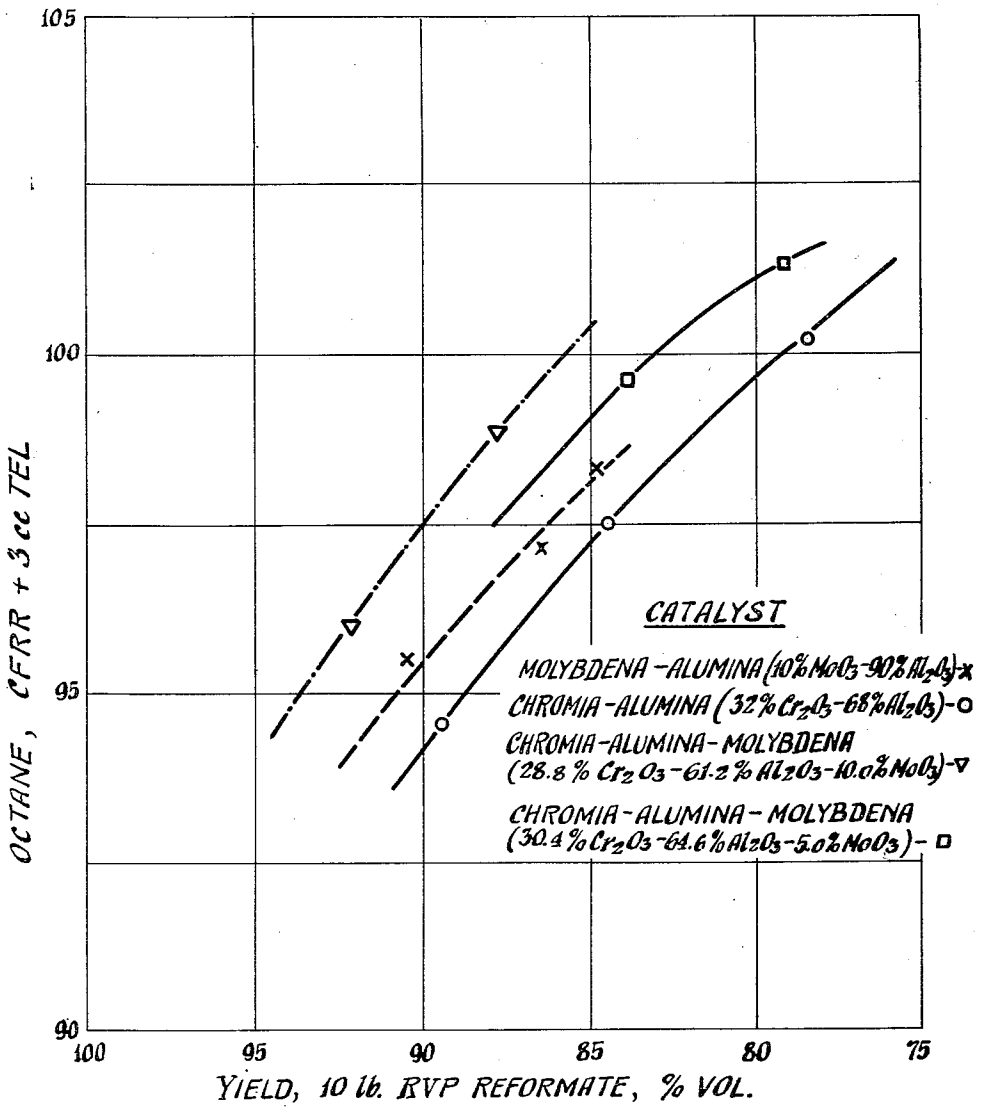
Dec. 11, 1956 W. A. STOVER 2,773,846

ALUMINA-CHROMIA-MOLYBDENA CATALYST

Filed June 13, 1952



INVENTOR.
William A. Stover
BY
Raymond W. Barclay
ATTORNEY

United States Patent Office 2,773,846 Patented Dec. 11, 1956

2,773,846

ALUMINA-CHROMIA-MOLYBDENA CATALYST

William A. Stover, Pitman, N. J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

Application June 13, 1952, Serial No. 293,412

2 Claims. (Cl. 252—465)

This invention relates to an improved catalytic reforming process for obtaining gasoline of high octant number. More particularly, the present invention is directed to catalytic reforming carried out in the presence of a catalyst consisting essentially of a co-gelled chromia-alumina composite of particularly defined composition impregnated with a specified amount of molybdena and to a process for preparing such catalyst.

