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ALUMINA-CHROMIA-PHOSPHORUS PENTOXIDE CATALYST
AND METHOD FOR PREPARING THE SAME
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Fig. 2.

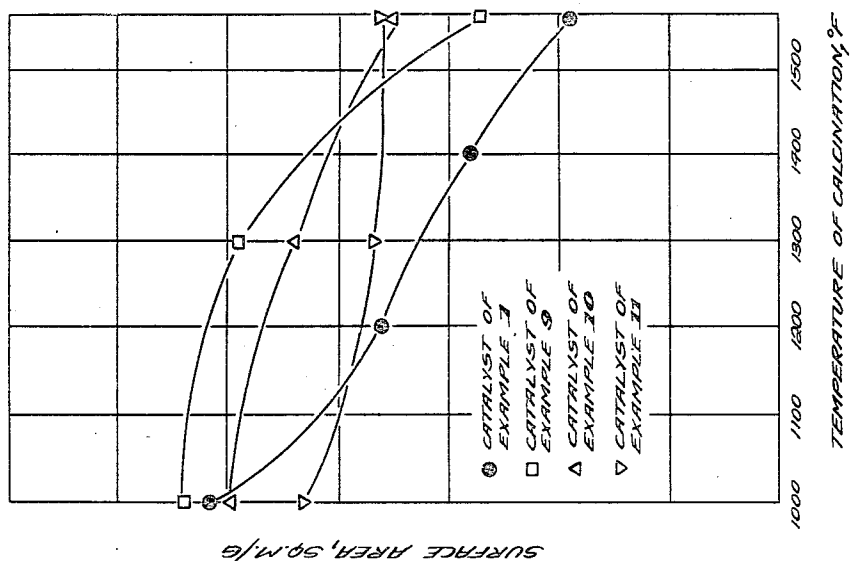
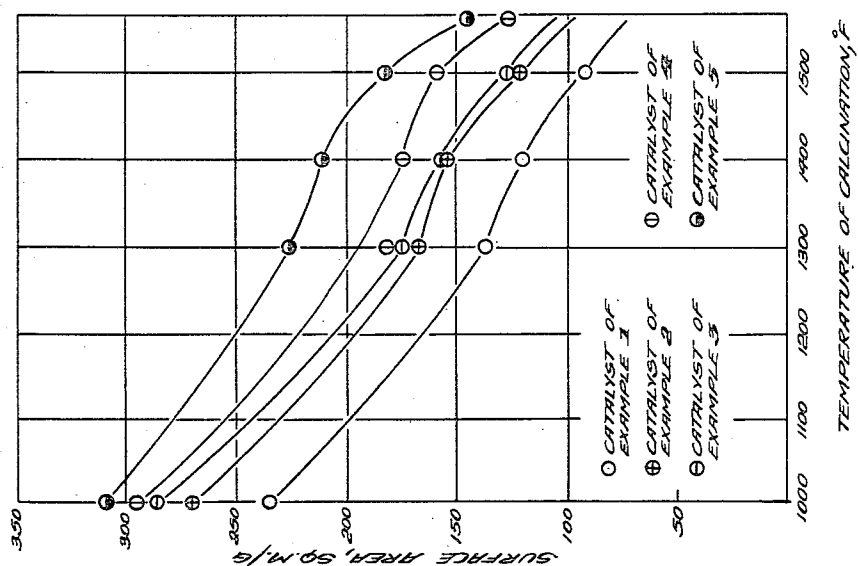


Fig. 1.



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ALUMINA-CHROMIA-PHOSPHORUS PENTOXIDE CATALYST AND METHOD FOR PREPARING THE SAME

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6 Claims. (Cl. 252—437)

This invention relates to an improved catalytic reforming process for obtaining gasoline of high octane number. More particularly, the present invention is directed to catalytic reforming carried out in the presence of a catalyst consisting essentially of a cogelled chromia-alumina composite of particularly defined composition impregnated with a specified amount of phosphorous pentoxide 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 cyclize 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 improved 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 occurs during reforming also results 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 hydrocarbon. 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

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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 overall 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 should also 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 cogelled chromia and alumina impregnated with a minor proportion of phosphorous pentoxide. The invention further comprises an improved catalytic composition and a method for preparing the same.

