalyst into the cracking unit at a temperature within the approximate range of 800°F . to 1500°F . for at least about 2 hours. Usually, steam at a temperature of about 1000°F . to 1300°F . will be used with the treating period extending from about 2 to about 100 hours. Temperatures above 1500°F . may be detrimental and should generally be avoided. Also, an atmosphere consisting of a substantial amount of steam, say at least about 10 percent by volume, but containing air or other gas substantially inert with respect to the composite being treated may be used and such mixtures may, in some instances, be desirable with the use of the more elevated temperatures to avoid possible deactivation of the catalyst. Exposure to steam may be that occurring during normal operation in a cracking unit or may be a separate step.

The cracking activity of the catalyst is illustrated by its ability to catalyze the conversion of a Mid-Continent gas oil to gasoline having an end point of 410°F . Vapors of the gas oil are passed through the catalyst at

temperatures of 875°F . or 900°F . substantially at atmospheric pressure at a feed rate of 1.5 to 8.0 volumes of liquid oil per volume of catalyst per hour for ten minutes. The method of measuring the instant catalyst was to compare the various product yields obtained with such catalyst with yields of the same products given by conventional silica-alumina catalyst at the same conversion level. The differences (Δ values) shown whereinafter represent the yields given by the present catalyst minus yields given by the conventional catalyst. These tests will sometimes hereinafter be referred to as CAT-C evaluations.

Cracking, utilizing the catalyst described herein, may be carried out at catalytic cracking conditions employing a temperature within the approximate range of 700°F . to 1200°F . and under a pressure ranging from sub-atmospheric pressure up to several hundred atmospheres. The contact time of the oil with the catalyst is adjusted in any case according to the conditions, the particular oil feed and the particular results desired to give a substantial amount of cracking to lower boiling products. Cracking may be effected in the presence of the instant catalyst utilizing well-known techniques including, for example, those wherein the catalyst is employed as a fluidized mass, fixed bed, or as a compact particle-form moving bed.

The catalysts of the present invention are especially suitable for use in both the "moving bed" and "fluid" cracking processes. In the "moving-bed process" (e.g. Thermoform Catalytic Cracking or TCC) catalyst particles are used which are generally in the range of about 0.08 to 0.25 inch in diameter. Useful reaction conditions include temperatures above about 850°F ., pressures from subatmospheric to approximately 3 atmospheres, catalyst to oil ratios of about 1.5-15 and liquid hourly space velocities of about 0.5 to 6. In the "fluidized catalytic cracking" process (or FCC) catalyst particles are used which are generally in the range of 10 to 150 microns in diameter. The commercial FCC processes include one or both of two types of cracking zones—a dilute bed (or "riser") and a fluid (or dense) bed. Useful reaction conditions in fluid catalytic cracking include temperatures above 850°F ., pressures from subatmospheric to three atmospheres, catalyst-to-oil ratios of 1 to 30, oil contact time less than about 12 to 15 seconds in the "riser," preferably less than about 6 seconds, wherein up to 100% of the desired conversion may take place in the "riser," and a catalyst residence (or contact) time of less than 15 minutes, preferably less than 10 minutes, in the fluidized (or dense) bed.

The following comparative examples serve to illustrate the advantages of the process and catalyst of the present invention without limiting the same:

EXAMPLE 1

Crystalline sodium aluminosilicate characterized by a structure having a uniform effective pore diameter in the range of 6 to 15 Angstrom units was prepared by admixture of the following solutions:

(A) Sodium silicate solution:		Lbs.
Water	-----	143
Sodium hydroxide (77.5% Na_2O)	-----	11
Sodium silicate (28.8% SiO_2)	-----	77.5
		231.5
(B) Sodium aluminate solution:		Lbs.
Water	-----	195
Sodium hydroxide (77.5% Na_2O)	-----	11
Sodium aluminate (43.5% Al_2O_3 and 30.2% Na_2O)	-----	25.6
		231.6

Solution B having a specific gravity at 111° F. of 1.128 was added to Solution A, having a specific gravity of 1.172 at 68° F. with vigorous agitation to form a creamy slurry. The resulting slurry was heated for 12 hours at 205° F. and was thereafter filtered. The filter cake was washed with water until the water in equilibrium with the washed solid had a pH of 11. The washed filter cake was then dried in air at a temperature of 280° F.

The dried product was then treated as follows: A 3.3 lb. portion of the dried cake was contacted with 4 batches of 6090 cc. each of 26 percent by weight aqueous solution of calcium chloride. Three contacts were made at a temperature of 180° F. for 24 hours each and one contact was made for about 72 hours at room temperature (approximately 75° F.). The filter cake obtained from the 4th concentrated calcium chloride treatment was further exchanged 4 times at room temperature (approximately 75° F.) with 6000 cc. each of an aqueous solution containing 2 percent by weight calcium chloride and 1 percent by weight ammonium chloride. Three of these were 2-hour exchanges and one was for approximately 19 hours. Thereafter, the filter cake was water-washed free of chloride ion and dried in air at 230° F. for 20 hours.

A silica hydrogel was prepared by admixture of the following solutions:

(C) Sodium silicate solution:

2882 cc. of sodium silicate solution containing 0.208 gram $\text{SiO}_2/\text{cc.}$ and having $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of .3/1.

(D) Acid solution:

384 cc. of 50% aqueous sulfuric acid solution
6734 cc. of water

Solution C was cooled to 40° F. and Solution D was cooled to 33° F. These solutions were mixed adding Solution C to Solution D. The resulting silica hydrosol was allowed to gel at 8.5 pH and the hydrogel so obtained was aged at room temperature (approximately 75° F.) for 20 hours. The hydrogel was then cut into cubes and base-exchanged with 1 percent aqueous sulfuric acid solution at a temperature of about 75° F. for four contact periods, two of which were overnight (approximately 20 hours), one of five hours, and one of two hours duration. The treated hydrogel was then washed free of sulfate ion.

The washed silica hydrogel in the amount of 7538 grams containing 5.97 weight percent SiO_2 was intimately mixed with 150 grams of the above-described calcium-ammonium aluminosilicate, equivalent to 25 percent by weight crystalline aluminosilicate on a finished catalyst basis, along with 1500 cc. of water by ball milling together for 24 hours at room temperature (about 75° F.). The resulting wet slurry was then dried at 275° F. for 20 hours in air and then calcined for 10 hours in air at 1000° F.

Before testing for gas oil cracking, this catalyst was treated with 100 percent steam at 1225° F. for 20 hours at atmospheric pressure. As will be evident from the cracking data hereinafter set forth in Table I, this catalyst afforded an approximately 57 percent conversion of the gas oil charge at 1.5 liquid hourly space velocity. In addition to the above activity, it is apparent from the data that the cracking selectivity of this catalyst also was good. Thus, at the 57 percent conversion level, this catalyst afforded 6 percent more gasoline as compared to the standard commercial silica-alumina catalyst. This gain was at the expense of 5.3 percent less C_4 's and 2 percent less dry gas than the standard silica-alumina catalyst.

EXAMPLE 2

Crystalline sodium aluminosilicate was prepared as in Example 1 having a weight mean particle diameter of 4.5 microns. The finely divided sodium aluminosilicate was incorporated into a silica gel resulting from admixture of the following solutions.

(A) Sodium silicate solution:

12.2 lbs. sodium silicate ($\text{Na}_2\text{O}/\text{SiO}_2=0.3/1$)

8.8 lbs. water

1.9 lbs. sodium aluminosilicate powder containing 55% solids at 230° F.

(B) Acid solution:

27.65 lbs. water

2.95 lbs. 97% aqueous sulfuric acid solution

Solution A having a specific gravity of 1.220 at 80° F. and Solution B having a specific gravity of 1.061 at 78° F. were continuously mixed together through a nozzle using 398 cc. per minute of the silicate solution at 46° F. and 328 cc. per minute of the acid solution at 46° F. The resulting hydrosol, containing 25 percent by weight dispersed crystalline sodium aluminosilicate powder on a finished catalyst basis, was formed into spheroidal hydrogel beads by introducing globules of the sol into an oil medium such as described in the aforementioned Marisic patent. The hydrosol particles so formed set to firm hydrogel beads in 2.7 seconds at a pH of 8.2-9.1.

The resulting hydrogel beads were placed in a 2 percent by weight aqueous solution of calcium chloride base-exchange solution using $\frac{1}{2}$ volume of solution per volume of beads. The calcium chloride base-exchange was continued for a total of three 2-hour and one overnight (approximately 20 hours) contact. This exchange was followed by 8 contacts with a combined exchange aqueous solution of 2 percent by weight calcium chloride and 1 percent by weight ammonium chloride. Six of these latter contacts were carried out for 2 hours and two were conducted for approximately 20 hours. The base-exchanged hydrogel was then washed continuously until the effluent water was free of chloride ion.

The washed hydrogel beads were then dried in air at 270° F. for 20 hours and calcined at 1000° F. in air for 10 hours. The resulting catalyst upon analysis was found to contain 0.13 weight percent sodium, 3.58 weight percent calcium, 8.05 weight percent alumina, less than 0.09 percent sulfate and the balance silica.

This catalyst was steam treated and evaluated for cracking characteristics as described in Example 1. The results of cracking with this catalyst are set forth in Table I hereinbelow. It will be seen from such data that this catalyst afforded approximately 74 percent conversion of the gas oil charge at 1.5 liquid hourly space velocity. Such results represent a marked improvement over those obtained with the catalyst of Example 1 and are in sharp contrast with those obtained with a standard silica-alumina cracking catalyst. In addition to its very high activity, it is apparent from the data set forth in Table I that the cracking selectivity of this catalyst was unusually good. Thus, at the 74 percent conversion level, this catalyst produced 14.5 percent more gasoline as compared to the standard commercial silicate-alumina catalyst. This exceptional gain was at the expense of 9.4 percent less C_4 's, 3.7 less dry gas and 2.8 percent less coke than the standard silica-alumina catalyst.

EXAMPLE 3

Another portion of the crystalline sodium aluminosilicate used in Example 2 was incorporated, to the extent of 25 percent by weight, in a silica-alumina gel matrix in a manner identical with that employed in the previous example.

The hydrogel in this instance was prepared by admixture of the following solutions.

(A) Sodium silicate solution:

42.6 wt. percent sodium silicate

($\text{Na}_2\text{O}/\text{SiO}_2=0.3/1$)

53.1 wt. percent water

4.3 wt. percent sodium aluminosilicate powder containing 55% solids at 230° F.

(B) Acid solution:

- 93.34 wt. percent water
3.43 wt. percent aluminum sulfate
3.23 wt. percent sulfuric acid

Solution A having a specific gravity of 1.191 at 76° F. and Solution B having a specific gravity of 1.059 at 79° F. were continuously mixed together through a mixing nozzle using 398 cc. per minute of the silicate solution at

more gasoline was obtained over the standard silica-alumina cracking catalyst along with 2.8 percent less dry gas and 4.4 percent less coke. At a liquid hourly space velocity of 3, this catalyst still provided a 65.8 volume percent conversion with a 10.4 percent gasoline advantage over the standard silica-alumina catalyst at the same conversion along with 2.9 percent less dry gas and 2.1 percent less coke.

Table I

Example No.-----	1	2	3
Physical Properties:			
Apparent Density g./cc. Steamed ¹ -----	0.54	0.50	0.55
Surface Area m. ² /g.:			
Fresh-----	577	442	526
Steamed ¹ -----	284	366	259
Composition:			
Na, wt. percent-----		0.13	0.31
Ca, wt. percent-----	2.2	3.58	3.96
Al ₂ O ₃ , wt. percent-----		8.05	13.1
SO ₄ , wt. percent-----		<0.09	<0.09

CRACKING DATA OF STEAMED¹ CATALYSTS

Conversion, Vol. Percent-----	56.7	74.5	52.0	80.4	65.8
LHSV-----	1.5	1.5	3.0	1.5	3.0
10 R.V.P. Gasol., Vol. Percent-----	46.8	62.3	46.1	59.1	55.0
XsC ₄ 's, Vol. Percent-----	10.1	12.8	6.8	19.9	12.7
C ₅ +Gaso., Vol. Percent-----	44.4	59.0	43.1	56.8	52.2
Total C ₄ 's, Vol. Percent-----	12.6	16.1	9.8	22.2	15.5
Dry Gas, Wt. Percent-----	5.2	6.7	4.4	8.8	5.9
Coke, Wt. Percent-----	4.5	5.7	3.4	6.8	3.8
H ₂ , Wt. Percent-----	0.05	0.02	0.01	0.03	0.02

A VALUES TO STANDARD SILICA-ALUMINA CATALYST.

10 R.V.P. Gasol., Vol. Percent-----	+6.0	+14.5	+7.4	+9.9	+10.4
XsC ₄ 's, Vol. Percent-----	-5.8	-10.3	-7.2	-5.6	-6.8
C ₅ +Gaso., Vol. Percent-----	+5.6	+13.7	+6.3	+10.0	+9.8
Total C ₄ 's, Vol. Percent-----	-5.3	-9.4	-6.1	-5.9	-6.2
Dry Gas, Wt. Percent-----	-2.0	-3.7	-1.9	-2.8	-2.9
Coke, Wt. Percent-----	+0.3	-2.8	-0.1	-4.4	-2.1

¹ Catalyst steamed 20 hours at 1,225° F. with 100% steam at atmospheric pressure.

² Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, 0.15 weight percent Cr₂O₃ and remainder SiO₂.

58° F. and 320 cc. per minute of the acid solution at 40° F. The resulting hydrosol, containing 25 percent by weight dispersed crystalline sodium aluminosilicate powder, on a finished catalyst basis, was formed into hydrogel beads at 63° F. with a gelation time of 1.7 seconds at a pH of 8.5.