Reforming operations wherein saturated gasoline fractions comprising straight run gasolines, natural gasolines, etc., are treated to improve the anti-knock characteristics thereof are well known in the petroleum industry. Straight run gasolines generally contain naphthenic hydrocarbons, particularly cyclohexane compounds and paraffinic hydrocarbons which are usually of straight chain or slightly branch chain structure, as well as varying proportions of aromatic hydrocarbons. During reforming, a multitude of reactions take place, including isomerization, dehydrogenation, cyclization, etc., to yield a product of increased aromatic content. Thus, in reforming, it is desired to dehydrogenate the naphthenic hydrocarbons to produce aromatics, to cyclisize the straight chain paraffinic hydrocarbons to form aromatics, and to effect a controlled type of cracking which is selective both in quality and quantity.

Controlled or selective cracking is highly desirable during reforming since such will result in a product of anti-knock characteristics. As a general rule, the lower molecular weight hydrocarbons exhibit a higher octane number, and a gasoline product of lower average molecular weight will usually have a higher octane number. In addition, the isomerization and molecular rearrangement which occur during reforming also result in products having higher anti-knock characteristics. The splitting or cracking of carbon to carbon linkages must, however, be selective and should be such as not to result in substantial decomposition of normally liquid hydrocarbon into normally gaseous hydrocarbons. The selective cracking desired ordinarily involves removal of one or two lower alkyl groups, such as methyl or ethyl, from a given molecule in the form of methane or ethane. Thus, during reforming, it is contemplated that heptane may be converted to hexane, nonane to octane or heptane, etc. Uncontrolled cracking, on the other hand, would result in decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons. For example, non-selective cracking of normal octane would ultimately lead to eight molecules of methane.

Uncontrolled reforming, moreover, generally results in rapid formation and deposition on the catalyst of large quantities of a carbonaceous material generally referred to as "coke." The deposition of coke on the catalyst surface diminishes or destroys its catalyzing effect and results in shorter processing periods with the accompanying necessity of frequent regeneration by burning the coke therefrom. In those instances where the activity of the catalyst is destroyed, it is necessary to

shut down the unit, remove the deactivated catalyst, and replace it with new catalyst. Such practice obviously is time-consuming and inefficient, imparting a greater over-all expense to the reforming operation.

The choice of catalyst for promoting reforming of hydrocarbons to gasolines of enhanced octane rating is dependent on several factors. Such catalyst should desirably be capable of effecting reforming in a controlled and selective manner as discussed above to yield a product of improved anti-knock characteristics. The catalyst selected should further be resistant to poisoning and particularly to sulfur poisoning so that sulfur-containing stocks may undergo reforming without the necessity of subjecting the same to a preliminary treatment for desulfurization. The catalyst also should desirably be characterized by high stability and be capable of easy regeneration, and the method for preparing such catalyst should be commercially attractive, requiring a minimum of equipment and processing stages.

In accordance with the present invention, a catalyst of the above-defined characteristics has been discovered. Broadly, the present invention comprises reforming a naphtha fraction of petroleum in the presence of a catalyst consisting essentially of co-gelled chromia and alumina impregnated with a critical minor proportion of molybdena. The invention further comprises a method for preparing the catalyst under conditions such that a completely homogeneous active surface is obtained.

It has heretofore been proposed to employ composites containing two or more of the oxides of chromium, aluminum, and molybdenum as catalysts for various reactions. Several methods for preparing such catalysts have been proposed, including alternate impregnation of an alumina support with suitable chromium and molybdenum compounds and co-precipitation of solutions containing salts of the desired metals. The difficulties encountered in the former method are well known in that a completely homogeneous active surface is seldom attained even when tedious methods are used. The latter technique, while overcoming this difficulty, is even more involved and requires extremely close control of pH and other variables to assure satisfactory results. Chromia-alumina composites heretofore recommended as reforming catalysts have been found to be characterized by a certain amount of instability, as indicated by the amount of Cr_2O_3 converted to the crystalline form during use. Catalysts of the present invention consisting essentially of co-gelled chromia-alumina impregnated with molybdena have been found to have an improved stability in comparison with the aforesaid chromia-alumina composites and have, further, been found to have improved reforming activity in comparison with chromia-alumina composites or molybdena-alumina composites.