It has heretofore been proposed to employ composites containing the oxides of chromium and aluminum as catalysts for various reactions. Several methods for preparing such catalysts have been proposed, including impregnation of an alumina support with suitable chromium compounds and co-precipitation of solutions containing salts of chromium and aluminum. The difficulties encountered in the former method are well known in that a completely homogeneous, active surface is seldom obtained 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 loss of surface area during use. Catalysts of the present invention, consisting essentially of cogelled chromia and alumina impregnated with P_2O_5 , have been found to have an improved thermal stability, i. e., ability to resist loss of surface area upon aging in comparison with the aforesaid chromia-alumina composites.

The method of reforming naphtha fractions of petroleum in the presence of a cogelled chromia-alumina composite impregnated with P_2O_5 as described herein has been found to have certain 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/or tempered material with a solution of a water-soluble phosphate. The acidity of the phosphate impregnating solution should not be such as to detrimentally affect the hydrogel or gel structure. Thus, strongly acidic impregnating solutions should be avoided. Mildly acidic impregnating solutions may be tolerated. Preferably, the phosphate impregnating solution is neutral or slightly alkaline. For example, a slightly ammoniacal solution

of ammonium phosphate has been found to provide an effective impregnating solution. The concentration of the water-soluble phosphate compound in the impregnating solution may be varied, depending upon the catalyst composition desired. The phosphate may be added by impregnation of either the chromia-alumina hydrogel or the dried or calcined chromia-alumina gel. Sufficient solution is used so that the particles of chromia-alumina hydrogel or gel may be completely impregnated. The hydrogel or 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 hydrogel or 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 heating the impregnated catalyst in an atmosphere of hydrogen. The impregnated dried catalyst, consisting essentially of a cogel of alumina and chromia impregnated with phosphorous pentoxide, is thereafter ready for use.

Composites consisting of a major proportion of alumina, a minor proportion of chromia, and a minor proportion of phosphorous pentoxide are suitably prepared by the method of the invention. Catalysts having a composition of 20 to 40 percent by weight of chromia, 50 to 80 percent by weight of alumina, and 0.2 to 10 percent by weight of phosphorous pentoxide are unusually effective for promoting reforming operations in which a petroleum naphtha is subjected to conversion to produce a reformed gasoline of improved anti-knock characteristics. Catalysts having phosphorous pentoxide concentration in the range of 2 to 5 percent are particularly preferred in the present invention. Thus, a composite having a composition in the range of 25 to 35 percent chromia, 60 to 73 percent alumina, and 2 to 5 percent phosphorous pentoxide, in which chromia and alumina in the form of a cogel are impregnated with phosphorous pentoxide, represents a preferred embodiment of the invention.

The method of the invention provides a simple but highly effective procedure for preparation of the catalyst. The cogel of chromia-alumina is a true gel prepared by forming a hydrosol of chromia and alumina, permitting said hydrosol to set to a hydrogel, and thereafter drying the hydrogel. If desired, the hydrogel may be impregnated before drying. The hydrogel or gel 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 hydrogel or 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. It is particularly preferred to prepare a cogelled 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 co-pending application Serial No. 201,537, filed December 14, 1950, by William A. Stover and Robert C. Wilson, Jr. Such process has been set forth in detail in the aforementioned patent. For convenience herein, the following is offered as a brief description of said process.

A true 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 but ordinarily alumina is present in major proportion and chromia in minor proportion. Generally, the composite contains a chromium oxide content in the range of 20 to 40 weight percent and an alumina content in the range of 60 to 80 weight percent. A particularly preferred composition is one containing approximately 30 to 35 weight percent chromic oxide and approximately 65 to 70 weight percent aluminum oxide.

It is preferred to use aqueous solutions of sodium aluminate and chromium acetate for preparation of the above-described hydrogels. 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 2.8 R-1.8 and not more than 4 R-2.4, and preferably in the range of 4 R-2.8 to 4 R-2.4.