The resulting hydrogel beads were placed in a 2 percent by weight aqueous solution of calcium chloride base-exchange solution immediately after forming, using ½ volume of solution per volume of beads. The calcium chloride base-exchange was continued for a total of three 2-hour and one overnight (approximately 20 hours) contacts at room temperature (approximately 75° F.). This exchange was followed by a combined exchange with an aqueous solution containing 2 percent by weight calcium chloride and 1 percent by weight ammonium chloride. Six of these contacts were carried out for 2 hours and two were conducted for approximately 20 hours. The base-exchanged hydrogel was then washed, dried, calcined and steam treated as in Example 2. The resulting catalyst contained, on a weight basis, 0.31 percent sodium, 3.96 percent calcium, 13.1 percent alumina, less than 0.09 percent sulfate and the balance silica. The surface area of the calcined catalyst before steam treatment was 526 m.²/gram and after steaming, the surface area was 259 m.²/gram.

This catalyst was evaluated for catalytic cracking in the manner described in the previous examples. The data obtained and summarized in Table I show the exceptionally high activity of this catalyst. Thus, an 80.4 percent conversion of the gas oil charge was obtained at 1.5 liquid hourly space velocity, along with good selectivity. A gasoline advantage of 9.9 percent

The catalyst of Example 3 was also further evaluated for gas oil cracking at various conversion levels. The conditions of cracking and data obtained are shown in Table II below:

Table II

LHSV-----	2	4	6	10
Cat./Oil-----	3	1.5	1.0	0.6
Temp., ° F-----	900	900	900	900
Yields:				
Conversion, Vol. Percent-----	77.0	64.6	51.0	34.4
C ₅ +Gaso., Vol. Percent-----	58.0	52.9	42.4	29.8
10# Gasol., Vol. Percent-----	61.3	56.9	45.9	32.6
Excess C ₄ , Vol. Percent-----	15.8	9.3	7.0	3.9
Total C ₄ , Vol. Percent-----	19.1	13.3	10.5	6.7
Dry Gas, Wt. Percent-----	8.9	6.3	4.8	3.3
Coke, Wt. Percent-----	4.9	2.9	2.1	1.3
Hydrogen, Wt. Percent-----	0.034	0.019	0.024	0.014

A VALUES TO STANDARD SILICA-ALUMINA CATALYST¹

C ₅ +Gaso., Vol. Percent-----	+8.5	+7.1	+3.9	+1.4
10# Gasol., Vol. Percent-----	+10.0	+8.9	+5.0	+2.0
Total C ₄ 's Vol. Percent-----	-4.0	-4.8	-2.8	-0.8
Dry Gas, Wt. Percent-----	-2.4	-2.1	-1.3	-0.4
Coke, Wt. Percent-----	-3.1	-2.6	-0.9	-0.1

¹ Silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃ and remainder SiO₂.

The change in selectivity at the above various conversion levels is shown graphically in the attached figure wherein the liquid hourly space velocity employed, the gasoline yield, and the amount of dry gas and coke produced are plotted against the volume percent conversion and compared with the results obtained under identical conditions with a standard silica-alumina cracking catalyst. It will be seen from the figure and the data of Table II, the

catalyst of the invention not only possessed marked selectivity and activity advantages over the conventional silica-alumina cracking catalyst but also was capable of efficient cracking at conversions far above the maximum prac-

These catalysts were evaluated for cracking characteristics in the same manner as the previous catalysts and the results are shown below together with the results of Examples 4-6 in Table III:

Table III

Example No.-----	4	5	6	7	8	9
Description:						
Matrix-----	(¹)	(¹)	(¹)	(²)	(²)	(²)
Wt. percent Crystalline Aluminosilicate-----	10	25	40	10	25	40
Composition:						
Na, Wt. percent-----	0.03	0.11	0.36	0.12	0.2	0.51
Ca, Wt. percent-----	2.39	3.65	4.67	3.06	4.03	3.35
Al ₂ O ₃ , Wt. percent-----				8.8	11.9	11.6
SO ₄ , Wt. percent-----	<0.09	<0.09	<0.09			<0.09

CRACKING DATA OF STEAMED * CATALYSTS

Conversion, Vol. percent-----	45.7	69.7	75.5	67.9	73	76.4
LHSV-----	1.5	1.5	1.5	1.5	1.5	1.5
10 R.V.P. Gasol., Vol. percent-----	41.5	60.1	54.7	54.9	57.7	55.5
XsC ₄ 's, Vol. percent-----	5.5	10.7	17.3	14.0	15.8	18.8
C ₂ + Gasol., Vol. percent-----	38.6	56.4	52.4	54.0	55.3	52.9
Total C ₄ 's, Vol. percent-----	8.0	14.4	19.6	16.4	18.3	21.0
Dry Gas, Wt. percent-----	3.5	5.4	8.3	6.5	7.3	8.3
Coke, Wt. percent-----	2.9	5.1	8.4	4.5	5.3	2.9
H ₂ , Wt. percent-----	0.01	0.02	0.05	0.02	0.03	0.03

A VALUES TO STANDARD SILICA-ALUMINA CATALYST *

10 R.V.P. Gasol., Vol. percent-----	+6.0	+12.6	+6.1	+9.4	+10.4	+6.7
XsC ₄ 's, Vol. percent-----	-6.3	-10.4	-7.1	-6.3	-6.7	-4.9
C ₂ + Gasol., Vol. percent-----	+4.9	+12.6	+6.2	+9.2	+10.4	+7.1
Total C ₄ 's, Vol. percent-----	-5.2	-9.0	-7.2	-6.2	-6.6	-5.2
Dry Gas, Wt. percent-----	-1.7	-4.2	-2.8	-2.7	-2.9	-2.5
Coke, Wt. percent-----	+0.2	-1.9	-1.6	-2.0	-2.8	-1.3

¹ SiO₂.

² SiO₂-Al₂O₃.

* Steamed 20 hours at 1,225° F. with 100% steam at atmospheric pressure.

* Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, 0.15 weight percent Cr₂O₃ and remainder SiO₂.

tical limit obtainable with the conventional catalyst. Indeed, if comparison is made at the higher conversions, the catalyst of the invention showed increasingly greater advantages over the standard silica-alumina catalyst.

EXAMPLES 4-6

The catalysts of these examples were prepared in a manner entirely analogous to that of Example 2 with the exception that the content of crystalline aluminosilicate incorporated in the silica gel matrix was varied as follows.

Example:	Percent weight of crystalline aluminosilicate
4 -----	10
5 -----	25
6 -----	40

These catalysts were evaluated for cracking characteristics in the manner described hereinabove and the results are shown hereinafter in Table III.

By reference to such data, it will be seen that as the content of crystalline aluminosilicate was increased, the sodium and calcium content of the finished catalyst increased and the conversion of gas oil was increased. In this series maximum selectivity was obtained with the catalyst of 25% weight crystalline material, affording a 12.6 percent volume gasoline advantage and 9.0 volume percent less C₄'s, 4.2 weight percent less dry gas and 1.9 weight percent less coke as compared to the standard silica-alumina catalyst.

EXAMPLES 7-9

The catalysts of these examples were prepared in a manner entirely analogous to that of Example 3 with the exception that the content of crystalline aluminosilicate incorporated in the silica-alumina gel matrix was varied as follows.

Example:	Percent weight of crystalline aluminosilicate
7 -----	10
8 -----	25
9 -----	40

Referring to the above tabulated data, it will again be seen that as the content of crystalline aluminosilicate was increased for the catalysts of these examples, the sodium and calcium content of the finished catalyst increased and conversion of the gas oil charge increased. Maximum selectivity was achieved with the catalyst of 25 percent weight crystalline material, affording a 10.4 volume gasoline advantage and 6.6 volume percent less C₄'s, 2.9 weight percent less dry gas and 2.8 weight percent less coke as compared to the standard silica-alumina catalyst.

EXAMPLE 10

The catalyst of this example was prepared in a manner analogous to that of Example 3 by admixture of the following solutions.

(A) Sodium silicate solution:

34.8 lbs. sodium silicate (Na₂O/SiO₂=0.3/1)

32.62 lbs. water

6.5 lbs. sodium aluminosilicate powder containing 55 percent solids at 230° F.

(B) Acid solution:

57.1 lbs. water

4.23 lbs. aluminum sulfate [Al₂(SO₄)₃·18H₂O]

1.98 lbs. sulfuric acid

Solution A having a specific gravity of 1.202 at 75° F. and Solution B having a specific gravity of 1.057 at 76° F. were continuously mixed together through a mixing nozzle using 362 cc./minute of the silicate solution and 350 cc./minute of the acid solution. The resulting hydrosol, containing 25 percent by weight dispersed crystalline sodium aluminosilicate powder, on a finished catalyst basis, was formed into hydrogel beads at 64° F. with a gelation time of 2.3 seconds at a pH of 8.5.

The resulting hydrogel beads were base-exchanged, water-washed, dried, calcined and steam treated in the same manner as Example 3. The resulting catalyst contained, on a weight basis, 0.32 percent sodium, 3.88

percent calcium, and 12.6 percent alumina, less than 0.03 percent sulfate and remainder silica.

This catalyst was evaluated for catalytic cracking as described hereinabove and the data obtained are herein-after summarized in Table IV. Referring to such data, it will be seen that conversion of the gas oil charge was 59.9 volume percent, affording a 9.0 volume percent gasoline advantage, together with 2.3 weight percent less dry gas and 1.3 weight percent less coke than the standard silica-alumina cracking catalyst.

EXAMPLE 11

For this catalyst, a batch of crystalline sodium aluminosilicate was prepared in a manner identical with that described in Example 1. This material was converted before drying to a mixed calcium-ammonium aluminosilicate by base-exchanging the filter cake with 4 batches of 6090 cc. each of a 27.5 percent by weight aqueous solution of calcium chloride. Three contacts were made at a temperature of 180° F. for 24 hours each and one contact was made for about 72 hours at room temperature (approximately 75° F.). The filter cake obtained from the 4th concentrated calcium chloride treatment was further exchanged 4 times at approximately 75° F. with 6090 cc. each of an aqueous solution containing 2 percent by weight calcium chloride and 1 percent by weight ammonium chloride. Three of these were 2-hour exchanges and one was for approximately 16 hours. Thereafter, the filter cake was washed free of chloride ion, dried in air at 230° F. for 20 hours.

The powdered calcium-ammonium aluminosilicate was then incorporated to the extent of 25 percent by weight based on the finished catalyst in a silica-alumina gel matrix containing approximately 93 percent SiO₂ and 7 percent Al₂O₃ and processed in a manner identical with that employed in preparing the catalyst of Example 10.

This catalyst was evaluated for catalytic cracking and the results together with those obtained with the catalyst of Example 10 are shown in Table IV below.

Table IV

Example No.	10	11
Composition:		
Na, Wt. Percent	0.32	0.06
Ca, Wt. Percent	3.88	3.9
Al ₂ O ₃ , Wt. Percent	12.6	11.7
SO ₄ , Wt. Percent	0.03	0.09

CRACKING DATA OF STEAMED¹ CATALYST

Conversion, Vol. Percent	59.9	56.5
LHSV	3.0	3.0
10 R.V.P. Gasol., Vol. Percent	51.3	49.2
XsC ₄ 's, Vol. Percent	9.9	9.8
C ₅ +Gasol., Vol. Percent	48.4	46.5
Total C ₄ 's, Vol. Percent	12.8	12.4
Dry Gas, Wt. Percent	5.5	5.1
Coke, Wt. Percent	3.4	3.0
H ₂ , Wt. Percent	0.02	0.02

Δ VALUES TO STANDARD SILICA-ALUMINA CATALYST²

10 R.V.P. Gasol., Vol. Percent	+9.0	+9.4
XsC ₄ 's, Vol. Percent	-7.2	-5.0
C ₅ +Gasol., Vol. Percent	+8.3	+8.1
Total C ₄ 's, Vol. Percent	-6.5	-5.4
Dry Gas, Wt. Percent	-2.3	-2.0
Coke, Wt. Percent	-1.3	-1.2

¹ Steamed 20 hours at 1,225° F. with 100% steam at atmospheric pressure.
² Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, 0.15 weight percent Cr₂O₃ and remainder SiO₂.

It will be seen from a comparison of the results obtained with the catalysts of Examples 10 and 11 that there was little difference in activity and selectivity between these two catalysts, showing that improved cracking characteristics of the resulting catalyst may be achieved by conversion through base-exchange to the desired form of the crystalline sodium aluminosilicate either before or after incorporation in the siliceous hydrogel.

EXAMPLES 12-14

These three examples were all prepared in a manner identical with that of Example 3 with the exception that the relative proportions of acid and silicate solutions were varied by changing their relative rates of addition through the mixing nozzle. Such variations served to control the pH of the resulting sol and hydrogel as follows:

Example:	pH
12	7-7.5
13	8.1-8.9
14	9.5-9.7

These catalysts were evaluated for cracking characteristics in the same manner as the previous catalysts and the results are shown in Table V below:

Table V

Example No.	12	13	14
Forming pH	7-7.5	8.1-8.9	9.5-9.7
Composition:			
Na, Wt. percent	0.19	0.59	0.15
Ca, Wt. percent	4.09	4.28	5.18
Al ₂ O ₃ , Wt. percent	12.6	12.6	12.2
SO ₄ , Wt. percent	<0.09	<0.09	<0.09

CRACKING DATA OF STEAMED¹ CATALYSTS

Conversion, Vol. percent	65.1	67.7	60.8
LHSV	3.0	3.0	3.0
10 R.V.P. Gasol., Vol. percent	56.1	55.9	52.8
XsC ₄ 's, Vol. percent	12.3	13.3	10.0
C ₅ +Gasol., Vol. percent	53.4	53.4	50.0
Total C ₄ 's, Vol. percent	15.0	15.9	12.8
Dry Gas, Wt. percent	5.5	6.4	5.2
Coke, Wt. percent	3.2	4.3	3.8
H ₂ , Wt. percent	0.02	0.02	0.02

Δ Values to standard silica-alumina catalyst²

10 R.V.P. Gasol., Vol. percent	+11.7	+11.6	+10.1
XsC ₄ 's, Vol. percent	-6.8	-6.9	-7.4
C ₅ +Gasol., Vol. percent	+11.3	+11.4	+9.5
Total C ₄ 's, Vol. percent	-6.4	-6.6	-6.8
Dry Gas, Wt. percent	-3.2	-2.8	-2.7
Coke, Wt. percent	-2.6	-2.2	-1.1

¹ Steamed 20 hours at 1,225° F. with 100% steam at atmospheric pressure.
² Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, 0.15 weight percent Cr₂O₃ and remainder SiO₂.