The method of reforming naphtha fractions of petroleum in the presence of a co-gelled chromia-alumina composite impregnated with molybdena as described herein has been found to have cetrain advantages over the processes commercially available. The advantages obtained upon reforming with the present catalyst, while not fully understood, are believed to result from the method of preparation of the catalyst employed. The instant method of catalyst preparation involves the formation of a hydrogel of chromia and alumina preferably containing a chromia-alumina content of at least 10 percent by weight and thereafter impregnating either the washed hydrogel or the dried and tempered material with a solution of a water-soluble molybdenum compound. A preferred embodiment of the invention involves the formation of co-gelled aluminum and chromium oxides which, after drying and/or tempering, are evacuated to a reduced pressure. The evacuated chromia-alumina gel,

generally in particle form, is then brought into contact with a solution of a water-soluble molybdenum compound. Molybdic acid or the alkaline salts thereof are preferred for such purpose. The concentration of the water-soluble molybdenum compound in the impregnating solution may be varied depending upon the catalyst composition desired. Sufficient solution is used so that the particles of chromia-alumina gel may be completely impregnated. The gel particles are permitted to remain in contact with the impregnating solution for a predetermined period of time which is sufficient to permit the solution to impregnate the gel. After completion of the impregnation, the catalyst is removed and slowly heated to an elevated temperature not exceeding about 1000° F. During this heating treatment, it is desirable that the atmosphere surrounding the material be free of oxygen. Such an atmosphere is provided in a preferred embodiment of the invention by permitting the steam produced during the course of heating from the moisture contained in the catalyst after impregnation to blanket the catalyst mass. The impregnated dried catalyst consisting essentially of a co-gel of alumina and chromia impregnated with molybdenum oxide is thereafter ready for use.

Composites consisting of a major proportion of alumina, a minor proportion of chromia, and a minor proportion of molybdena are suitably prepared by the method of the invention. Catalysts having a composition of 10 to 30 percent by weight of chromia, 50 to 89 percent by weight of alumina, and 1 to 20 percent by weight of molybdena are unusually effective for promoting reforming operations in which a saturated gasoline is subjected to conversion to produce a reformed gasoline of improved anti-knock properties. Catalysts having a molybdena concentration in the range of 8 to 12 percent are particularly preferred in the present invention. Thus, a composite having a composition in the range of 20 to 30 percent chromia, 58 to 72 percent alumina, and 8 to 12 percent molybdena, in which chromia and alumina in the form of a co-gel are impregnated with molybdena, represents a preferred embodiment of the invention and has been found to afford an improved yield of reformate of the same octane number as compared to an operation carried out under identical reforming conditions employing a chromia-alumina gel catatlyst of corresponding composition but which had not been impregnated with molybdena.

The method of the invention provides a simple but highly effective procedure for preparation of molybdena-containing reforming catalyst. The co-gel of chromia-alumina is a true gel prepared by forming a hydrosol of chromia and alumina, permitting said hydrosol to set to an all-embracing hydrogel and thereafter drying the hydrogel. The gel, as indicated above, is suitably, but not necessarily, in particle form prior to impregnation. The particles may be of irregular size such as those produced by breaking up a previously set dried gel or the particles may be in the form of extruded or pressed pellets. Preferably, however, the alumina-chromia gel particles are in the form of spheroids prepared by introducing the hydrosol in the form of globules into a water-immiscible medium wherein the hydrosol globules set to spheroidal hydrogel particles which are thereafter removed and dried to form hard gel spheroids highly resistant to attrition. It is particularly preferred to prepare a co-gelled catalytic composite of chromia and alumina from a hydrosol having an inorganic oxide content of at least about 10 percent by weight in accordance with the process described in copending application Serial No. 201,537, filed December 14, 1950, by myself and Robert C. Wilson, Jr. Such process has been set forth in detail in the aforementioned patent application. For convenience herein, the following is offered as a brief description of said process.

A true, all-embracing chromia-alumina hydrogel having a metal oxide product concentration of at least about 10 percent by weight and a relatively short gelation time, i.e., less than 2 hours and preferably less than 60 seconds,

is prepared by intimately admixing an organic chromium salt, such as chromic acetate, and an alkali metal aluminate, such as sodium aluminate to produce a chromia-alumina hydrosol. The hydrosol so formed is permitted to set to a hydrogel. The resulting hydrogel is thereafter subjected to aging and then water-washed, dried, and calcined to yield a catalytic chromia-alumina gel composite. The relative proportions of chromia and alumina may be varied over a wide range. In accordance with the instant invention, however, the concentrations of reactants employed should be such as to afford a chromia-alumina gel of composition within the range set forth hereinabove.