The control of the mole ratios discussed above is readily achieved in the manufacture of the 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 U. S. 2,615,031.

Sodium aluminate is conveniently prepared from caustic soda of 50° Bé. and aluminum trihydrate. At a sodium to aluminum mole ratio in the range 1.25/1 to 1.5/1, the sodium aluminate is advantageously manufactured in an open, agitated kettle at 220° F. to 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° F. to 300° F. and 10 to 30 pounds per square inch gage at the same reaction time. Sodium aluminate solutions having a low sodium to aluminum ratio of 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 be dependent upon the particular composition of the chromia-alumina hydrogel desired.

Temperature, acidity, and product concentration are inter-related 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 have been experienced at temperatures between about 120° F. and about 140° F. The pH of the chromia-alumina hydrogels is generally between 10 and 13. For bead formation, a pH of about 12 has been found to yield excellent results.

For the production of chromia-alumina hydrogel beads, preparation is carried out substantially the same

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as that described in the above-noted Marisc patent for producing silica-alumina beads. Thus, a chromic 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 at a constant temperature 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 6.0 by the addition of sulfuric 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 re-circulated 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. Thereafter, the solution may be maintained in contact with the hydrogel for an additional period of about 2 to 24 hours without pH control. During this latter period, the pH of the aging solution may rise from 6.0 to 9.0-9.5. Such treatment of the freshly formed hydrogel is designated herein as "aging."

After aging treatment, the chromia-alumina hydrogel is washed free of anions introduced during aging. The washed hydrogel can be satisfactorily dried in either superheated steam or air. The hydrogel so dried has been tempered in an atmosphere of hydrogen, nitrogen, carbon dioxide, carbon monoxide, steam, and air. The use of mixtures containing oxygen results in the production of a gel of low mechanical strength. The chromia-alumina gel should, accordingly, be tempered in an inert or reducing atmosphere.

In accordance with the process of the present invention, it has been found that the heat stability of the chromia-alumina gel catalyst described above for promoting reforming is markedly increased by bringing the chromia-alumina hydrogel after the alumina content has been fixed by the aforementioned aging procedure into contact with a solution of a phosphorous compound decomposable upon heating into phosphorous pentoxide, thereafter removing the hydrogel from said solution and heating to yield a resultant chromia-alumina gel impregnated with a minor proportion of P_2O_5 . In general, the chromia-alumina hydrogel may be brought into contact with the impregnating solution of phosphorous compound at any time subsequent to the above-described aging and washing steps. Thus, the hydrogel, after aging and washing, but before drying, may be contacted with the impregnating solution and the resultant composite dried and heated to a temperature sufficient to effect decomposition of the phosphorous compound to phosphorous pentoxide, or the dried hydrogel, i. e., gel, may be brought into contact with the impregnating solution and thereafter dried and calcined. Alternatively, the calcined chromia-alumina gel may be impregnated with a soluble phosphate compound and thereafter dried and heated to a temperature sufficient to convert such phosphate compound to phosphorous pentoxide.

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Contact of the chromia-alumina composite with the impregnating solution should, in accordance with the instant invention, be maintained for a sufficient period of time to effect the deposition of a small amount of phosphorous compound on the surface of the composite. The critical factor in this step is the amount of phosphorous compound incorporated. If either too much or too little phosphorous compound is incorporated, the resulting catalyst does not have the improved characteristics of the catalyst prepared by the method of the invention. The amount of phosphorous compound employed in this step is dependent upon the concentration of phosphorous pentoxide which it is desired to incorporate by impregnation in the finished catalyst and is adjusted by controlling the concentration of phosphorous compound in solution or the amount of the impregnating solution such that when the specified amount of phosphorous compound is incorporated, the ultimate catalyst contains the final amount of phosphorous pentoxide which it is desired to deposit by impregnation. It has been found that the concentration of phosphorous pentoxide impregnated on the chromia-alumina cogelled catalyst in accordance with the process of the invention should desirably be between about 0.2 and about 10 percent by weight, and preferably between about 2 and about 5 percent by weight of the original catalyst. Amounts smaller than about 0.2 percent P_2O_5 have not been found to appreciably increase the thermal stability of the chromia-alumina cogelled catalyst, while large amounts in excess of about 10 percent P_2O_5 impregnated on the catalyst surface have been found to unduly increase the extent of coke formation as the catalyst ages.