It will be evident from the foregoing data that change in forming pH of the hydrosol and hydrogel had no marked effect on the ability of the catalysts to efficiently crack the gas oil charge stock. These data show that while the activity is somewhat lower for the catalyst prepared at 9.5 pH, the selectivity of this catalyst is still very good.

EXAMPLE 15

The catalyst of this example was prepared in a manner identical to that of Example 13 with the exception that it was not subjected to steam treatment prior to testing for cracking characteristics. The catalyst of Example 13 was steamed 20 hours at 1225° F. with 100 percent steam before testing. The benefits of steam treatment are clearly evident from a comparison of the cracking data shown for the steamed and unsteamed catalyst in Table VI below:

Table VI

	Example 15	Example 13
Conversion, Vol. percent	74.9	67.7

Δ VALUES TO STANDARD SILICA-ALUMINA CATALYST

C ₅ +Gasoline, Vol. percent	-1.3	+11.4
Total C ₄ 's, Vol. percent	+0.9	-6.6
Dry Gas, Wt. percent	-0.5	-2.8
Coke, Wt. percent	-0.3	-2.2

It will be seen from the above data, an initial steam treatment at essentially atmosphere pressure is very bene-

ficial to the product distribution obtained with such catalyst. While such benefit may be gained by slow steaming at low temperatures or low steam partial pressures in a commercial catalytic cracking operation using unsteamed catalyst, pretreating of the catalyst described herein with steam before introduction into a cracking unit is, as shown by the above data, very beneficial.

EXAMPLES 16-18

These catalysts were prepared in the form of bead hydrogels, containing 25 percent by weight of crystalline sodium aluminosilicate, in a manner identical with that of Example 3. These materials were processed in a manner comparable to that used in Example 3 except that the composition of the base-exchange solutions was varied. The nature of the exchange solutions used in each of these examples together with the results obtained upon cracking with the catalysts in each instance as shown in Table VII below:

Table VII

Example No.	16	17	18
Forming pH	8.5	8.4-8.5	8.4-8.5
Base Exchange:			
Solution	CaCl ₂	CaCl ₂ -MgCl ₂	(¹)
pH	8.5-9		6.4
Conc. Wt. percent	2	2	2
2 hours	9	9	9
Exchange 16 hours	3	3	3

Physical Properties of washed, dried (20 hrs. at 275° F. in air) and calcined (10 hrs. in air at 1,000° F.) product

Apparent density, g./cc.:			
Fresh	0.55	0.56	
Steamed ²			
Surface Area, m. ² /g.:			
Fresh	505	503	
Steamed ²	339	303	
Composition:			
Na, Wt. percent	0.21	0.24	0.44
Ca, Wt. percent		Ca 4.13	
Al ₂ O ₃ , Wt. percent	5.74	Mg 1.32	
SiO ₂ , Wt. percent	13.0	12.7	11.5
Conversion, Vol. percent	61.3	59.4	74.8
LHSV	3.0	3.0	3.0
10 R.V.P. Gaso., Vol. percent	54.5	51.8	57.4
XsC ₃ 's, Vol. percent	8.9	9.1	16.8
C ₂ +Gaso., Vol. percent	51.0	48.7	55.0
Total C ₄ 's, Vol. percent	12.4	12.2	19.3
Dry Gas, Wt. percent	5.0	5.3	7.8
Coke, Wt. percent	3.6	3.5	6.1
H ₂ , Wt. percent	0.02	0.02	0.03

Δ Values to Standard Silica-Alumina Catalyst ³

10 R.V.P. Gaso., Vol. percent	+11.5	+9.7	+9.6
XsC ₃ 's, Vol. percent	-8.6	-7.7	-6.4
C ₂ +Gaso., vol. percent	+10.3	+8.7	+9.5
Total C ₄ 's, Vol. percent	-7.4	-6.8	-6.3
Dry Gas, Wt. percent	-3.0	-2.4	-2.7
Coke, Wt. percent	-1.4	-1.1	-2.5

¹ Rare earth metal chloride.

² Steamed 20 hours at 1,225° F. with 100% steam at atmospheric pressure.

³ Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, 0.15 weight percent Cr₂O₃ and remainder SiO₂.

It will be seen from the above data of Example 16 that use of a calcium chloride base-exchange solution afforded a catalyst possessing highly effective cracking characteristics.

The results of Example 17 show that a mixture of calcium and magnesium ions used for base-exchange afforded a resulting catalyst characterized by high activity and high selectivity.

The catalyst of Example 18 was prepared employing a 2 percent by weight aqueous solution of rare earth chloride derived from monazite sand and containing cerium chloride, along with the chlorides of praseodymium, lanthanum, neodymium and samarium. The finished catalyst product, upon analyses, showed a sodium content of less than 0.5 weight percent and a total rare earth oxide content of about 15 weight percent. From the cracking results set forth in Table VII, it will be seen

that this catalyst possessed a high activity with a volume percent conversion of 75 and an excellent selectivity affording a gasoline advantage of 9.6 volume percent with 2.7 weight percent less dry gas and 2.5 weight percent less coke than the standard silica-alumina cracking catalyst.

EXAMPLE 19

This example illustrates that other siliceous gels having acidic cracking sites, in addition to silica-alumina, may be used as the matrix through which the crystalline aluminosilicate is dispersed with results comparable to the catalysts made with silica-alumina.

In accordance with this example, crystalline sodium aluminosilicate, such as used in Example 2, was incorporated, to the extent of 25 percent by weight of the finished catalyst, in silica-zirconia gel matrix.

The hydrogel in this instance was prepared by admixture of the following solutions.

- (A) Sodium silicate solution:
12.2 lbs. sodium silicate (Na₂O/SiO₂=0.3/1)
8.95/lbs. water
1.9 lbs. sodium aluminosilicate powder containing 55 percent solids at 230° F.
- (B) Acid solution:
18.85 lbs. water
1.49 lbs. zirconium sulfate [Zr(SO₄)₂·2.4 H₂O]
0.76 lb. sulfuric acid.

Solution A having a specific gravity of 1.238 at 76° F. and Solution B having a specific gravity of 1.060 at 60° F. were continuously mixed together through a mixing nozzle using 380 cc./minute of the silicate solution and 336 cc./minute of the acid-zirconium sulfate solution. The resulting hydrosol was formed into hydrogel beads at 57° F. with a gelation time of 1.4 seconds at a pH of 8.3.

The resulting hydrogel beads were base-exchanged, washed, dried, calcined and steam treated in the same manner as in Example 3. The finished catalyst contained, on a weight basis, 0.19 percent sodium, 3.55 percent calcium, 7.9 percent zirconia and 6.36 percent alumina.

Catalytic cracking evaluation of this catalyst showed it to be characterized by substantially the same activity and selectivity as the catalyst of Example 10 which had a matrix of silica-alumina gel. The comparative cracking data obtained with each of these catalysts are shown below in Table VIII:

Table VIII

Catalyst of Example	10	19
Type of Gel Matrix	(¹)	(²)

CRACKING DATA ON STEAMED CATALYSTS:

Conversion, Vol. Percent	59.9	64.0
LHSV	3.0	3.0
10 R.V.P. Gaso., Vol. Percent	51.3	54.9
XsC ₃ 's, Vol. Percent	9.9	10.4
C ₂ +Gaso., Vol. Percent	48.4	51.9
Total C ₄ 's, Vol. Percent	12.8	13.5
Dry Gas, Wt. Percent	5.5	5.9
Coke, Wt. Percent	3.4	3.8
H ₂ , Wt. Percent	0.02	

Δ VALUES TO STANDARD SILICA-ALUMINA CATALYST ³

10 R.V.P. Gaso., Vol. Percent	+9.0	+8.0
XsC ₃ 's, Vol. Percent	-7.2	-7.0
C ₂ +Gaso., Vol. Percent	+8.3	+7.1
Total C ₄ 's, Vol. Percent	-6.5	-6.1
Dry Gas, Wt. Percent	-2.3	-2.0
Coke, Wt. Percent	-1.3	-0.1

¹ SiO₂/Al₂O₃.

² SiO₂/ZrO₂.

³ Steam treated 20 hours at 1225° F. in 100% steam at atmospheric pressure.

⁴ Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, 0.15 weight percent Cr₂O₃ and remainder SiO₂.

It will be evident from the above that the catalyst of this example possessed good activity and high selectivity affording a gasoline advantage of 8.0 volume percent and 2.0 weight percent less dry gas than the standard silica-alumina cracking catalyst.

EXAMPLE 20

This example illustrates the use of silica as a matrix for an active calcium acid crystalline aluminosilicate. The composition was prepared by admixture of the following solutions:

(A) Sodium silicate solution:	Lbs.
Water -----	8.1
Sodium Silicate (28.9 wt.% SiO ₂ , 8.9 wt.% Na ₂ O, 62.2 wt.% H ₂ O) -----	12.2
	20.3
(B) Aluminosilicate slurry:	
Water -----	0.66
Sodium aluminosilicate (13X) -----	1.9

Solutions A and B were mixed together to form a silicate slurry solution having a specific gravity at 80° F. of 1.2220. The resulting solution was mixed with—

(C) Acid solution:	Lbs.
Water -----	41.47
Sulfuric acid (96.7%) -----	4.42
Specific gravity at 80° F. -----	1.060

These solutions were mixed together through a nozzle using 410 cc./min. of the silicate solution at 50° F. with 300 cc./min. of the acid solution at 44° F. The resulting hydrosol, containing dispersed crystalline sodium aluminosilicate powder, was formed into spheroidal hydrogel beads by introducing globules of the sol into an oil medium. The hydrosol particles so formed set to firm hydrogel beads in 2 seconds at 64° F. The resulting hydrogel beads were base exchanged initially with an aqueous solution of 2 percent by weight calcium chloride, using four contacts of 2 hours each. This exchange was

followed by eight contacts of 2 hours each with a combined exchange aqueous solution of 2 percent by weight calcium chloride and 1 percent by weight ammonium chloride. The base-exchanged hydrogel was washed with water until free of chloride ion. The washed hydrogel beads were then dried in air at 270° F., calcined at 1000° F. in air for 10 hours and treated with steam at atmospheric pressure for 20 hours at 1225° F. The resulting catalyst, upon analysis, was found to contain 0.11 weight percent sodium and 3.65 weight percent calcium.

This catalyst was evaluated for cracking characteristics as described in Example 1 at a temperature of 875° F., using a catalyst to oil ratio of 4 and a liquid hourly space velocity of 1.5. The results of such evaluation are set forth in Table IX. As will be seen, the catalyst afforded a 69.7 volume percent conversion of the gas oil charge and at this level produced an exceptional 12.6 percent more gasoline as compared to the standard commercial silica-alumina catalyst.

EXAMPLE 21

The catalyst of this example was prepared in a manner similar to that of Example 20 using the same type silicate solution with an acid solution containing aluminum sulfate to form a silica-alumina hydrogel matrix for the crystalline aluminosilicate component. The hydrogel product was base-exchanged, dried, calcined and steamed as described in the preceding example. The finished catalyst analyzed 0.2 weight percent sodium, 12.2 weight percent alumina and 4.01 weight percent calcium.

The results of evaluating this catalyst for cracking characteristics are set forth in Table IX. As will be seen by reference to such table, this catalyst was as active as the catalyst of Example 21 wherein a silica matrix was employed, but less selective, yielding +8.2 volume percent C₅+ gasoline advantage over the conventional silica-alumina cracking catalyst at the same conversion, which is approximately 4 volume percent less selective than the catalyst of Example 20.

Table IX

Examples	20	21
Description:		
Matrix	Silica	Silica/Alumina
Fines:		
Type	NaX	NaX
Conc.	25	25
Base Exchange:		
Solution	CaCl ₂ →CaCl ₂ -NH ₄ Cl	CaCl ₂ →CaCl ₂ -NH ₄ Cl
Conc., Wt. percent	2 2 1	2 2 1
Contacts (No. X Hrs.)	4 (2 hr.) 8 (2 hr.)	4 (2 hr.) 8 (2 hrs.)
Composition:		
Na, Wt. percent	0.11	0.2
Al ₂ O ₃ , Wt. percent	3.65	12.2
Ca, Wt. percent		4.01
Physical Properties:		
App. Dens. g./cc.	0.49	
Surface Area, m. ² /g.	414	512
Steamed	342	217

CRACKING DATA OF STEAMED¹ CATALYSTS

Conversion, Vol. percent	69.7	70.8
LHSV	1.5	1.5
10 R.V.P. Gaso., Vol. percent	60.1	54.1
Excess C ₄ 's, Vol. percent	10.7	14.4
C ₅ + Gasoline, Vol. percent	56.4	51.4
Total C ₄ 's, Vol. percent	14.4	17.2
Dry Gas, Wt. percent	5.4	6.8
Coke, Wt. percent	5.1	4.6
H ₂ , Wt. percent	0.02	0.02

ADVANTAGE OVER STANDARD SILICA-ALUMINA CATALYST²

10 R.V.P. Gaso., Vol. percent	+12.6	+8.7
Excess C ₄ 's, Vol. percent	-10.4	-6.1
C ₅ + Gasoline, Vol. percent	+12.6	+8.2
Total C ₄ 's, Vol. percent	-9.0	-5.5
Dry Gas, Wt. percent	-4.2	-2.5
Coke, Wt. percent	-1.9	-1.9

¹ Steam treated 20 hrs. at 1,225° F., 1 atm.

² Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, 0.15 weight percent Cr₂O₃ and remainder SiO₂.

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Examples 22-24 illustrate the catalytic advantages of using silica as matrix for a rare earth metal exchanged crystalline aluminosilicate of the X faujasite type.

EXAMPLE 22

The catalyst of this example was prepared by continuously mixing through a nozzle a silicate solution containing the active crystalline aluminosilicate component along with raw clay for diffusivity control, with a solution of acetic acid. The solution compositions were as follows.

(A) Sodium silicate slurry solution:

(1) Silicate clay slurry:	Lbs.
Water -----	6.55
Sodium Silicate (28.9 wt.% SiO ₂ , 8.9 wt.% Na ₂ O, 62.2 wt.% H ₂ O) -----	9.83
McNamee Clay (87 wt.% solids at 1000° F.) -----	0.652
(2) Aluminosilicate slurry:	
Water -----	57.0
Rare earth exchanged X-type faujasite (52.2% wt.% solids at 1000° F.) ----	0.66

These two parts of solution A were mixed together and maintained in an agitated condition. The specific gravity of the mixed solution at 78° F. was 1.174.

(B) Acid solution:

Water -----	lbs. 27.5
Acetic acid (99%) -----	lbs. 2.61
Specific gravity at 80° F. -----	1.010

Solutions A and B were mixed through a nozzle using 528 cc./min. at 68° F. of solution A and 442 cc./min. at 42° F. of solution B. The resulting hydrosol, having a pH of 8.3, was formed into spheroidal hydrogel beads by introducing globules of the sol into an oil medium. The hydrosol particles so formed set to firm hydrogel beads in 7.1 seconds at 68° F.

A portion of the resulting hydrogel beads were base exchanged at room temperature continuously for 24 hours with a 1.4 weight percent aqueous solution of (NH₄)₂SO₄. The base exchanged hydrogel was washed with water until free of sulfate ions, dried in air at 270° F. for 20 hours, calcined in air for 10 hours at 1000° F. and finally treated with steam at 15 p.s.i.g. for 24 hours at 1200° F. The final catalyst analyzed 0.03 weight percent sodium and 2.85 weight percent rare earth metal oxides [(RE)₂O₃].

Catalytic data obtained utilizing this catalyst are summarized in Table X. These data show a progressive activity increase from 54.6 to 56 volume percent conversion at 4 LHSV as the steam treat was increased from 24 hours to 72 hours. At the same conversion level, the C₆+ gasoline advantage over conventional silica-alumina cracking catalyst increased from +7.1 to +9.4 volume percent.

EXAMPLE 23

The preparation of the catalyst of this example differed from that of the previous example in method of base exchange.

Another portion of the hydrogel beads, prepared as described in Example 22, was exchanged for 24 hours continuously using a 1 weight percent aqueous solution of a mixture of rare earth metal chlorides (RECl₃·6H₂O) having a composition expressed as oxides as follows:

	Weight percent
CeO ₂ -----	48
La ₂ O ₃ -----	24
Pr ₆ O ₁₁ -----	5
Nd ₂ O ₃ -----	17
Sm ₂ O ₃ -----	3
Gd ₂ O ₃ -----	2
Other rare earth metal chlorides -----	0.8

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The base exchanged hydrogel was washed with water, dried, calcined and steam treated in exactly the same manner as in Example 22. The final catalyst analyzed 0.05 weight percent sodium and 8.72 weight percent rare earth metal oxides [(RE)₂O₃].

Catalytic evaluation data are summarized in Table X. These data show a progressive increase in activity from 53.3 to 58.5 volume percent conversion at 4 LHSV as the time of exposure to steam increases from 24 to 72 hours at 1200° F. and 15 p.s.i.g.

EXAMPLE 24

The catalyst of this example was prepared in a manner entirely analogous to Example 22 except that the acid used was sulfuric acid and the active ingredient was a rare earth metal exchanged synthetic faujasite of the X type which had been precalcined 10 hours at 1000° F. prior to dispersing in the silicate solution.

The resulting hydrogel was processed in the same manner as in Example 22, base exchanging continuously for 24 hours with a 1.4 weight percent aqueous solution of (NH₄)₂SO₄, followed by water washing, drying, calcining and steam treatment. The final catalyst analyzed 0.066 weight percent sodium and 2.92 weight percent rare earth metal oxides [(RE)₂O₃].

Catalytic evaluation data are summarized below in Table X. These data show this catalyst to be quite similar to Examples 22 and 23 giving increased conversion from 54.6 to 57.3 at 4 LHSV as steaming is increased from 24 to 72 hours at 1200° F. with steam at 15 p.s.i.g.

Particularly important are the data of the last line of Table X. They show that these catalysts with the low activity silica matrix exhibit superior selectivity for gasoline production.

The following examples demonstrate that a low activity matrix of silica-rare earth metal oxide afforded catalytic selectivity advantages similar to those realized with use of a silica matrix. The catalytic activity of catalysts wherein matrices of silica-rare earth metal oxides were employed are described below:

EXAMPLE 25

The catalyst of this example was prepared by admixture of the following solutions.

(A) Silicate solution:

(1) Sodium silicate solution:	Lbs.
Water -----	10.52
Sodium Silicate (28.9 wt.% SiO ₂ , 8.9 wt.% Na ₂ O, 62.2 wt.% H ₂ O) -----	20.85
(2) Aluminosilicate slurry	
Water -----	9.95
Sodium aluminosilicate (13X) -----	1.22

These two parts of solution A were mixed together yielding a solution having a specific gravity of 1.189 at 72° F.

(B) Acid solution:

	Lbs.
Water -----	29.68
Sulfuric acid (97.6 wt. percent) -----	1.97
Rare earth metal chloride (RECl ₃ ·6H ₂ O) ----	0.87
Specific gravity at 74° F. -----	1.054

Solutions A and B were mixed together continuously in a nozzle using 444 cc./min. at 74° F. of solution A and 404 cc./min. at 60° F. of solution B. The resulting hydrosol having a pH of 8.4 was formed into hydrogel beads with a gelation time of 2 seconds at 75° F.

Table X

Silica Matrix Durabead Catalysts

Example	22			23			24		
Steaming ¹ Time, hrs.	24	48	72	24	48	72	24	48	72
Forming pH	8.2			8.2			8.4		
Base Exchange:									
Solution	(NH ₄) ₂ SO ₄			RECl ₃ ·6H ₂ O			(NH ₄) ₂ SO ₄		
Conc., wt. percent	1.4			1			1.4		
Composition:									
Na, wt. percent	0.03			0.05			0.066		
(RE) ₂ O ₃ , wt. percent	2.85			8.72			2.92		
Physical Properties: Surface Area, m. ² /g., Steamed	266	234	206	312	292	277	229	208	181
Catalytic Evaluation Conditions:									
LHSV	4	4	4	4	4	4	4	4	4
Catalyst/oil	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Conversion, vol. percent	54.6	54.9	56.8	56.0	53.3	58.5	54.6	55.8	57.3
10 RVP Gasol., vol. percent	49.3	50.4	52.1	52.5	47.1	52.3	49.9	50.9	53.5
Excess C ₄ 's vol. percent	8.1	7.3	7.8	6.9	8.1	7.5	8.0	7.5	7.5
C ₅ + Gasoline, vol. percent	46.7	47.5	49.3	49.6	44.5	49.3	50.8	47.2	50.5
Total C ₄ 's, vol. percent	10.7	10.2	10.6	9.9	10.6	10.5	11.0	10.7	10.5
Dry Gas, wt. percent	5.2	5.0	4.6	5.2	5.5	5.0	4.7	4.9	4.5
Coke, wt. percent	1.61	1.77	1.6	1.4	2.3	1.8	1.9	2.0	1.5
H ₂ , wt. percent	0.44	0.44	0.01	0.03	0.05	0.04	0.03	0.05	0.03

A ADVANTAGE OVER STANDARD SILICA-ALUMINA CATALYST²

10 RVP Gasol., vol. percent	+8.2	+9.1	+9.8	+10.6	+6.8	+9.7	+10.4	+8.9	+9.2	+10.9
Excess C ₄ 's, vol. percent	-4.8	-5.7	-5.9	-6.4	-4.3	-6.3	-6.1	-4.9	-5.7	-8.3
C ₅ + Gasoline, vol. percent	+7.1	+7.7	+8.7	+9.4	+5.7	+8.6	+9.2	+7.5	+8.1	+9.5
Total C ₄ 's, vol. percent	-3.7	-4.4	-4.5	-5.0	-3.4	-4.8	-4.8	-3.8	-4.6	-4.8
Dry Gas, wt. percent	-1.8	-2.0	-2.3	-2.6	-1.7	-1.9	-2.5	-2.3	-2.2	-2.9
Coke, wt. percent										
C ₅ + Gasoline Delta Over REHX in silica-alumina matrix	+1.7	+2.1	+3.0	+3.6	+0.5	+2.6	+2.5	+2.1	+3.0	+3.5

¹ Steam treated at 1200° F. and 15 p.s.i.g.

² Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, and 90 percent SiO₂.

The resulting hydrogel beads were base exchanged initially with a single contact for 16 hours with a 2 weight percent aqueous solution of rare earth metal chlorides followed by a continuous exchange for 24 hours with a 1 weight percent aqueous solution of NH₄Cl. The base exchanged hydrogel product was washed with water until free of chloride. The washed product was dried in air at 270° F. for 20 hours, calcined 10 hours in air at 1000° F. and then treated for 24 hours with 15 p.s.i.g. steam at 1200° F. The final catalyst analyzed 0.03 weight percent sodium and 12.2 weight percent rare earth metal oxides [(RE)₂O₃].

Catalytic data obtained utilizing this catalyst and summarized in Table XI show that the catalyst is characterized by exceptional selectivity.

EXAMPLE 26

The catalyst of this example was prepared in essentially the same manner as that of the preceding example except that the rare earth component was lanthanum instead of the composite rare earths. The hydrogel was formed at 7.3 pH. In this example, the lanthanum oxide content was lower in the final catalyst since the catalyst was base exchanged only with a 1 weight percent solution of ammonium chloride continuously for 24 hours.

The preparational details and catalytic results obtained upon use of this catalyst are hereinafter summarized in Table XI.

EXAMPLE 27

The catalyst of this example was prepared in essentially the same manner as that of Example 25 except that the matrix was a silica-lanthanum oxide gel formed at 7.4 pH and the aluminosilicate was a synthetic sodium faujasite prepared by caustic silica fusion of raw McNamee clay.

The hydrogel product was also base exchanged with a 2 weight percent aqueous solution of LaCl₃·6H₂O for a single 15 hour contact followed by continuous treatment with a 1 weight percent aqueous NH₄Cl solution for 24 hours. Washing, drying, calcining and steaming were carried out as described in Example 25. The final

catalyst analyzed 0.03 weight percent sodium and 6.3 weight percent lanthanum oxide.

Catalytic data obtained utilizing this catalyst establish the same to be characterized by unusual selectivity.

Such data, together with those for Examples 25 and 26, are set forth in Table XI below:

The following examples demonstrate advantages from reduced matrix contribution through controlled alumina content.

EXAMPLE 28

The catalyst of this example was prepared by dispersing the sodium X form of active aluminosilicate into a silica-alumina hydrogel matrix having an alumina content of 2.5 weight percent Al₂O₃. The hydrogel was prepared in bead form utilizing techniques described hereinabove. the resulting hydrogel was base exchanged with an aqueous solution containing 1 weight percent of rare earth metal chlorides (RECl₃·6H₂O) and 1 weight percent of NH₄Cl continuously for 24 hours. Such exchange was with a flow of base exchange solution equal to ½ volume of solution per hour per volume of bead hydrogel. The hydrogel particles were thereafter washed, dried, calcined and steam treated in the manner described in Example 22. The final catalyst analyzed 0.09 weight percent sodium and 7.92 weight percent rare earth metal oxides [(RE)₂O₃].

Catalyst preparational details and evaluation data are shown hereinafter in Table XII.

EXAMPLE 29

The catalyst of this example was prepared by dispersing a high silica synthetic faujasite of the Y type pre-exchanged with a combined rare earth chloride and ammonium chloride solution into a silica-alumina hydrogel matrix having an alumina content of 1.5 weight percent Al₂O₃. In addition, raw McNamee clay was added for diffusivity control. The resulting hydrogel, in bead form, was base exchanged with an aqueous solution containing a combined 1.4 wt. percent (NH₄)₂SO₄+0.2 wt. percent RECl₃·6H₂O continuously for 24 hours. Such exchange was with a flow of base exchange solution equal to ½ volume of solution per hour per volume of bead hydrogel.

The hydrogel particles were thereafter washed, dried, calcined and steam treated as described in the preceding example. The final catalyst analyzed 0.07 weight percent sodium and 3.39 weight percent rare earth metal oxide [(RE)₂O₃].

EXAMPLE 30

The catalyst of this example was prepared by incorporating rare earth exchanged XY faujasite, formed from clay by a caustic-silicate fusion method followed by rare earth exchange into some of the original natural clay.