It is preferred, in preparing the above-described hydrogels, to use aqueous solutions of sodium aluminate and chromic acetate. Neither of these substances is a true chemical compound. The ratio of sodium to aluminum can be varied widely as can the ratio of acetate to chromium ion. Variation in the sodium to aluminum ratio of the aluminate solution requires compensating adjustment of the acetate to chromium ratio of the second solution in order to achieve satisfactory gelation. Hydrosols capable of setting to hydrogels in less than about 20 seconds are particularly desirable for the production of bead-like spheroidal particles by methods well known in the art, for example, those described in patents to Marisic, such as U. S. Patent No. 2,384,946.

Quick-setting hydrosols of low viscosity which can be readily handled at bead-forming nozzles are those prepared from sodium aluminate solutions which have a sodium to aluminum mole ratio referred to as "R" of between 1 and 1.5. The acetate to chromium mole ratio in the chromic acetate solution employed should be not less than 2.8R–1.8 and not more than 4R–2.4 and preferably in the range of 4R–2.8 to 4R–2.4.

The control of the mole ratios discussed above is readily achieved in the manufacture of reactant solutions. Chromium acetate is readily formed without introduction of undesirable extraneous materials by reducing sodium dichromate with glycolic acid in the presence of acetic acid as described more fully in my copending application Serial No. 174,594, filed July 18, 1950, now U. S. 2,2615,031, issued October 21, 1952.

Sodium aluminate is conveniently prepared from caustic soda of 50° Bé. and aluminum trihydrate. At a sodium to aluminum mole ratio in the range of 1.25/1 to 1.5/1, the sodium aluminate is advantageously manufactured in an open agitated kettle at 220–230° F. with a reaction time of 1 to 3 hours. Solutions having a lower mole ratio down to about 1.0/1 are made in an autoclave at 240–300° F. and 10 to 30 pounds per square inch gauge at the same reaction time. Sodium aluminate solutions having a low sodium to aluminate ratio less than 1.3 are relatively unstable and may be stabilized by the addition of such organic materials as glycerine, starch, sugar, and the like.

Thus, chromia-alumina hydrogels having a short time of set and a high solids content generally between about 10 and about 30 percent by weight may readily be prepared by controlling the sodium to aluminum mole ratio of the sodium aluminate solution employed and the acetate to chromium mole ratio of the chromic acetate solution. The specific ratios employed will depend upon the particular composition of the chromia-alumina hydrogel desired.

Temperature, acidity, and product concentration are interrelated variables effecting gelation and within the limits in which formation of hydrogels occurs they control gelation time. In general, the other factors can be controlled to achieve gelation at any practical solution temperature. Thus, temperatures from 30° F. to 130° F. are suitable. Best gelation times are experienced at temperatures between about 120 and about 140° F. The pH of the chromia-alumina hydrogels is generally be-

tween 10 and 13. For bead formation, a pH of about 12 yields excellent results.

For the production of chromia-alumina hydrogel beads, preparation is carried out substantially the same as that described in the above noted Marisic patent for producing silica-alumina beads. Thus, a chromium acetate solution and a sodium aluminate solution are contacted in a mixing nozzle and discharged onto the apex of a dividing cone from which a number of small streams flow into a column of water-immiscible liquid. The temperature of said water-immiscible liquid is desirably maintained constant by circulation through a heat exchanger outside the bead-forming tower.

The freshly formed chromia-alumina hydrogel above described is subject to a loss of aluminum as sodium aluminate if immediately washed with water. This tends to weaken the hydrogel to such an extent that it disintegrates in the wash water. That adverse effect can be avoided by immediately treating the freshly formed hydrogel in a slightly alkaline aqueous medium. This is generally accomplished by bringing the freshly formed chromia-alumina hydrogel into contact with an aqueous solution of an ammonium salt of a mineral acid or a mineral acid or a mixture of such salt and acid. In a typical operation, the freshly formed hydrogel beads are sluiced out of the forming tower with oil. The hydrogel beads are then separated from the oil and treated with a 20 percent by weight solution of ammonium sulfate. The solution is advantageously kept at a pH of 8.0 to 9.5 by the addition of sulphuric acid. It is advisable to maintain a solution of this type in contact with the freshly formed hydrogel for some time after formation. For example, the solution is recirculated through the freshly formed hydrogel or otherwise maintained in contact therewith for a period of from about 2 to about 24 hours after forming in order to fix the alumina. Such treatment of the freshly formed hydrogel is designated herein as "aging."