The chromia-alumina composite, i. e., the aged hydrogel or gel derived therefrom, is thus impregnated with a solution of a soluble phosphorous compound, which compound may be converted to phosphorous pentoxide by heating. While aqueous solutions are to be preferred for practical reasons, other solutions, such as alcoholic solutions or ammoniacal solutions may be used. A concentrated solution of just sufficient volume to wet the chromia-alumina composite may be used or a large volume of a more dilute solution may be used. An important factor in the impregnation of calcined chromia-alumina gel is the presence of soluble chromate ions on the catalyst surface. If a large volume of dilute solution is used for impregnation, sufficient chromium may be removed from the spent solution to lower the activity of the base catalyst. Accordingly, it is preferred, when impregnating the dried or calcined chromia-alumina gel, to subject the same to a preliminary treatment with hydrogen to anchor the chromium before such gel is brought into contact with the impregnating solution. Excess solution may be drained from the chromia-alumina composite or it may be evaporated in the presence of such composite to increase the amount of composite impregnated. The impregnation may be carried out under vacuum or under pressure or under a combination of vacuum and pressure. When the composite is a dry gel, it is preferred to evacuate the pores thereof before impregnation in order to avoid shattering of the gel when the same is brought into contact with aqueous impregnating solution. If, due to the solubility of the phosphorous compound, it is not possible to incorporate the desired amount of compound in one impregnation, the composite may be dried after the first impregnation and the impregnation repeated until the desired amount of compound is incorporated. While soluble phosphorous compounds capable of conversion to phosphorous pentoxide by heating may generally be used for effecting impregnation, providing the acidity thereof is not such as to adversely affect the gel structure, it is preferred to employ slightly alkaline compounds of phosphorous. Thus, compounds, such as diammonium hydrogen phosphate, ammonium phosphate, and ammonium dihydrogen phosphate are easily decomposed by heating at moderate temperatures to yield phosphorous pentoxide.

For impregnation of the wet hydrogel, the use of a strongly acid impregnating solution should be avoided in order not to injure the catalyst structure. However, mildly acidic impregnating solutions, i. e., those having a pH not less than about 6, may be used for impregnation of the dried or calcined chromia-alumina catalyst.

The impregnation may be carried out either as a batch or continuous operation. Thus, the chromia-alumina hydrogel, after aging and washing, may be permitted to soak in the impregnating solution under substantially static conditions for the requisite time, or the chromia-alumina gel composite in the form of spheroidal globules or particles of other desired shape may be passed through a bath of the impregnating solution or, alternatively, the impregnating medium may be circulated through a stationary bed of the hydrogel or gel particles. Likewise, contact between the impregnating solution and the hydrogel or gel particles may be accomplished by counter-current passage thereof through an elongated treating zone.

After the chromia-alumina composite has been impregnated with a suitable amount of a soluble phosphorous compound decomposable to phosphorous pentoxide by heating, the impregnated composite is dried and then calcined. The calcination is carried out to convert a phosphorous compound to phosphorous pentoxide. The minimum calcination temperature is the temperature of decomposition of the impregnating compound. Usually, temperatures somewhat above the minimum decomposition temperature are preferred. On the other hand, very high temperatures cause sintering and are to be avoided. The rate of heating should be comparatively slow, generally not in excess of 10° F. per minute. Where spheroidal particles are being treated, the rate of heating should ordinarily not exceed about 4° F. per minute. Temperatures in the range of 300° F. to 1000° F. are quite suitable in nearly all cases, but somewhat lower temperatures may be applied in some cases and higher temperatures up to about 1400° F. may be employed if desired. During this heating treatment, it is desirable that the atmosphere surrounding the composite be free of oxygen. It is particularly feasible, although not essential, to flush the chromia-alumina composite with a reducing gas such as hydrogen during the calcination to avoid chromate formation during the initial heat treatment. This is especially desired for composites, the structure of which has not been set by previous calcination, such as hydrogels in the wet or dry state. The calcination is usually continued until the impregnated phosphorous compound is completely decomposed but is discontinued before sintering occurs. The finished catalyst is a chromia-alumina gel impregnated with an activating amount of phosphorous pentoxide. While certain details referred to in the foregoing description have been directed to the formation of the hydrogel in the form of chromia-alumina gel beads, it is to be realized that the treating procedure of this invention may be practiced upon chromia-alumina cogelled composites of any other desired form or shape. The following non-limiting illustrative examples will serve to more specifically point out the catalyst and process of the invention and the improved results in thermal 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.—Diluted sodium aluminate containing approximately 18.3 percent Al_2O_3 , 14.4 percent Na_2O , and 67.3 percent H_2O .