Table XI

Example	25	26	27
Steaming ¹ Time, hrs	24	24	24
Forming pH	8.4	7.3	7.4
Base Exchange:			
Solution	RECl ₃ →NH ₄ Cl	NH ₄ Cl	LaCl ₃ →NH ₄ Cl
Conc., wt. percent	2	1	2
Composition:			
Na, wt. percent	0.03	0.04	0.03
(RE) ₂ O ₃ , wt. percent	12.2	4.09 La ₂ O ₃	6.3 La ₂ O ₃
Physical Properties:			
Surface Area, m. ² /g., Steamed	356	376	367
Catalytic Evaluation Conditions:			
LHSV	4	4	4
Catalyst/oil	1.5	1.5	1.5
Conversion, vol. percent	56.0	52.9	58.6
10 RVP Gasol., vol. percent	52.2	48.9	54.9
Excess C ₄ 's, vol. percent	7.2	7.2	5.7
C ₃ +Gasoline, vol. percent	49.2	46.3	51.2
Total C ₄ 's, vol. percent	10.2	9.8	9.4
Dry Gas, wt. percent	4.8	4.4	5.3
Coke, wt. percent	1.7	1.7	1.7
H ₂ , wt. percent	0.02	0.02	0.03

Δ ADVANTAGE OVER STANDARD SILICA-ALUMINA CATALYST²

10 RVP Gasol., vol. percent	+9.4	+7.9	+10.7
Excess C ₄ 's, vol. percent	-5.3	-4.2	-7.6
C ₃ +Gasoline, vol. percent	+8.7	+7.5	+9.2
Total C ₄ 's, vol. percent	-4.6	-3.9	-6.1
Dry Gas, wt. percent	-2.1	-2.0	-2.1
Coke, wt. percent	-2.1	-1.6	-2.6
Delta to REHX in silica-alumina matrix	+2.5	+1.9	+2.8

¹ Steam treated at 1200° F. and 15 p.s.i.g.

² Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, and 90 percent SiO₂.

Catalyst preparational details and evaluation data showing the unusual selectivity of this catalyst are set forth in Table XII below:

The active component was prepared by the caustic fusion method described in the co-pending application, Serial No. 186,804, filed April 11, 1962. The activated

Table XII

LOW ALUMINA MATRIX CATALYSTS

Example	29	30
Steaming ¹ Time, hrs	30	24
Forming pH	8.5	8.4
Description:		
Matrix SiO ₂ /Al ₂ O ₃	97.5/2.5	98.5/1.5
Fines:		
A. Type	NaX	REHY
Conc.	10	4
B. Type		McNamee Clay
Conc.		21
Base Exchange:		
Solution	RECl ₃ .6H ₂ O+NH ₄ Cl	(NH ₄) ₂ SO ₄ +RECl ₃ .6H ₂ O
Conc., wt. percent	1	1.4
Contacts (No.X.hrs.)	1-24 hr. continuous	0.2
Composition:		
Na, wt. percent	0.09	0.07
(RE) ₂ O ₃ , wt. percent	7.92	3.39
Physical Properties:		
Surface Area, m. ² /g., Steamed	221	190
Catalytic Evaluation Conditions:		
LHSV	4	4
Catalyst/oil	1.5	1.5
Conversion, vol. percent	54.8	55.6
10 RVP Gasol., vol. percent	48.3	51.0
Excess C ₄ 's, vol. percent	9.1	8.5
C ₃ +Gasoline, vol. percent	45.8	48.5
Total C ₄ 's, vol. percent	11.6	11.1
Dry Gas, wt. percent	4.9	4.8
Coke, wt. percent	2.5	1.0
H ₂ , wt. percent	0.03	0.05

ADVANTAGE OVER STANDARD SILICA-ALUMINA CATALYST²

10 RVP, Gasol., vol. percent	+6.1	+9.3
Excess C ₄ 's, vol. percent	-2.9	-4.7
C ₃ +Gasoline, vol. percent	+6.0	+8.5
Total C ₄ 's, vol. percent	-2.7	-3.7
Dry Gas, wt. percent	-1.9	-2.4
Coke, wt. percent	-1.1	-2.8

¹ Steamed at 1200° F. with 100% steam at 15 p.s.i.g.

² Commercial silica-alumina gel cracking catalyst containing about 10 wt. per cent Al₂O₃, and 90 per cent SiO₂.

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clay was base exchanged with a combined 5 percent rare earth chloride plus 2 percent ammonium chloride solution at 180° F. to reduce the sodium content to 0.43 percent.

A plastic composite was formed from 167 grams of the above wet cake containing 60 weight percent solids with 300 grams raw McNamee clay and sufficient water to render the mixture plastic. The plastic material was then extruded hydraulically into $\frac{3}{16}$ " pellets. The pellets were dried at 230° F., sized 4 x 10 mesh, calcined 10 hours at 1000° F. and steam treated at 1200° F. for 24 hours with 15 p.s.i.g. steam.

The final catalyst containing 25 weight percent of the active aluminosilicate component and 75 weight percent of the dry matrix analyzed 5 weight percent rare earth metal oxides [(RE)₂O₃].

Catalytic evaluations presented in Table XIII show that this catalyst was very active and very selective. At 4 LHSV the catalyst gave 73.2 volume percent conversion with a C₅+ gasoline advantage of +9.1 volume percent over the standard silica-alumina. At 8 LHSV the conversion was 58.7 volume percent and the selectivity was +8.4 volume percent over the standard silica-alumina.

EXAMPLE 31

The catalyst of this example was prepared using 10 weight percent of the same active rare earth component used in Example 30. The clay matrix component was kaolinite. In the preparation, 20 grams of the above active aluminosilicate component were mixed with 213 grams of the kaolinite clay slurry (50.7 weight percent solids). The mixture was not extruded but merely dried. The dry material was further sized, calcined and steamed as described above in Example 30.

Catalytic evaluations in Table XIII show that this catalyst was highly selective.

EXAMPLE 32

The catalyst of this example was prepared to contain 10 weight percent of active component in McNamee clay. The active component was prepared by base-exchanging 13X crystalline aluminosilicate with a combined 5 percent rare earth chloride plus 2 weight percent ammonium chloride solution to a low sodium level of 0.22 weight percent. A homogeneous slurry was blended containing 21.6 grams of active component (77.1 weight percent solids at 1000° F.), 172.5 grams McNamee clay (87 weight percent solids at 1000° F.) and sufficient water to convert the mixture to a slurry. The slurry was dried at 230° F. then sized, calcined and steamed as described above in Example 30.

Catalytic evaluation of this catalyst in Table XIII shows increased selectivity over conventional silica-alumina of +7.9 volume percent C₅+ gasoline at 4 LHSV.

EXAMPLE 33

This preparation differs from the previous preparations in that the active component is a rare earth acid type prepared by exchanging a high silica synthetic faujasite with a combined 5 percent rare earth chloride and 2 percent ammonium chloride solution, by contacting 2 pounds of high silica faujasite with 360 pounds of the solution at 180° F. Following this treatment a calcined sample analyzed 1.54 weight percent sodium.

The catalyst of this example was prepared by blending 21.2 grams of the above rare earth faujasite (78.0 weight percent solids) and 172.5 grams of raw McNamee clay (87 weight percent solids) with enough water to make a homogeneous slurry. The resulting composite was dried at 230° F. in air, sized 4 x 10 mesh, calcined 10 hours at 1000° F. and steam treated at 1200° F. with 15 p.s.i.g. steam for 24 hours.

Catalytic data summarized in Table XIII show that the catalyst of this example, containing only 10 weight percent of a relatively active component, is extremely active, comparing favorably with the catalyst of Example

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30 containing 25 weight percent of a relatively active component of the X type. At 4 LHSV the catalyst was extremely selective showing a +11.2 volume percent C₅+ gasoline advantage over the standard silica-alumina catalyst at 74.7 volume percent conversion. When the LHSV is increased to 8, thereby reducing the conversion, the catalyst is still +10.5 volume percent more selective in gasoline production than standard silica-alumina at the same conversion of 57.7 volume percent.

EXAMPLE 34

This example demonstrates the catalytic advantages of incorporating a synthetic Y faujasite into a clay matrix. This example was prepared mixing, on dry basis, 10 wt. percent sodium Y aluminosilicate with 90 wt. percent McNamee Clay matrix by slurring with water in a blender, then dried at 230° F., sized 4 x 10 mesh, calcined 10 hours at 1000° F. and steamed for 24 hours at 1200° F. with steam at 15 p.s.i.g. The final catalyst analyzed 0.87 wt. percent sodium.

Catalytic evaluation data summarized in Table XIII clearly show the high selectivity of the catalyst. At 62.3 volume percent conversion at 4 LHSV, the catalytic advantage in C₅+ gasoline was +10.0 volume percent over the standard silica-alumina.

EXAMPLE 35

This example demonstrating the advantages of acid Y type aluminosilicate in a clay matrix was prepared as follows. A sample of NaY was base exchanged with 25% NH₄Cl solutions at 180° F. until the product had a sodium content of 0.58. This material was then composited after washing and drying at 230° F. with McNamee Kaolinite Clay (10% NH₄Y-90% clay) in the same manner as in Example 34 and processed in the same manner.

Catalytic evaluation data at 4 LHSV are as follows:

	Yields	Yields (to Silica-Alumina)
Conversion, vol. percent.....	53.4	-----
C ₅ + Gasoline, vol. percent.....	45.8	+7.0
Total C ₅ 's, vol. percent.....	10.5	-3.4
Dry Gas, wt. percent.....	5.1	-1.8
Coke, wt. percent.....	1.0	-2.5

The following examples will serve to illustrate that alumina can also be used as a matrix with particular catalytic advantages. The catalysts of these examples were prepared by blending alumina with the active component, then pelleting and activating.

EXAMPLE 36

The catalyst of this example was prepared by blending the matrix alumina with a lanthanum/ammonium pre-exchanged faujasite of the Y type. The alumina base was prepared by reacting aluminum metal with water at room temperature in presence of mercury. The resulting alumina was mainly beta trihydrate which upon calcination yields eta alumina. The active component, a lanthanum acid Y faujasite, was prepared by base-exchanging a sodium faujasite with a combined 5 percent lanthanum chloride plus 2 weight percent ammonium chloride solution at 180° F., water washing to remove chloride ions and drying at 230° F. in air.

For the preparation of the final catalyst 30 grams of lanthanum/ammonium - exchanged Y faujasite were blended with 135 grams of hydrated alumina (66.5 weight percent solids at 1000° F.).

Catalytic evaluation at 4 LHSV, after pressure steaming 24 and 48 hours at 1200° F., at 15 p.s.i.g., shows in Table XIV that the catalyst is exceptionally selective, having a +11.1 volume percent C₅+ gasoline advantage over the conventional silica-alumina catalyst at 64.5 volume percent conversion.

Table XIII
CLAY MATRIX CATALYSTS

Example	30	31	32	33	34
Steaming Time, hrs	24	24	24	24	24
Description:					
Matrix	McNamee ²	Kaolin slurry	McNamee Clay	McNamee Clay	McNamee Clay
Conc.	75	90	90	90	90
Fines:					
Type	REXY ³	³ REXY	REHX	REHY	NaY
Conc.	25	10	10	10	10
Composition:					
Na, wt. percent			0.07	0.26	
(RE) ₂ O ₃ , wt. percent	5.0		2.60	1.42	
Physical Properties:					
App. Dens., g./cc	0.69	0.81			
Surface Area, m. ² /g	119				
Steamed	93	48	51	60	58
Catalytic Evaluation Conditions:					
LHSV	4	8	4	4	4
c/o	1.5	0.75	1.5	1.5	1.5
Conversion, vol. percent	73.2	58.7	58.9	74.7	62.3
10 RVP Gasol., vol. percent	60.4	54.1	51.2	63.0	56.4
Excess C ₄ 's, vol. percent	14.5	5.4	8.4	13.9	10.0
C ₅ + Gasoline, vol. percent	57.9	50.4	48.3	60.4	53.6
Total C ₄ 's, vol. percent	17.0	9.1	11.4	16.5	12.9
Dry Gas, wt. percent	7.8	5.4	5.7	7.8	5.4
Coke, wt. percent	3.9	2.5	2.2	2.4	1.3
H ₂ , wt. percent	0.11	0.07	0.11	0.11	0.10

DELTA ADVANTAGE OVER SILICA-ALUMINA

10 RVP, Gasol., vol. percent	+9.7	+9.9	+7.5	+8.7	+12.1	+11.6	+11.3
Excess C ₄ 's, vol. percent	-5.1	-7.9	-4.6	-4.4	-5.9	-6.2	-5.5
C ₅ + Gasoline, vol. percent	+9.1	+8.4	+6.7	+7.9	+11.2	+10.5	+10.0
Total C ₄ 's, vol. percent	-4.4	-6.4	-3.8	-3.5	-4.9	-5.0	-4.2
Dry Gas, wt. percent	-2.3	-2.1	-1.6	-1.9	-2.2	-2.7	-2.7
Coke, wt. percent	-3.3	-1.8	-2.0	-2.8	-4.8	-3.4	-3.4

¹ Steam treated at 1,200° F. and 15 p.s.i.g.

² Clay and REX mixed to extrudable state then extruded hydraulic 10 tons, dried 20 hrs, at 230° F. calcined at 1,000° F.

³ Rare earth exchanged sodium XY faujasite from clay fusion process.

EXAMPLE 37

The catalyst of this example was prepared in a manner similar to that of Example 36. The sodium Y faujasite was exchanged with a rare earth chloride and ammonium chloride solution. The catalyst was prepared by blending 22 grams of dried rare earth Y faujasite with 99.2 grams of the same alumina used in Example 37.

As shown in Table XIV, catalytic performance of the catalyst at 4 LHSV was similar to that of Example 37, showing about +10.4 volume percent C₅+ gasoline advantage over the conventional silica-alumina catalyst.