After the aging treatment, the chromia-alumina hydrogel is water-washed free of anions introduced during aging. The washed hydrogel can be satisfactorily dried in either superheated steam or heated air. Hydrogels so dried may be tempered at an elevated temperature generally in the range of 500° F. to 1200° F. in an inert or reducing atmosphere, such as flue gas.

The resulting particles of chromia-alumina gel are evacuated to a reduced pressure of generally less than 10 mm. of mercury and preferably less than 2 mm. of mercury. Evacuation of the gel particles serves a twofold purpose. First, it assures substantial removal of air from the pores of the gel which, if permitted to remain, would cause breakage of the gel particles when the same are subsequently contacted with aqueous impregnating solution. Second, evacuation of the gel particles affords a uniform and rapid distribution of the impregnating solution throughout the evacuated particles and thus provides a uniform, active surface of molybdena on the chromia-alumina gel.

The gel particles in evacuated condition are brought into contact with an aqueous solution of a water-soluble molybdenum compound. A solution of molybdic acid or ammonium molybdate is preferred for such purpose although the alkaline salts of this acid or other readily available molybdenum-containing compounds which are soluble in water may likewise be used. The concentration of the impregnating solution may be varied depending upon the composition of the catalyst desired. Sufficient solution is used to cover the chromia-alumina gel particles during impregnation. The particles are permitted to remain in contact with the impregnating solution for a length of time sufficient to permit the solution to impregnate the chromia-alumina gel. Under the usual conditions contemplated for impregnation, this time will generally range from one second up to about ten minutes.

At the completion of the impregnation, the catalyst is removed from the vacuum chamber and the wet impregnated particles are slowly heated to an elevated temperature in the range of 800 to 1000° F. The rate of such heating should be comparatively slow, generally not in excess of 10° F. per minute. During the period of heating the wet catalyst particles, the atmosphere surrounding such particles should be desirably free of oxygen. This may be accomplished by maintaining an inert atmosphere in contact with the particles during the course of heating. In a preferred embodiment of the invention, a non-oxidizing atmosphere may be provided by permitting the steam produced from the moisture contained in the wet catalyst to blanket the mass of particles being heat-treated. The resulting catalyst is a composite consisting essentially of the chromia-alumina gel impregnated with an effective amount of molybdena.

The evacuation, impregnation and subsequent heat treatment of the chromia-alumina gel particles in accordance with this invention may be carried out either as a batch or continuous operation. Thus, the chromia-alumina gel particles after evacuation may be permitted to contact the molybdic acid or other impregnating solution under substantially static conditions for the requisite time or the gel particles may be passed through a solution of the impregnating solution or, alternatively, the impregnating solution may be circulated through a stationary bed of the gel particles. Likewise, contact between the impregnating solution and the chromia-alumina gel particles may be accomplished by countercurrent passage thereof through an elongated treating zone. Heat treatment of the impregnated particles may also be effected as a batch or continuous operation. An alternate method of preparation for the cogelled chromia-alumina composite impregnated with molybdena as described herein involves contacting the aged, water-washed chromia-alumina hydrogel prepared as hereinabove described with an aqueous solution of a water-soluble molybdenum compound such as molybdic acid or the alkaline salts thereof. In this method of operation, the period of impregnation will generally be within the range of 2 to 48 hours. The impregnated composite is thereafter dried preferably in superheated steam at a temperature of 220–250° F. and subsequently tempered at an elevated temperature of about 1000° F. Also, in some instances, it may be desirable to prepare the catalyst by purging the dried, tempered chromia-alumina gel particles under atmospheric pressure with steam at a temperature above 212° F., thereby replacing the air which normally occupies the gel pores with steam. The gel particles so treated may then be brought into contact with the aqueous impregnating solution of molybdenum compound without encountering gel breakage and impregnation thereafter effected as in the case of the above-described evacuated particles.