Solution B.—Diluted chromic acetate prepared by reduction of sodium chromate with glycolic acid and containing approximately 26.0 percent $\text{Cr}(\text{CH}_3\text{COO})_3$, 1.4

percent $\text{Cr}(\text{OH})_3$, 2.3 percent CH_3COONa , 5.5 percent $(\text{COONa})_2$, 0.6 percent HCOONa , 0.8 percent

$\text{CH}_2\text{OHCOONa}$

and 63.4 percent H_2O .

Solutions A and B were pumped separately under pressure to an efficient mixing nozzle. The solutions were heated to 120–125° F. and mixed in equal volumes at a rate of 1.06 gallons per minute. The resulting stream of hydrosol flowed over a divider into a column of oil. The hydrosol set to beads of hydrogel and the resulting hydrogel beads were sluiced from the bottom of the forming tower in a stream of oil. After separating oil from the hydrogel beads, the latter were aged in a 20 percent by weight aqueous solution of ammonium sulfate. Since the pH of the aging solution rises as it flows through the fresh hydrogel beads, sulfuric acid was added in sufficient amount to maintain a pH of about 6.0. The bead hydrogel was aged in this solution for 24 hours, after which it was allowed to age an additional 8 hours without pH control. During this latter period, the pH of the aging solution rose from about 6.0 to about 9.5. After aging, the hydrogel was washed until a sulfate-free wash water was indicated. The washed hydrogel had a product concentration of 18.3 percent by weight. The hydrogel was thereafter dried in 100 percent steam at 230–235° F. for 7 hours, then gradually raised to 350° F. over a period of about 2 hours, and then tempered by heating in a closed vessel to 1100° F. at the rate of 2½° F. per minute. The resulting beads of gel contained 24 mole percent Cr_2O_3 and 76 mole percent Al_2O_3 . This catalyst is representative of that produced by the aforementioned process of Stover and Wilson and may be considered as a blank for comparison with the catalysts which have undergone treatment in accordance with the present process.

Example 2

A chromia-alumina hydrogel, prepared as in Example 1, was treated, after aging and washing, with an aqueous solution containing enough diammonium hydrogen phosphate so that the phosphate ions, upon complete absorption, produced 1.5 percent by weight P_2O_5 after calcination. After allowing the hydrogel to soak for about 16 hours, the hydrogel particles were removed, drained, and washed slightly to remove adhering solution. Analyses of the drained liquid showed substantially complete removal of the phosphate ions and no extraction of chromium. The wet impregnated particles were dried at 175° F. in a closed vessel, thereby providing a water-saturated atmosphere during the early drying stage and preserving a maximum proportion of whole gel particles. The partially dry particles were then heated to 1000° F. in a hydrogen atmosphere over a 4-hour period and then maintained at 1000° F. in hydrogen for 12 hours.

Example 3

The chromia-alumina hydrogel of Example 1 was impregnated with 2.0 percent P_2O_5 by the procedure of Example 2.

Example 4

The chromia-alumina hydrogel of Example 1 was impregnated with 3.0 percent P_2O_5 by the procedure of Example 2.

Example 5

The chromia-alumina hydrogel of Example 1 was impregnated with 5.0 percent P_2O_5 by the procedure of Example 2.