Table XIV

Example	36	37
Steaming Time, hrs	24	24
Description:		
Matrix	Al ₂ O ₃	Al ₂ O ₃
Fines:		
Type	LaHY	REHY
Conc., wt. percent	25	25
Physical Properties:		
App. Dens., g./cc	172	167
Surface Area, m. ² /g., Steamed		
Catalytic Evaluation Conditions:		
LHSV	4	4
c/o	1.5	1.5
Conversion, vol. percent	64.5	62.3
10 RVP Gasol., vol. percent	59.2	57.5
Excess C ₄ 's, vol. percent	8.9	7.8
C ₅ + Gasoline, vol. percent	55.9	54.2
Total C ₄ 's, vol. percent	12.2	11.1
Dry Gas, wt. percent	5.6	5.5
Coke, wt. percent	2.0	2.2
H ₂ , wt. percent	0.08	0.09

DELTA ADVANTAGE OVER SILICA-ALUMINA

10 RVP Gasol., vol. percent	+12.2	+11.5
Excess C ₄ 's, vol. percent	-6.5	-6.8
C ₅ + Gasoline, vol. percent	+11.1	+10.4
Total C ₄ 's, vol. percent	-5.4	-5.7
Dry Gas, wt. percent	-2.9	-2.5
Coke, wt. percent	-3.4	-2.8

¹ Steam treated at 1200° F. and 15 p.s.i.g.

EXAMPLE 38

Twenty-five (25) parts by weight of a synthetic crystalline aluminosilicate identified as Zeolite 13X was dispersed in 75 parts of a silica alumina matrix, and the resulting composition treated with two percent by weight solution of calcium chloride continuously for 8 hours, followed by treatment with an aqueous solution consisting of two percent by weight of calcium chloride, and 0.5% by weight of ammonium chloride continuously for 16 hours, and then treated with a two percent by weight aqueous solution of rare earth chlorides for two contacts each of two hours. The aluminosilicate was then washed with water until there were no chloride ions in the effluent, dried and then treated for 20 hours at 1225° F. with 100% atmospheric steam to yield a catalyst having a calcium content of 2.15% by weight and a rare earth content, determined as rare earth oxides, of 7.2% by weight.

The following table shows the cracking data of the catalyst when evaluated for cracking gas oil at 900° F.:

Table XV

Cracking data:	
Conversion, vol. percent	57.3
LHSV	4
10 R.V.P. gasol., vol. percent	46.1
Excess C ₄ 's, vol. percent	11.3
C ₅ + gasoline, vol. percent	43.3
Total C ₄ 's, vol. percent	14.1
Dry gas, wt. percent	6.6
Coke, wt. percent	4.0
H ₂ , wt. percent	0.03
Δ Advantage:	
10 R.V.P., vol. percent	+2.7
Excess C ₄ 's, vol. percent	-1.6
C ₅ + gasoline, vol. percent	+2.0
Total C ₄ 's, vol. percent	-1.0
Dry gas, wt. percent	-0.6
Coke, wt. percent	-0.1

EXAMPLE 39

Ten (10) parts by weight of a synthetic crystalline aluminosilicate identified as Zeolite 13X was dispersed into 90 parts by weight of a silica didymium matrix consisting of 97% by weight SiO_2 and 3% by weight didymium oxides. The resulting composition was then treated for 16 continuous hours with an aqueous solution consisting of 2% by weight of lanthanum chloride and then for 24 continuous hours with 1% by weight aqueous solution of ammonium chloride. The aluminosilicate was then washed with water until the effluent contained no chloride ions, dried and then treated for 24 hours at 1200° F. with steam at 15 p.s.i.g. to yield a catalyst having a rare earth content of 7.78% by weight, determined as rare earth oxides.

The resulting catalyst had the cracking data shown in the following table when evaluated for cracking gas oil at 900° F.:

Table XVI

Cracking data:	
Conversion, vol. percent	53.3
LHSV	4
10 R.V.P. gaso., vol. percent	47.8
Excess C_4 's, vol. percent	7.8
C_5 + gasoline, vol. percent	45.3
Total C_4 's, vol. percent	10.3
Dry gas, wt. percent	5.1
Coke, wt. percent	2.0
H_2 , wt. percent	0.05
Δ Advantage:	
10 R.V.P., vol. percent	+6.4
Excess C_4 's, vol. percent	-5.4
C_5 + gasoline, vol. percent	+6.2
Total C_4 's, vol. percent	-5.1
Dry gas, wt. percent	-1.4
Coke, wt. percent	-1.4

EXAMPLE 40

Ten (10) parts by weight of a synthetic crystalline aluminosilicate identified as Zeolite 13X was dispersed in 90 parts by weight of a silica alumina lanthanum matrix consisting of 91% by weight SiO_2 , 3% by weight Al_2O_3 and 6% by weight of lanthanum oxides. The resulting composition was treated with a combined 1% by weight aqueous solution of lanthanum chloride and a 1% by weight solution of ammonium chloride for 24 continuous hours. The composite was then washed with water until the effluent contained no chloride ions, dried and then treated for 24 hours at 1200° F. with steam at 15 p.s.i.g. to yield a catalyst having a sodium content of 0.15% by weight and a rare earth content of 11.5% by weight, determined as rare earth oxides.

The cracking data of the resulting catalyst are shown in the following table, when the catalyst was evaluated for cracking gas oil at 900° F.:

Table XVII

Cracking data:	
Conversion, vol. percent	54.0
LHSV	4
10 R.V.P. gaso., vol. percent	49.8
Excess C_4 's, vol. percent	7.5
C_5 + gasoline, vol. percent	46.9
Total C_4 's, vol. percent	10.4
Dry gas, wt. percent	4.8
Coke, wt. percent	1.8
H_2 , wt. percent	0.01
Δ Advantage:	
10 R.V.P., vol. percent	+8.0
Excess C_4 's, vol. percent	-5.9
C_5 + gasoline, vol. percent	+7.4
Total C_4 's, vol. percent	-5.2
Dry gas, wt. percent	-2.7
Coke, wt. percent	-2.6

EXAMPLE 41

Ten (10) parts by weight of a crystalline aluminosilicate identified as the sodium form of Zeolite Y was dispersed into 90 parts by weight of a silica alumina matrix, and the resulting composition was treated for 16 continuous hours with an aqueous solution comprising a 2% by weight mixture of rare earth chlorides and then for 24 continuous hours with a 1% by weight aqueous ammonium chloride solution. The aluminosilicate was then washed with water until the effluent contained no chloride ions, dried and then treated for 24 hours at 1200° F. with steam at 15 p.s.i.g. to yield a catalyst having a rare earth content of 3.35 weight percent.

The cracking data of the resulting catalyst are shown in the following table when evaluated for cracking gas oil at 900° F.:

Table XVIII

Cracking data:

Conversion, vol. percent	58.2
LHSV	4
10 R.V.P. gaso., vol. percent	50.8
Excess C_4 's, vol. percent	10.6
C_5 + gasoline, vol. percent	48.3
Total C_4 's, vol. percent	13.1
Dry gas, wt. percent	5.4
Coke, wt. percent	2.0
H_2 , wt. percent	0.01
Δ Advantage:	
10 R.V.P., vol. percent	+6.8
Excess C_4 's, vol. percent	-2.5
C_5 + gasoline, vol. percent	+6.5
Total C_4 's, vol. percent	-2.3
Dry gas, wt. percent	-1.9
Coke, wt. percent	-2.2

EXAMPLE 42

Twenty-five hundred (2500) grams of a silica zirconia hydrogel (10% ZrO_2), 45 grams of McNamee clay and 300 grams of a rare earth-hydrogen aluminosilicate, prepared by reacting the sodium form of Zeolite Y with rare earth ions and a source of hydrogen ions, and 1,000 milliliters of water were mixed vigorously in a Waring Blender for 5 minutes. The resulting slurry was then dried at 230° F. for 48 hours, sized to 4 x 10 mesh and calcined in air for 10 hours at 1000° F. to yield a catalyst having a sodium content of 0.22 weight percent.

The following table shows the cracking data obtained when the catalyst was evaluated for cracking gas oil at 900° F. and at a catalyst to oil ratio of 1.5:

Table XIX

Cracking data:

Conversion, vol. percent	57.7
LHSV	4
10 R.V.P. gaso., vol. percent	47.5
Excess C_4 's, vol. percent	10.7
C_5 + gasoline, vol. percent	45.0
Total C_4 's, vol. percent	13.1
Dry gas, wt. percent	6.4
Coke, wt. percent	3.5
H_2 , wt. percent	0.10
Δ Advantage:	
10 R.V.P., vol. percent	+4.2
Excess C_4 's, vol. percent	-2.1
C_5 + gasoline, vol. percent	+3.8
Total C_4 's, vol. percent	-1.8
Dry gas, wt. percent	-0.6
H_2 , wt. percent	-0.7

EXAMPLE 43

Ten (10) parts by weight of the synthetic crystalline aluminosilicate identified as Zeolite 13X were dispersed into 90 parts by weight of a silica-alumina rare earth oxide matrix consisting of 91 parts by weight of SiO_2 , 6 parts

by weight of Al_2O_3 , 3 parts by weight of rare earth oxides ($\text{RE})_2\text{O}_3$. The resulting composition was treated with a 2 percent aqueous solution of rare earth chlorides for 24 continuous hours, washed with water, dried and then treated for 24 hours at 1200°F . with steam at 15 p.s.i.g. to yield a catalyst having a rare earth content determined as rare earth oxides of 16.7 percent by weight and a sodium content of 0.15 percent by weight.

The following cracking data were obtained when the catalyst was evaluated for cracking gas oil at 900°F .:

Table XX

Cracking data:

Conversion, volume percent	56.8
LHSV	4
10 R.V.P. gaso., vol. percent	49.4
Excess C_4 's, vol. percent	10.0
C_5 + gasoline, vol. percent	47.0
Total C_4 's, vol. percent	12.4
Dry gas, wt. percent	5.6
Coke, wt. percent	2.8
H_2 , wt. percent	0.04

 Δ Advantage:

10 R.V.P. gaso., vol. percent	+6.2
Excess C_4 's, vol. percent	-2.6
C_5 + gasoline, vol. percent	+6.0
Total C_4 's, vol. percent	-2.5
Dry gas, wt. percent	-1.5
Coke, wt. percent	-1.2

EXAMPLE 44

Ten (10) parts by weight of a synthetic crystalline aluminosilicate, identified as Zeolite 13X, was dispersed into 90 parts by weight of silica-alumina consisting of 94 percent by weight of SiO_2 and 6 percent by weight of Al_2O_3 . The resulting composition was then subjected to a 16 continuous hour contact with a 1 percent by weight aluminum sulfate and then to twelve 2 hour contacts with a 2 percent by weight solution of rare earth chlorides. The composition was then washed with water until the effluent contained no chloride or sulfate ions, dried, and then treated for 30 hours at 1200°F . with steam at 15 p.s.i.g. to yield a catalyst having a sodium content of 0.05 percent by weight, and a rare earth content of 11.5 percent by weight determined as rare earth oxides.

The following cracking data were obtained when the catalyst was evaluated for cracking gas oil at 900°F .:

Table XXI

Cracking data:

Conversion, volume percent	52.1
LHSV	4
10 R.V.P. gaso., vol. percent	45.1
Excess C_4 's, vol. percent	8.4
C_5 + gasoline, vol. percent	42.8
Total C_4 's, vol. percent	10.7
Dry gas, wt. percent	5.8
Coke, wt. percent	2.5
H_2 , wt. percent	0.04

 Δ Advantage:

10 R.V.P. gaso., vol. percent	+4.5
Excess C_4 's, vol. percent	-2.8
C_5 + gasoline, vol. percent	+4.4
Total C_4 's, vol. percent	-2.8
Dry gas, wt. percent	-0.5
Coke, wt. percent	-1.0

EXAMPLE 45

Twenty-five (25) parts by weight of a synthetic crystalline aluminosilicate, identified as Zeolite 13X, was dispersed into 75 parts by weight of silica-alumina consisting of 94 percent by weight SiO_2 and 6 percent Al_2O_3 . The composition was then treated with an aqueous solution of rare earth chloride and manganese chloride, washed with water until there were no chloride ions in the effluent, dried, and then treated for twenty hours at 1225°F . with steam at atmospheric pressure to yield a catalyst having a sodium content of 0.57 percent by weight, a manganese content of 1.2 percent by weight, and a rare earth content of 11.6 percent by weight determined as rare earth oxides.

The following cracking data were obtained when the catalyst was evaluated for cracking gas oil at 900°F .

Table XXII

Cracking data:

Conversion, volume percent	64.6
LHSV	4.0
10 R.V.P. gaso., vol. percent	56.0
Excess C_4 's, vol. percent	10.5
C_5 + gasoline, vol. percent	52.6
Total C_4 's, vol. percent	13.9
Dry Gas, wt. percent	6.4
Coke, wt. percent	3.6
H_2 , wt. percent	0.034

 Δ Advantage:

10 R.V.P. gaso., vol. percent	+9.0
Excess C_4 's, vol. percent	-5.0
C_5 + gasoline, vol. percent	+7.7
Total C_4 's, vol. percent	-3.7
Dry gas, wt. percent	-2.1
Coke, wt. percent	-1.8

EXAMPLE 46

Ten (10) parts by weight of a synthetic crystalline aluminosilicate, identified as Zeolite 13X, were dispersed into 90 parts by weight of a silica-alumina matrix, and the resulting composition treated with a 2 percent by weight aqueous solution of rare earth chlorides for 24 continuous hours, followed by three 16 hour contacts and nine 2 hour contacts with a 2 percent by weight aqueous solution of manganese chloride. The treated composition was then washed with water until the effluent contained no chloride ions, dried, and then treated for 30 hours at 1200°F . with steam at 15 p.s.i.g. to yield a catalyst having a sodium content of 0.29 percent by weight, a rare earth content determined as rare earth oxides of 4.48 percent by weight, and a manganese content determined as manganese at 3.18 percent by weight.