The advantage of the present catalyst and procedures of preparation over those of the prior art is that a homogeneous, active catalytic surface is obtained and that the stability of the resultant three-component composite is distinctly improved as compared with chromia-alumina composite which had not been impregnated with molybdena. Thus, the catalyst described herein, comprising an intimate composite of alumina, chromia, and molybdena in specified amounts possesses both greater selectivity, activity, and stability than does a chromia-alumina composite of corresponding composition which had not undergone impregnation with molybdena. It would appear that the advantages derived in reforming with the present catalyst are due to the specific promoting effect of the specified quantities of molybdena when the same are combined with chromia-alumina gel of the above-recited composition range.

Selectivity in a reforming catalyst is highly desirable since it further increases the octane number of the reformed gasoline, produces a gasoline of higher volatility

and converts higher boiling fractions to lower boiling fractions within the range of gasoline. The improved catalysts of the present invention are particularly desirable for reforming operations using a wide variety of stocks because the catalyst is unaffected by the presence of sulfur and is capable of effecting the desired aromatization and controlled cracking under selected conditions of operations.

While certain details referred to in the foregoing description have been directed to catalyst preparation in which chromia-alumina gel is employed in the form of spheroidal particles, it is to be realized that it is within the purview of this invention to use chromia-alumina gels of any other desired form or shape.

The following non-limiting illustrative examples will serve to more specifically point out the process of the invention and the improved results in activity and stability obtained with the catalyst prepared in accordance with said process.

Example 1

A chromia-alumina hydrogel was prepared from the following reactants:

Solution A: 47.5 pounds sodium aluminate made up to a volume of 10 gallons with distilled water;

Solution B: 48 pounds chromic acetate, the acetate to chromium ratio of which is adjusted within the approximate range of 2.6 to 2.8 and then made up to a volume of 13 gallons with distilled water, providing a solution containing 0.92 mole Cr_2O_3 per liter.

Solutions A and B were pumped separately under pressure through heating coils to an efficient mixing nozzle. The solutions were heated to about 110° F. and mixed in equal volumes at a total rate of 1200 cc. per minute. The resulting stream of hydrosol flowed over a divider into a column of D. T. E. (diesel turbine engine) light oil. The hydrosel set to beads of hydrogel and the resulting hydrogel beads were sluiced from the bottom of the forming tower with a 20 percent by weight aqueous solution of ammonium sulfate. The sluicing solution was maintained at a pH of 8.5 by the addition of sulfuric acid. Since the pH of the hydrogel was about 10.5, it was necessary to add sulfuric acid to the sluicing solution in order to maintain the pH at 8.5. The bead hydrogel was aged for 24 hours in the same solution that was used to sluice from the forming tower. After aging, the gel was washed until a sulfate-free wash water was indicated. The washed hydrogel had a product concentration of 21 percent by weight. The hydrogel was thereafter dried in 100 percent steam at 260–270° F. for 3 to 4 hours and then tempered 4 hours at 1100° F. in a hydrogen atmosphere. The resulting beads of gel contained approximately 32 percent by weight of chromia and 68 percent by weight of alumina.

One thousand grams of the above-described chromia-alumina gel beads were placed in a suitable chamber and evacuated to a pressure of 2 mm. of mercury. An aqueous solution of 494 grams of ammonium molybdate solution having a concentration of 23 percent by weight of MoO_3 was then introduced into the chamber. The gel beads were permitted to remain in contact with the ammonium molybdate solution for a period between 1 and 60 seconds, after which the impregnated gel beads were removed from the vacuum chamber and slowly heated to 1000° F. over a period of 250 minutes. During the heating period, the atmosphere surrounding the impregnated gel particles was maintained free of oxygen by permitting steam from the moisture contained in the catalyst to blanket the mass of gel particles. The resulting catalyst had the following composition:

Chromia, percent weight	28.8
Alumina, percent weight	61.2
Molybdena, percent weight	10.0

Example 2

A chromia-alumina hydrogel was prepared by a procedure similar to that of Example 1. The hydrogel after aging was water-washed until a sulfate-free wash water was indicated. The washed hydrogel had a product concentration of 18 percent by weight.

The washed hydrogel (8,640 grams) was brought into contact with 6,520 grams of molybdic acid solution having a concentration of 3.8 percent by weight of MoO_3. The hydrogel was permitted to remain in contact with the molybdic acid solution for a period of 24 hours, after which the impregnated hydrogel product was removed from the impregnating solution, dried in superheated steam for 5 hours at 233–240° F., and thereafter tempered for 3 hours at 1000° F. The resulting catalyst had the following composition:

Chromia, percent weight	24.6
Alumina, percent weight	65.4
Molybdena, percent weight	9.0

The catalyst of Example 1 together with a similarly prepared catalyst but containing 5 percent molybdena (30.4 percent Cr_2O_3—64.6 percent Al_2O_3—5.0 percent MoO_3), a chromia-alumina cogel prepared as described in Example 1 but not impregnated with molybdena (32 percent Cr_2O_3—68 percent Al_2O_3), and a catalyst consisting essentially of molybdena on alumina (10 percent MoO_3—90 percent Al_2O_3) were tested in reforming a naphtha petroleum fraction under the following conditions:

Liquid hourly space velocity	1
Time on stream, hours	2
Recycle to naphtha mole ratio	6.0
Hydrogen to hydrocarbon mole ratio	4
Total pressure, p. s. i. g.	175

The results obtained in this operation are shown graphically in the attached drawing for the above-described catalysts. Referring more particularly to the drawing showing the yield-octane number relationship, it will be noted that at the 98 octane (CFRR+3 cc. TEL) level the cogelled chromia-alumina catalyst impregnated with 10 percent by weight molybdena (Example 1) produced a yield advantage of 5.5 percent volume as compared with chromia-alumina composite and a 4 percent volume advantage over the alumina-molybdena composite, indicating the greater selectivity of the present catalyst. The similar cogelled chromia-alumina catalyst containing 5 percent by weight of molybdena also showed an advantage over both the chromia-alumina catalyst and the alumina-molybdena catalyst although such advantage in this case was somewhat less than that obtained with the catalyst of higher molybdena content. The higher activity of the latter is further shown by the fact that an average temperature of 50° F. less than that required for chromia-alumina was sufficient to produce a product of the same octane level.

The improvement in stability of the present cogelled chromia-alumina composites impregnated with molybdena prepared in the manner herein described as illustrated in the table set forth below using the conversion of Cr_2O_3 to the crystalline form as the measure of the instability. The test conditions employed involved heating the catalyst at a temperature of 1400° F. in air for a predetermined length of time. The amount of chromia converted to the crystalline form was determined by X-ray diffraction. The results obtained were as follows:

	Time, Hrs.	Percent Crystalline Cr_2O_3
Chromia-alumina (32% Cr_2O_3—68% Al_2O_3)	10	16
Chromia-alumina-molybdena (32% Cr_2O_3—67.25% Al_2O_3—0.75% MoO_3)	4.5	12
Chromia-alumina-molybdena (31.5% Cr_2O_3—67.0% Al_2O_3—1.5% MoO_3)	4.5	9
Chromia-alumina-molybdena (29.1% Cr_2O_3—61.9% Al_2O_3—9.0% MoO_3)	11	1
	23	8

It will be noted from the above-tabulated data that the catalyst containing 9.0 percent molybdena showed no appreciable crystalline Cr_2O_3 under the same conditions at which chromia-alumina showed 16 percent by weight of crystalline Cr_2O_3. At the more severe test conditions, with an exposure time more than twice that of the chromia-alumina, the improved catalyst showed only one-half the crystalline Cr_2O_3 content of the former.

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

What is claimed is:

1. A catalytic composite consisting essentially of 10 to 30 percent by weight of chromia, 50 to 89 percent by weight alumina, and 1 to 20 percent by weight of molybdena, having chromia and alumina components intimately combined in the form of a dried hydrogel, which hydrogel is impregnated with the molybdena component.

2. A catalytic composite consisting essentially of 20 to 30 percent by weight of chromia, 58 to 72 percent by weight of alumina, and 8 to 12 percent by weight of molybdena, having the chromia and alumina components intimately combined in the form of a dried hydrogel, which hydrogel is impregnated with the molybdena component.

References Cited in the file of this patent

UNITED STATES PATENTS

1,778,517	Benner	Oct. 14, 1930
2,270,165	Groll et al.	Jan. 13, 1942
2,397,350	Hayden et al.	Mar. 26, 1946
2,451,471	Burke et al.	Oct. 19, 1948
2,492,167	Marisic et al.	Dec. 27, 1949
2,577,823	Stine	Dec. 11, 1951
2,602,771	Munday et al.	July 8, 1952
2,635,082	Smith	Apr. 14, 1953
2,670,322	Krebs et al.	Feb. 23, 1954