Example 6

A chromia-alumina gel, prepared as in Example 1, was treated after aging, washing, and calcining, with an aqueous solution of diammonium hydrogen phosphate dissolved in just enough water to completely cover the gel particles and to form 0.6 percent by weight P_2O_5

upon ignition. After allowing to stand 16 hours, the impregnated gel particles were drained and dried in air about 16 hours at about 180° F. and then calcined in a hydrogen atmosphere at 1000° F. for 12 hours.

Example 7

Chromia-alumina gel particles, prepared as in Example 1, were impregnated with 1.9 percent P_2O_5 by the procedure of Example 6.

Example 8

Chromia-alumina gel particles, prepared as in Example 1, were impregnated with 3.1 percent P_2O_5 by the procedure of Example 6.

Example 9

A chromia-alumina gel, prepared as in Example 1, was treated, after aging, washing, drying, and calcining, with hydrogen for 12 hours to fix the chromium. The reduced calcined chromia-alumina gel was then brought into contact with an ammoniacal solution containing sufficient ammonium phosphate to form 2.5 percent by weight P_2O_5 upon ignition. After allowing to stand 16 hours, the impregnated gel particles were dried 12 hours in air at 180° F. and then heated to 1000° F. in a hydrogen atmosphere over a 4-hour period and calcined at 1000° F. in hydrogen for 12 hours.

Example 10

A chromia-alumina gel, prepared as in Example 1, was treated and impregnated with 6.2 percent P_2O_5 by the procedure of Example 9.

Example 11

A chromia-alumina gel, prepared as in Example 1, was treated and impregnated with 12.4 percent P_2O_5 by the procedure of Example 9.

The foregoing catalysts were tested for stability under thermal conditions encountered in the reforming of petroleum naphthas. The data obtained upon testing are shown graphically by the attached curves wherein:

Figure 1 represents the change in surface area, in square meters per gram, of the untreated and treated chromia-alumina catalyst impregnated with varying amounts of P_2O_5 in the hydrogel state.

Figure 2 represents the change in surface area, in square meters per gram, of the untreated and treated chromia-alumina catalyst impregnated with varying amounts of P_2O_5 after the gel has been dried and calcined.

Figure 1 shows that, when the chromia-alumina gel particles are impregnated before drying, there is an increase in the initial surface area after calcination in hydrogen with an increase in the phosphate content up to 5 percent P_2O_5 . There is a parallel increase in surface area stability with phosphate content for heat treatment in air at 1300° F. or 1400° F. At higher calcination temperatures, the surface area stability drops off rapidly for all these catalysts. If the gel particles are impregnated after calcination as shown by the data of Figure 2, appreciable phosphate addition results in reduced initial surface area. This decrease in surface area is apparent for the chromia-alumina gel impregnated with 12.4 weight percent P_2O_5 . For relatively high phosphate concentrations, an increase in surface area stability with increasing phosphate concentrations is shown even after heat treatment at 1560° F. The results of Figures 1 and 2 show that the heat stability of the catalyst increased with increasing concentrations of P_2O_5 impregnated on chromia-alumina gel particles.

The present catalyst, comprising a major proportion of alumina and a minor proportion of chromia in the form of a cogel impregnated with phosphorous pentoxide generally possesses improved thermal stability over a chromia-alumina composite of corresponding composition which has not undergone impregnation with phosphorous pentoxide. It would accordingly appear that the advantages achieved with the treated catalyst of the invention are

due to the effects of the specified quantities of phosphorous pentoxide when the same are deposited on a chromia-alumina gel prepared as described herein.

What is claimed is:

1. A catalytic composite consisting essentially of 20 to 40 percent by weight of chromia, 50 to 80 percent by weight alumina, and 0.2 to 10 percent by weight of phosphorous pentoxide, wherein the chromia and alumina components in the form of a cogel are impregnated with the phosphorous pentoxide component.
2. A catalytic composite consisting essentially of 25 to 35 percent by weight of chromia, 60 to 73 percent by weight alumina, and 2 to 5 percent by weight of phosphorous pentoxide, wherein the chromia and alumina components in the form of a cogel are impregnated with the phosphorous pentoxide component.
3. A method for preparing an intimate catalytic composite of chromia, alumina, and phosphorous pentoxide, which comprises forming a chromia-alumina cogel consisting of a major proportion of alumina and a minor proportion of chromia, calcining said chromia-alumina gel, reducing said calcined chromia-alumina gel with hydrogen, bringing said reduced gel into contact with an aqueous solution of a water-soluble phosphorous compound, maintaining said contact for a predetermined time sufficient to effect impregnation of said gel with said solution, removing the gel from the impregnating solution, and drying the same to yield a chromia-alumina gel containing 20 to 40 percent by weight of chromia, 50 to 80 percent by weight of alumina and impregnated with between about 0.2 and about 10 percent by weight of phosphorous pentoxide, and thereafter slowly heating the resulting gel product in a hydrogen atmosphere to an elevated temperature not exceeding about 1000° F. at a rate not in excess of 10° F. per minute.
4. A method for preparing an intimate catalytic composite of chromia, alumina, and phosphorous pentoxide, which comprises preparing a chromia-alumina cogel consisting of a major proportion of alumina and a minor proportion of chromia by mixing aqueous solutions of sodium aluminate and chromic acetate to yield a hydrosol having a chromia-alumina content of at least about 10 percent by weight, controlling the sodium to aluminum ion ratio and the acetate to chromium ion ratio in said solutions to effect rapid gelation of said hydrosol to a hydrogel, aging the hydrogel so obtained, washing the aged hydrogel, drying and tempering the same to yield a resulting hard chromia-alumina gel, reducing said gel with hydrogen, bringing the reduced gel into contact with an aqueous solution of a water-soluble phosphorous compound, and maintaining said contact for a predetermined time sufficient to effect impregnation of said gel with said solution, removing the gel from the impregnating solution, and drying and calcining the same in an oxygen-free atmosphere to yield a chromia-alumina gel containing 20 to 40 percent by weight of chromia, 50 to 80 percent by weight of alumina and impregnated with a small amount in the range of 0.2 to 10 percent by weight of phosphorous pentoxide.
5. A method for producing an intimate catalytic composite of chromia, alumina, and phosphorous pentoxide, which comprises preparing a chromia-alumina cogel by mixing aqueous solutions of sodium aluminate and chromic acetate to yield a hydrosol having a chromia-alumina content of at least about 10 percent by weight, controlling the sodium to aluminum ion ratio and the acetate to chromium ion ratio in said solutions to effect rapid gelation of said hydrosol to a hydrogel, aging the hydrogel so obtained, washing the aged hydrogel, bringing the washed hydrogel into contact with an aqueous solution of a water-soluble phosphorous compound and maintaining said contact for a predetermined time sufficient to effect impregnation of said hydrogel with said solution, removing the hydrogel from the impregnating solution, and drying the same to yield a chromia-alumina gel containing 20 to 40 percent by weight of chromia, 50 to 80 percent

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by weight of alumina and impregnated with between 0.2 and 10 percent by weight of phosphorous pentoxide, and thereafter slowly heating the resulting gel product in a hydrogen atmosphere to an elevated temperature not exceeding about 1000° F. at a rate not in excess of 10° F. per minute.

6. A method for producing an intimate catalytic composite of chromia, alumina, and phosphorous pentoxide, which comprises forming spheroidal particles of chromia-alumina gel, calcining the gel particles, reducing the calcined gel particles with hydrogen, bringing the reduced particles into contact with an aqueous ammonium phosphate solution, maintaining said contact for a predetermined time sufficient to effect impregnation of said particles with said solution, removing the particles from the impregnating solution, and drying the same to yield

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spheroidal particles of chromia-alumina gel containing 25 to 35 percent by weight of chromia, 60 to 73 percent by weight alumina and impregnated with phosphorous pentoxide in the amount of 2 to 5 percent by weight, and thereafter slowly heating the resulting gel product in a hydrogen atmosphere to an elevated temperature not exceeding about 1000° F. at a rate not in excess of about 4° F. per minute.

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