The following cracking data were obtained when the catalyst was evaluated for cracking gas oil at 900°F .:

Table XXIII

Cracking data:

Conversion, vol. percent	42.4
LHSV	4.0
10 R.V.P. gaso., vol. percent	38.0
Excess C_4 's, vol. percent	6.5
C_5 + gasoline, vol. percent	35.9
Total C_4 's, vol. percent	8.6
Dry gas, wt. percent	4.1
Coke, wt. percent	1.6
H_2 , wt. percent	0.04

 Δ Advantage:

10 R.V.P. Gaso., vol. percent	+2.8
Excess C_4 's, vol. percent	-1.9
C_5 + gasoline, vol. percent	+2.9
Total C_4 's, vol. percent	-2.1
Dry gas, wt. percent	+0.6
Coke, wt. percent	-0.4

EXAMPLE 47

Twenty-five (25) parts by weight of a synthetic crystalline aluminosilicate, identified as Zeolite 13X, were dispersed into 75 parts by weight of a silica-alumina matrix and the resulting composition treated with an aqueous solution containing 1 percent by weight rare earth chloride and 1 percent by weight calcium chloride. The composition was then washed with water until there were no chloride ions in the effluent, dried, and then treated for 10 hours at 1200° F. with steam at 15 p.s.i.g. to yield a catalyst having a sodium content of 0.14 percent by weight.

The following cracking data were obtained when the catalyst was evaluated for cracking gas oil at 875° F.:

Table XXIV

Cracking data:

Conversion, vol. percent	71.5
LHSV	3.0
10 R.V.P. Gas., vol. percent	52.5
Excess C ₄ 's, vol. percent	18.4
C ₅ + gasoline, vol. percent	50.7
Total C ₄ 's, vol. percent	20.3
Dry Gas, wt. percent	7.9
Coke, wt. percent	6.4

Δ Advantage:

10 R.V.P. Gas., vol. percent	+5.7
Excess C ₄ 's, vol. percent	-3.3
C ₅ + gasoline, vol. percent	+6.3
Total C ₄ 's, vol. percent	-3.9
Dry Gas, wt. percent	-2.0
Coke, wt. percent	-1.1

EXAMPLES 48-88

To demonstrate the benefit in octane number achieved by use of the composite catalysts described herein, wherein the porous matrix was silica-alumina, there were prepared a series of pure aluminosilicate catalysts and a series of composite catalysts comprising aluminosilicates in combination with silica and with silica-alumina matrix materials.

The aluminosilicates used were rare earth faujsites, of the X and Y type, and the acid Y type. Preparation of these materials is described below:

Rare earth crystalline aluminosilicate of the X type

Rare earth X aluminosilicate was prepared by base exchanging a sodium aluminosilicate (13X) prepared in a manner described in Example 1. Such sodium aluminosilicate (0.6 lbs.) was given seventeen 2-hour and seven overnight (16-hour) contacts at 180° F. with 600 cc. of 5% solution of rare earth chlorides. Following the rare earth chloride base exchange the wet cake was washed continuously at room temperature with a water flow rate of 20 cc./min. for seven days, until essentially free of chloride ion. It was then dried in air at 230° F. for 20 hours, pelleted and sized to 4-10 mesh, calcined 10 hours at 1000° F. and steamed for 20 hours at 1225° F. with steam at atmospheric pressure prior to catalytic evaluation.

A modification of the above process was used in the preparation of the catalyst of Example 49. This modification involved a continuous base exchange with a solution 5% RECl₃·6H₂O and 2% NH₄Cl, using 60 lbs. of solution for 1½ lbs. of starting wet sodium aluminosilicate.

The rare earth aluminosilicate catalysts of the X type described in Table XXV, were prepared essentially in accordance with one or the other of these basic procedures.

Rare earth crystalline aluminosilicate of the Y type

Rare earth Y aluminosilicate of Example 61, was prepared in essentially the same manner as described for the modified rare earth X aluminosilicate, differing in that a solution of 5% RECl₃·6H₂O+5% NH₄Cl was used. In this case, 90 lbs. of solution were used for ½ lb. of wet sodium aluminosilicate of the Y type.

Catalysts identified as those of Examples 63, 64 and 65 differ from the above in that the starting sodium aluminosilicate of the Y type was first pretreated with a chelating agent, ethylene-diaminetetra acetic acid

(H₄EDTA)

The catalyst of Example 63 was treated at 200° F. for four 24-hour contacts using 20 g. H₄EDTA in each contact per ½ lb. of starting sodium Y aluminosilicate. The treated chelated sodium aluminosilicate was subsequently base exchanged continuously with a combined 5%

RECl₃·6H₂O

and 2% NH₄Cl solution. The catalysts of both Examples 64 and 65, were treated only twice with the H₄EDTA prior to the RECl₃·6H₂O-NH₄Cl base exchange.

The remaining REY catalysts reported in Table XXVI were prepared essentially in accordance with one or the other of these basic procedures.

Crystalline aluminosilicate of the acid Y type

The catalyst of Example 76, a crystalline aluminosilicate of the acid Y type, was prepared by base exchanging 1 lb. of a chelated sodium aluminosilicate Y type with ammonium EDTA resulting from the mixture of 80 g. H₄EDTA and 18 cc. NH₄OH for four contacts at 200° F., one for 72 hours and three for 24 hour periods. This was followed by washing, drying, pelleting, calcining and steaming.

Usually acid Y aluminosilicate catalysts were prepared by base exchanging continuously at 180° F. with 5 or 25% NH₄Cl solutions for periods extending from several days to several weeks depending on the desired level of residual sodium. The amount of solution generally used was about 240 lbs. of 5% NH₄Cl solution per 2 lbs. wet sodium Y aluminosilicate over an 8 day period.

All HY catalysts reported in Table XXVII were prepared essentially in accordance with these basic procedures.

Catalysts with silica-alumina matrix

Silica-alumina matrix catalysts were prepared by dispersing the active component, i.e., sodium or exchanged forms of the crystalline aluminosilicate first in water and then dispersing this slurry into a diluted water glass solution. The silicate fines slurry was then gelled by mixing continuously in a mixing nozzle with an acid alum solution at controlled rates to give the desired pH. The alumina content of the matrix was controlled by the composition of the acid solution. Flow rates of the solution were essentially equal to give good mixing.

The hydrosols resulting from the intermixing of the silicate-fines slurry and the acid alum solution were formed into bead catalyst by the conventional bead forming method.

Illustrative of the above method was that used in preparing the catalyst of the following example:

EXAMPLE 84

Preparation of silicate-fines solution:

(A) Dilute water glass solution

34.8 lbs. N-Brand silicate solution (28.9 wt. percent SiO₂, 8.9 wt. percent Na₂O, 62.2 wt. percent water)
17.55 lbs. water

(B) Sodium aluminosilicate slurry:

14.62 lbs. water
6.50 lbs. sodium aluminosilicate (13X) (approx. 55% solids at 1000° F.)

Solution B was added to solution A while mixing vigorously. This solution was kept mixing before and during the forming run to insure consistent composition of resulting catalyst. The specific gravity of the mixture was 1.202 at 76° F.

Preparation of the acid-alum solution:

57.1 lbs. water
4.23 lbs. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
1.98 lbs. H_2SO_4 97.6%
Sp. gr. 1.057 at 76° F.

These solutions were mixed together through a nozzle mixing the silicate solution at 362 cc./min. at 73° F. with 350 cc./min. acid-alum solution at 40° F. The resulting 8.5 pH hydrosol had a 2.5 second gel time at 64° F. The hydrosol was formed into bead catalyst in the conventional bead forming method.

The catalysts having a silica-alumina matrix reported in Tables XXV to XXVIII were prepared essentially in accordance with these basic procedures.

Catalysts with silica matrix

The silica matrix catalysts were prepared by a method essentially the same as that described above for the silica-alumina catalysts, but excluding the $\text{Al}_2(\text{SO}_4)_3$ from the acid solution. In the preparation of the catalysts of Examples 52, 53 and 54, the acid used was acetic acid while in the preparation of the catalyst of Example 55, the forming acid was sulfuric acid.

Illustrative of reactant solution utilized in preparing the silica matrix catalysts is that of Example 52 which was prepared as follows:

Preparation of silicate fines slurry:

(A) Diluted water glass solution

9.83 lbs. N-Brand silicate (28.9 wt. percent SiO_2 , 8.9 wt. percent Na_2O , 62.2 wt. percent water)

6.55 lbs. water

(B) Aluminosilicate-clay fines slurry

6.36 lbs. water

0.652 lb. Raw McNamee Clay (87.1% solids at 1000° F.)

0.484 lb. Rare Earth X aluminosilicate (78.1 wt. percent solids at 1000° F.)

Solution B was mixed into solution A while stirring vigorously. Mixing was continued before and during forming to insure uniform composition. The specific gravity of the mixture was 1.168 at 80° F.

Preparation of acid solution:

27.5 lbs. H_2O
2.61 lbs. glacial acetic acid (99.9 wt.)
Sp. gr. 1.010 at 84° F.

The catalysts reported in Tables XXV to XXVIII having a silica matrix were prepared essentially in accordance with these basic procedures.

Preparation of gasoline for octane evaluation of catalysts

All catalysts were run in an autocyclic unit at the liquid hourly space velocity and catalyst to oil ratio recorded in Tables XXV to XXVIII for the CAT-C evaluations. Cracking temperatures were 900° F. for both CAT-C and octane evaluation. The charge stock was wide range Mid-Continent straight run gas oil. The cycle in the autocyclic unit, in addition to the cracking step, described above, consisted of air regeneration for one hour at about 1050° F. and nitrogen purges before and after cracking.

About one liter of synthetic crude was accumulated for each run, including liquid condensate from the cracking gases in a cold trap. The synthetic crude was distilled to yield a 50°–410° F. gasoline.

The gasoline prepared as above contains some C_4 's; and some C_5 's are lost. The octane number was determined on the gasoline as prepared. From the analysis for C_4 's and C_5 's, and from the CAT-C evaluation, the octane number was corrected to a C_4 -free basis, with a C_5 content equal to that of the calculated CAT-C C_5 +gasoline. Octane blending values of 107.0 for the C_4 's and 106.5 for the C_5 's were used to correct the octane numbers.

In some of the runs recorded in Tables XXV to XXVIII, the gasoline was prepared by repeated CAT-C runs until enough gasoline was accumulated for the micro octane evaluation. In these cases, the gasolines were re-distilled in a Podbielniak column to yield C_4 free gasolines.

The results are set forth below in Tables XXV to XXVIII:

Table XXV

Example	Alumino-silicate	Matrix	Wt. percent REX in Catalyst	Steam Treatment	CAT-C Evaluation					Gasoline Octane Number R+3 corr.
					LHSV	Cat./Oil	Con. Vol. percent	C_5 + Gasol., Vol. percent	Values to Standard Silica-Alumina Catalyst ¹	
48	REX		100	SR	16	0.38	61.4	51.6	+8.4	96.3
49	REHX		100	SP24	16	0.38	65.2	52.9	+7.8	95.7
50	REHX		100	SP48	16	0.38	65.7	54.5	+9.2	95.6
51	REX		100	SR	16	0.38	62.5	49.4	+5.7	96.6
Average										96.0
52	REHX	Silica	10	SP24	4	1.5	50.6	43.6	+6.4	97.4
53	REHX	do	10	SP24	3	2.0	49.4	41.0	+4.6	96.3
54	REHX	do	10	SP72	4	1.5	56.0	49.6	+9.2	94.9
55	REHX	do	10	SP72	4	1.5	57.3	50.5	+9.4	96.1
Average										96.2
56	REX	Silica-Alumina	10	SP30	4	1.5	46.9	38.9	+4.0	97.1
57	REHX	do	10	SP24	4	1.5	64.2	50.2	+5.6	97.2
58	REHX	do	10	SP24	4	1.5	56.5	45.6	+5.0	97.2
59	REHX	do	10	SP24	4	1.5	59.2	48.1	+6.0	97.4
60	REHX	do	10	SP24	4	1.5	59.1	47.0	+5.0	96.9
Average										97.2

¹ Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al_2O_3 , and remainder SiO_2 .

SR=Steamed at 1225° F., atmospheric pressure, 100% steam, 20 hours.

SP=Steamed at 1200° F., 15 p.s.i.g., 100% steam for indicated number of hours.

Table XXVI

Example	Alumino-silicate	Matrix	Wt. percent REX in Catalyst	Steam Treatment	CAT-C Evaluation					Gasoline Octane Number R+3 corr.
					LHSV	Cat./Oil	Con. Vol. percent	C ₅ +Gaso., Vol. percent	Values to Standard Silica-Alumina Catalyst ¹	
61	REHY		100	SP72	16	0.38	68.8	57.1	+10.3	95.5
62	REHY		100	SP120	16	0.38	68.0	59.5	+13.0	95.2
63	REHY		100	SP48	16	0.38	49.2	44.8	+8.5	95.7
64	REHY		100	SP72	16	0.38	58.9	52.1	+10.2	94.5
65	REHY		100	SP72	16	0.38	51.5	46.6	+8.9	94.6
Average										95.1
66 (NC)	REHY	Silica	10	SP24	4.0	1.5	57.3	49.8	+8.7	94.6
67 (NC)	REHY	do	10	SP48	4.0	1.5	55.7	49.8	+9.6	94.4
68 (NC)	REHY	do	10	SP48	4.0	1.5	55.7	49.8	+9.6	94.6
Average										94.5
69	REHY	Silica-Alumina	10	SP60	4.0	1.5	60.8	50.5	+7.6	96.3
70	REHY	do	10	SP24	4.0	1.5	64.7	53.7	+8.9	96.6
71	REHY	do	10	SP24	4.0	1.5	64.2	52.6	+8.0	96.0
72	REHY	do	10	SP24	4.0	1.5	63.3	51.4	+7.3	96.6
73	REHY	do	10	SP24	4.0	1.5	69.6	57.1	+9.9	96.3
74	REHY	do	10	SP24	4.0	1.5	62.4	51.1	+7.4	96.8
75	REHY	do	10	SP24	4.0	1.5	65.6	52.8	+7.5	96.1
Average										96.4

¹ Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, and remainder SiO₂.

NC=Not calcined before steaming.

SP=Steamed at 1200° F., 15 p.s.i.g., 100% steam for indicated number of hours.

Table XXVII

Example	Alumino-silicate	Matrix	Wt. percent HY in Catalyst	Steam Treatment	CAT-C Evaluation					Gasoline Octane Number R+3 corr.
					LHSV	Cat./Oil	Con. Vol. percent	C ₅ +Gaso., Vol. percent	Values to Standard Silica-Alumina Catalyst ¹	
76	HY		100	SP24	8.0	0.75	60.3	53.2	+10.6	96.4
77	HY		100	SP24	10.0	0.60	66.1	56.9	+11.4	97.1
78	HY		100	SP24	16	0.38	57.8	49.9	+8.5	97.4
Average										97.0
79 (NC)	HY	Silica	15	SP24	2.0	3.0	66.2	53.5	+7.9	96.6
80	HY	Silica-alumina	10	SP30	2.0	3.0	59.8	46.9	+4.5	97.7
81	HY	do	10	SP24	2.0	3.0	61.9	47.9	+4.5	98.2
82	HY	do	10	SP24	2.0	3.0	67.0	48.4	+2.4	98.7
83	HY	do	10	SP24	2.0	3.0	62.7	49.6	+5.8	98.0
Average										98.2

¹ Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, and remainder SiO₂.

SP=Steamed at 1200° F., 15 p.s.i.g., 100% steam for indicated number of hours.

NC=Not calcined before steaming.

Table XXVIII

Example	Catalyst	Steam Treatment	CAT-C Evaluation					Gasoline Octane Number R+3 Corr.
			LHSV	Cat./Oil	Con., Vol. Percent	C ₅ +Gaso., Vol. Percent	Values to Standard Silica-Alumina Catalyst ¹	
85	Silica-Alumina	SR	2.0	3.0	50.4	37.7	+0.7	98.8
86	do	SR	2.0	3.0	50.4	37.7	+0.7	99.0
87	do	SR	2.0	3.0	50.4	37.7	+0.7	98.7
88	do	SR	2.0	3.0	60.7	45.1	+2.3	98.4
Average								98.7

¹ Commercial silica-alumina gel cracking catalyst containing about 10 wt. percent Al₂O₃, and remainder SiO₂.

SR=Steamed at 1225° F., atmospheric pressure, 100% steam, 20 hours.

It will be evident from the foregoing tabulated data that the catalysts of active crystalline aluminosilicate contained in a porous silica-alumina matrix when utilized for cracking afforded a gasoline product of enhanced octane number over comparable catalysts wherein the matrix was silica. Catalysts in which the matrix is silica, on the other hand, as shown by the data of Table X, are superior in selectivity to gasoline production over those in which the matrix is silica-alumina. Accordingly, the catalysts described herein are not only exceptionally well adapted for use in the conversion of hydrocarbons, but

highly versatile with the versatility being in part controlled by the nature of the matrix material in which the active crystalline aluminosilicate component is contained.

It will further be evident from the examples and data set forth herein that crystalline aluminosilicates of low sodium content possessing substantial catalytic activity when incorporated in a matrix likewise exhibiting substantial catalytic activity, but of an appreciably lower order than that of the crystalline aluminosilicate with which it is combined, become vastly improved catalytic components. When used in conventional hydrocarbon

cracking processes, the present catalyst compositions exhibit activity and selectivity unexpectedly superior to conventional commercial cracking catalysts. 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 appended hereto.

We claim:

1. In a continuous cyclic process of cracking a petroleum gas oil to produce a selectively large yield of high octane gasoline, and selectively small yields of dry gas and coke, the steps of:

- (a) continuously passing a gas oil through a cracking zone maintained under catalytic cracking conditions;
- (b) in contact with a composite catalyst in said cracking zone;
- (c) said composite catalyst comprising as a major proportion porous silica-alumina;
- (d) which silica-alumina is capable, as a catalyst, of effecting at least 15 percent conversion of Mid-Continent gas oil having a boiling range of 450° to 950° F. at a liquid hourly space velocity of 2, a catalyst to oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure;
- (e) and not more than about 25 percent by weight of a finely divided crystalline aluminosilicate intermixed with said silica-alumina, at least a substantial proportion of the original alkali metal content of said crystalline aluminosilicate having been replaced by ion exchange;
- (f) said crystalline aluminosilicate having a structure of rigid three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 4 Angstroms and less than 15 Angstroms, the cavities being connected with each other in three dimensions by said pore openings;
- (g) said crystalline aluminosilicate having a catalytic activity which is substantially greater than that of said silica-alumina;
- (h) the exchangeable sodium content of said composite catalyst being less than about 1% by weight;
- (i) continuously recovering a liquid fraction rich in high octane gasoline;
- (j) continuously withdrawing spent composite catalyst from the cracking zone;
- (k) subjecting said withdrawn spent catalyst to an operation to regenerate catalytic activity of both said silica-alumina and said zeolite;
- (l) and returning regenerated composite catalyst to said cracking zone.

2. The process of claim 1, wherein the crystalline aluminosilicate is derived from caustic treated clay.

3. The process of claim 1, wherein the porous silica-alumina comprises a member selected from the group consisting of natural clay, chemically treated clay and thermally treated clay.

4. The process of claim 1, wherein the porous silica-alumina comprises a synthetic gel.

5. The process of claim 1, wherein the total sodium content of the composite catalyst is less than 3 percent by weight.

6. A process for cracking a petroleum gas oil to produce a selectively large yield of gasoline, and selectively small yields of dry gas and coke, which comprises:

- (a) passing a gas oil through a cracking zone maintained under catalytic cracking conditions;
- (b) in contact with a composite catalyst in said cracking zone;
- (c) said composite catalyst comprising as a major proportion a porous matrix material;

(d) said matrix material being capable, as a catalyst, of effecting at least 15 percent conversion of Mid-Continent gas oil having a boiling range of 450° to 950° F. at a liquid hourly space velocity of 2, a catalyst to oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure;

(e) and not more than about 25 percent by weight of a finely divided crystalline aluminosilicate having a structure of rigid three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 6 Angstroms and less than 15 Angstroms, the cavities being connected with each other in three dimensions by said pore openings, said crystalline aluminosilicate being intermixed with said matrix material, at least a substantial proportion of the original alkali metal content of said crystalline aluminosilicate having been replaced by ion exchange;

(f) said crystalline aluminosilicate having a catalytic activity which is substantially greater than that of said matrix material;

(g) the sodium content of said composite catalyst being less than about 1 percent by weight;

(h) and recovering as a liquid effluent product from said cracking zone a fraction rich in gasoline.

7. The process of claim 6, wherein the porous matrix material comprises a member selected from the group consisting of natural clay, chemically treated clay and thermally treated clay.

8. The process of claim 7, wherein the crystalline aluminosilicate comprises a material having the crystallographic structure of faujasite.

9. The process of claim 6, wherein the crystalline aluminosilicate comprises a material having the crystallographic structure of faujasite.

10. The process of claim 6, wherein the porous matrix material comprises silica.

11. The process of claim 6, wherein the porous matrix material comprises silica-metal oxide.

12. The process of claim 6, wherein particles of said porous material and particles containing said crystalline aluminosilicate are free to move independently of each other.

13. A process for cracking a petroleum gas oil to produce a selectively large yield of gasoline, and selectively small yields of dry gas and coke, which comprises:

- (a) passing a gas oil through a cracking zone maintained under catalytic cracking conditions;
- (b) in contact with a composite catalyst in said cracking zone;

(c) said composite catalyst comprising as a major proportion a porous matrix material;

(d) said matrix material being capable, as a catalyst, of effecting at least 15 percent conversion of Mid-Continent gas oil having a boiling range of 450° to 950° F. at a liquid hourly space velocity of 2, a catalyst/oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure;

(e) and not more than about 25 percent by weight of a finely divided crystalline aluminosilicate having a structure of rigid three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 6 Angstroms and less than 15 Angstroms, the cavities being connected with each other in three dimensions by said pore openings, said crystalline aluminosilicate being intermixed with said matrix material;

(f) said crystalline aluminosilicate having a catalytic activity which is substantially greater than that of said matrix material;

(g) the sodium content of said composite catalyst being less than about 3 percent by weight;

(h) and recovering as a liquid effluent product from said cracking zone a fraction rich in gasoline.

14. A catalytic conversion process which comprises contacting a hydrocarbon charge under catalytic cracking conditions with a catalyst characterized by:

- (a) a sodium content of less than 4 percent by weight;
- (b) a major proportion of a porous matrix material capable, as a catalyst, of effecting at least 15 percent conversion of Mid-Continent gas oil having a boiling range of 450° to 950° F. at a liquid hourly space velocity of 2, a catalyst to oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure;
- (c) not more than 25 percent by weight of a finely divided crystalline aluminosilicate having a structure of three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 4 Angstroms and less than 15 Angstroms, the cavities being connected with each other in three dimensions by said pore openings, said crystalline aluminosilicate being intermixed with said matrix material, and;
- (d) said crystalline aluminosilicate having a catalytic activity substantially greater than that of said matrix material.

15. A catalytic composition comprising a minor proportion not exceeding about 25 percent by weight of a finely divided crystalline aluminosilicate having a structure of rigid three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 6 Angstroms and less than 15 Angstroms, the cavities being connected with each other in three dimensions by said pore openings, suspended in and distributed throughout a major portion of a porous matrix material, which composition has a sodium content of less than about 4 weight percent, said crystalline aluminosilicate exhibiting substantial catalytic activity for the conversion of hydrocarbons, and said porous matrix material likewise exhibiting a lesser, but substantial catalytic activity capable of effecting at least 15 percent conversion of Mid-Continent gas oil having a boiling range of 450° F. to 950° F. at a liquid hourly space velocity of 2, a catalyst to oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure.

16. A catalytic composition characterized by:

- (a) a sodium content of less than 1 percent by weight;
- (b) a major proportion of a porous matrix material capable, as a catalyst, of effecting at least 15 percent conversion of Mid-Continent gas oil having a boiling range of 450° to 950° F. at a liquid hourly space velocity of 2, a catalyst to oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure;
- (c) not more than about 25 percent by weight of a finely divided crystalline aluminosilicate having a structure of rigid three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 6 Angstroms and less than 15 Angstroms, the cavities being connected with each other in three di-

mensions by said pore openings, said crystalline aluminosilicate being intermixed with said matrix material and;

(d) said crystalline aluminosilicate having a catalytic activity substantially greater than that of said matrix material.

17. A catalytic composition characterized by:

- (a) a sodium content of less than 3 percent by weight;
- (b) a major proportion of a porous matrix material capable, as a catalyst, of effecting at least 15 percent conversion of Mid-Continent gas oil having a boiling range of 450° to 950° F. at a liquid hourly space velocity of 2, a catalyst to oil volume ratio of 3, a temperature of 900° F. and substantially atmospheric pressure;
- (c) not more than about 25 percent by weight of a finely divided crystalline aluminosilicate having a structure of rigid three-dimensional networks characterized by a system of cavities with interconnecting pore openings having minimum diameters of greater than 4 Angstroms and less than 15 Angstroms, the cavities being connected with each other in three dimensions by said pore openings, said crystalline aluminosilicate being intermixed with said matrix material.

18. The catalytic composition of claim 16, wherein the porous matrix material comprises a member selected from the group consisting of natural clay, chemically treated clay and thermally treated clay.

19. The catalytic composition of claim 16, wherein the crystalline aluminosilicate is derived from caustic treated clay.

20. The catalytic composition of claim 16, wherein the porous matrix material is a synthetic silica-alumina composite.

21. The catalytic composition of claim 16, wherein particles of said porous material and particles containing said crystalline aluminosilicate are free to move independently of each other.

22. The catalytic composition of claim 17, wherein the porous matrix material comprises silica-alumina.

23. The catalytic composition of claim 17, wherein the porous matrix material comprises a member selected from the group consisting of natural clay, chemically treated clay and thermally treated clay.

24. The catalytic composition of claim 16 wherein the crystalline aluminosilicate comprises a material having the crystallographic structure of faujasite.

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60 DELBERT E. GANTZ, *Primary Examiner.*

A. RIMENS, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,271,418

September 6, 1966

Charles J. Plank et al.

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

Column 1, line 58, for "usual" read -- unusual --;
column 3, line 23, and column 8, line 60, for "catalystic",
each occurrence, read -- catalytic --; column 12, line 8,
for "whereinafter" read -- herein after --; line 32, for
"inch" read -- inches --; column 14, line 11, for "1,061"
read -- 1.061 --; column 18, line 62, for "75" read -- 76 --;
column 19, line 23, for "exchanges" read -- exchanged --;
column 20, line 48, for "stock" read -- stock. --; column 21,
line 58, for " Al_2O_3 " read -- Al_2O_3 --; column 22, Table
VIII, line 55, for "CATALYSTS²" read -- CATALYSTS³ --; same
Table VIII, line 65, for "CATALYST³" read -- CATALYST⁴ --;
column 23, Example 20, section (C) for the right-hand column
reading

Lbs.		
41.47	read	41.47 lbs.
4.42		4.42 lbs.
1.060		1.060

column 29, Table XI, first column, line 8, for " $(\text{NE})_2\text{O}_3$ "
read -- $(\text{RE})_2\text{O}_3$ --; column 33, Table XIV, second and third
columns, line 6 thereof, for "172 167" read -- --- ---
--; same table, second and third columns, opposite "Surface
Area, m.²/g., Steamed" insert -- 172 167 --; columns
41 and 42, Table XXV, eighth column, line 11 thereof, for
"46.9" read -- 49.6 --;

3,271,418

columns 43 and 44, Table XXVI, fourth column, in the heading, line 2 thereof, for "REX" read -- REHY --.

Signed and sealed this 5th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents