United States Patent Office 2,849,382 Patented Aug. 26, 1958

2,849,382

SILICA-ALUMINA-CHROMIUM FLUORIDE CATALYTIC COMPOSITIONS; THEIR PREPARATION; AND THEIR USE IN HYDROCARBON CONVERSIONS

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No Drawing. Application June 7, 1955
Serial No. 513,893

7 Claims. (Cl. 196—52)

This invention relates to a catalytic composition effective in catalytic processes for coverting hydrocarbons. More particularly, this invention relates to new and improved catalytic compositions having specific physical properties consisting essentially of silica, alumina and chromium fluoride, their preparation, and to a process for converting hydrocarbons employing the new catalyst wherein a specific hydrocarbon fraction, boiling above the gasoline range, is converted to gasoline of high octane rating.

The conversion of various petroleum hydrocarbon fractions by processes such as cracking, reforming, hydroforming, and the like, using a variety of catalysts and reaction conditions, has been described. Such heretofore described processes, however, are not suitable for converting the hydrocarbon fraction boiling substantially within the range of from about 375° F. to 500° F. to high octane gasoline in a single stage. Instead of achieving a good yield of high octane gasoline, there is produced gasoline hydrocarbons of relatively low octane rating usually in low yields, the production of normally gaseous hydrocarbons, such as propanes and butanes, is excessive, and the reduction of catalyst activity is rapid. It has heretofore been necessary to employ at least two stages to convert a petroleum hydrocarbon fraction boiling above the gasoline range, especially a fraction boiling within the range of from about 375° F. to 500° F., to high octane gasoline. Such processes usually involve a cracking stage wherein a portion of the hydrocarbons are converted to hydrocarbons boiling in the gasoline range, and a reforming, or hydroforming, stage to upgrade the octane rating of the gasoline. In the upgrading stage, the use of two catalysts in separate reactors with a hydrocarbon separation step between the reactors, or the use of two catalysts in a single reactor, has heretofore commonly been required.

An object of this invention is to provide a new and improved catalytic composition effective for converting hydrocarbons.

Another object is to provide a process for converting a hydrocarbon fraction boiling within the range of from about 375° F. to 500° F. to high octane gasoline in a single stage and in good yield.

A still further object is to provide a process for the preparation of a new and improved catalyst.

Other objects and their achievement, in accordance with the invention will be apparent from the following specification.

General

A new catalytic composition has been discovered which gives improved results in converting hydrocarbons. The new catalytic composition contains defined quantities of chromium fluoride, silica and alumina as hereinafter discussed. The new catalytic composition must have physical properties, namely surface area and pore radius, within defined limits, also as hereinafter discussed. It has been found that this new catalytic composition is especially effective in converting relatively high boiling petroleum fractions, e. g., a fraction boiling within the range of from about 375° F. to 500° F., to gasoline hydrocarbons of high octane number, and that the formation of coke and normally gaseous hydrocarbons, such as butane, is low and the olefinic content of the normally gaseous hydrocarbons that are formed is high as compared to heretofore described processes.

The reactions involved in the process of the invention are primarily the cracking of the relatively high molecular weight hydrocarbons to hydrocarbons boiling in the gasoline range, and the dehydrogenation of hydrocarbons to produce hydrocarbons of higher octane number, such as the dehydrogenation of naphthenes to produce aromatic hydrocarbons. Hence, the process of the present invention is conveniently designated herein as "dehydrocracking." Other reactions, however, are involved and assist in producing the high octane hydrocarbons prepared by the process, such as the isomerization of paraffins to produce more highly branched chain paraffins of relatively high octane number, and cyclization followed by dehydrogenation to produce aromatics from paraffins.

The new catalyst of the invention may be prepared by a variety of means. However, a new method has been discovered which gives an especially effective catalyst. This new method of preparation is described hereinafter.

It is of primary importance that the limits on the ranges of components of the catalytic composition and that the limits on the surface area and pore radius be observed as hereinafter discussed.

The catalyst

As above stated, the catalytic composition of the present invention consists essentially of chromium fluoride, alumina, and silica. It is important that the weight percent, based on the final composition, of each component be within the following ranges: chromium fluoride=4 to 19; alumina=6 to 21; and silica=75 to 90. The values herein reported for chromium fluoride have been calculated for the trifluoride (CrF_3), but it is realized that other fluorides of chromium may be present. As used herein, "chromium fluoride" is intended to include the various fluorides of chromium and mixtures thereof.

When the quantity of chromium fluoride in the catalytic composition is below 4% by weight, a substantial loss of octane rating of the gasoline hydrocarbons and a decrease in the olefinic content of the normally gaseous hydrocarbons are observed, whereas in quantities above 19% by weight, conversion of the charge stock to gasoline hydrocarbons is substantially decreased. If the quantities of alumina or silica are varied from the stated ranges, the conversion of the high molecular weight hydrocarbons to hydrocarbons boiling in the gasoline range is adversely effected. Accordingly, it is of primary importance that the components of the catalytic composition be within the stated ranges.

It is also of primary importance that the surface area and pore radius of the catalytic composition be within defined ranges. The surface area of the catalytic composition must be within the range of from about 20 to 90 square meters per gram ($m.^2/g.$) and the pore radius must be within the range of from about 135 to 300 A. (Angstrom units). When the pore radius falls below the minimum value stated therefore or when the surface area falls above the maximum value stated therefor, the gasoline yield is small as compared to the yield of normally gaseous hydrocarbons and coke, whereas when the pore radius is above the maximum value stated therefor, or the surface area is below the minimum value stated therefor, no improvement in the catalyst is obtained and the proportion of unsaturated hydrocarbons in the normally gaseous hydrocarbons is decreased and conversion

of the charge stock to lower boiling materials is decreased.

The surface area values, as herein reported, were determined by adsorption of an aromatic hydrocarbon as described by Eagle and Scott, Ind. Eng. Chem. 42 1287 (1950), the published procedure being modified by determing the adsorption, for each catalyst, at an equilibrium concentration of 10% by volume benzene in isooctane. Pore radius, by which is meant the mean pore radius, was determined from the pore volume and surface area using the equation described by Emmett and DeWitt, J. A. C. S. 65 1253 (1943), the pore volume being determined as described by Hirschler and Mertes, Ind. Eng. Chem. 47 193 (1955).

Preparation of catalyst

Although the catalytic composition of the present invention may be prepared by various means, it is preferred to first prepare a synthetic silica-alumina composition, and to deposit the remaining component thereon. Synthetic silica-alumina compositions are well known as cracking catalysts, and heretofore described methods for their preparation may be employed in preparing the silica-alumina portion of the present catalyst. For example, the silica-alumina portion of the catalyst may be prepared by impregnating silica with aluminum salts, by directly combining precipitated hydrated alumina and silica, or by joint preparation of alumina and silica from aqueous solutions of their salts, and by washing, drying, and heating the resulting composition. The resulting silica-alumina composition should have an activity index of at least 30, and preferably from 40 to 50. "Activity index," as used herein, is a measure of the efficiency of a catalyst for cracking hydrocarbons and is determined by a method described by Alexander, Proceedings Am. Pet. Inst. 27 (III) 51 (November 1947). The surface area of the synthetic silica-alumina composition will be above 150 m.^{2}/g., and usually will be about 190 m.^{2}/g. The pore radius of the silica-alumina will be below about 70 A., and usually will be below 55 A. The surface area of the silica-alumina catalyst can be modified prior to the deposition of chromium fluoride if desired. This modification, which will generally be a decrease in the surface area and/or an increase in the pore radius, can be accomplished by steaming the catalyst at an elevated temperature or by thermal aging, i. e., by aging the catalyst at an elevated temperature, or by a combination of steaming and thermal aging. However, it is preferred to employ a method of deposition which adjusts the surface area and pore diameter within the required limits without such additional operation. This is accomplished in accordance with a preferred embodiment of the invention by a procedure involving the formation of a water soluble chromium chelate compound as follows: by dissolving a water-soluble salt of chromium in water, adding ammonium fluoride and subsequently adding methyl alcohol to precipitate chromium fluoride. Ammonium nitrate should then be removed from the precipitate and the resulting aqueous solution containing chromium evaporated to obtain a desired concentration of the chromium. Prior to the evaporation step, oxalic acid is added to form a chelate compound of chromium which maintains the chromium in solution. The chromium chelate compound can be formed with other materials, such as ethylene diamine or 2, 4-pentanedione with substantially equivalent results. This permits sufficient evaporation to obtain an aqueous solution of a concentration sufficient to impregnate the silica-alumina composition with a desired quantity of the chromium fluoride. The impregnated silica-alumina composition is then dried and calcined at about 600° C. say from 500° C. to 750° C. for from about 2 to 10 hours, and advantageously about 6 hours. By this method of preparation, as has been found, the surface characteristics of the resulting composition fall within the defined limits therefor, although the precise step wherein the adjustment occurs is not known with certainty. It is known, however, that other metallic fluorides when deposited on silica-alumina compositions do not impart a surface area or pore radius to the resulting composition within the herein defined limits. The foregoing procedure and the failure of other metallic compositions to give comparable results are specifically set forth hereinafter.

Although the foregoing procedure is preferred, other methods of catalyst preparation which give a composition consisting essentially of chromium fluoride, silica and alumina in quantities within the defined ranges and having a surface area and pore radius within the defined ranges are within the scope of the invention.

Dehydrocracking

The reactions involved in the present process for converting relatively high boiling petroleum hydrocarbons to gasoline hydrocarbons of high octane rating are primarily dehydrogenation and cracking, and hence the overall process is conveniently designated as "dehydrocracking." The gasoline product preferably contains only hydrocarbons having a molecular weight lower than the hydrocarbons of the charge stock, and hence includes only the hydrocarbons which have been cracked in the process.

As above stated, the new catalytic composition of the invention is especially suitable for dehydrocracking hydrocarbon fractions boiling in the range of from 375° F. to 500° F. to gasoline hydrocarbons of high octane rating, heretofore described processes and catalysts being unsuitable for this conversion. Accordingly, the use of the present catalyst will be described in terms of this preferred embodiment.

Especially suitable charge stocks are straight-run fractions having a naphthene content of at least 10%, and preferably above 30%, say from about 30% to 75% by volume. Other fractions such as those obtained from catalytic cracking, and recycle gas oils in general, may be used.

In the process, temperatures within the range of from 450° C. to 540° C. give good results and with the preferred hydrocarbon charge stock must be observed in order to obtain suitable conversion without excessive coke formation. The pressure is preferably maintained at about atmospheric pressure, but superatmospheric pressure up to about 100 p. s. i. g. can be used if desired. The space velocity must be maintained within the range of from about 0.5 to 3. It is preferred to employ a space velocity of from 0.8 to 1.5 since within this range there is obtained a high gasoline yield of high octane number. By "space velocity," as used herein, is meant the liquid hourly space velocity, which is the liquid volume of hydrocarbons charged per volume of catalyst per hour.

In carrying out the process of the invention, it is preferred to pass the hydrocarbon charge through a bed of catalyst under the above conditions. By such operation the activity of the catalyst is gradually decreased, principally due to the deposition of carbonaceous materials thereon. Periodic regeneration of the catalyst, such as by discontinuing the operation, flushing the catalyst bed with an inert gas such as steam, flue gas, nitrogen, or the like, and burning off the carbonaceous materials by passing an oxygen containing gas, such as air, through the hot catalyst bed, is advantageously employed. Regeneration is generally advantageously employed at intervals of from about 10 minutes to 2 hours, depending upon the particular operation and reaction variables being used.

Hydrogen preferably is not employed in the process, but a small partial pressure thereof is not deleterious. In some other uses of the present catalyst, however, an atmosphere of hydrogen is advantageous, especially where operation is at superatmospheric pressure, as hereinafter described.

Examples

In order to illustrate a preferred catalytic composition of the invention and its use in dehydrocracking, a catalytic composition, in accordance with the invention, was prepared as follows, in which "parts" refers to parts by weight.

141.6 parts of chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) was dissolved in water and the resulting aqueous solution introduced with stirring into 250 parts of water containing 44 parts of ammonium fluoride. The admixed solutions were heated to boiling for 2 hours, cooled and a equal volume of absolute methyl alcohol added to precipitate chromium trifluoride. The precipitate was filtered and digested with methyl alcohol in an extractor to remove ammonium nitrate. The precipitate was then heated with water to form a solution and the solution evaporated to 400 parts at which point a precipitate formed. 52.6 parts of oxalic acid was added to form the water soluble chelate chromium compound, and the evaporation continued until the solution was reduced to 290 parts. No precipitate was evident in the solution.

The resulting solution was used to impregnate a synthetic silica-alumina cracking catalyst prepared by coprecipitation and containing about 13% by weight alumina. The synthetic silica-alumina catalyst had an activity index of about 46, a surface area of about 195 m.²/g., a pore radius of about 49 A. and a pore volume of about 0.44 milliters per gram (ml./g.). The impregnated synthetic silica-alumina composition was dried by heating at about 93° C. in contact with air for 16 hours. The dried composition was calcined in contact with air at about 600° C. for 6 hours. The resulting composition contained 7.9% by weight chromium trifluoride and had a surface area of 23.8 m.²/g., a pore radius of 309 A. and a pore volume of about 0.38 ml./g. In the following table the resulting composition is designated as Catalyst A.

Another catalyst was prepared, as above described, except that oxalic acid was not used and instead the aqueous solution (made acid with nitric acid) was used while hot (about 90° C.) to impregnate the same synthetic silica-alumina composition heated to about 90° C. The resulting composition contained 7.5% chromium fluoride, had a surface area of 47.5 m.²/g. and a pore radius of 160.4 A. In the following table the resulting composition is designated as Catalyst B.

In order to illustrate the efficacy of the new catalytic compositions for converting hydrocarbon fractions boiling in the range of from 375° F. to 500° F. to high octane gasoline hydrocarbons, a straight-run petroleum hydrocarbon fraction boiling in the range of from about 375° F. to 460° F., having an aromatic content of about 13% by volume and a naphthene content of about 50% by volume was contacted therewith. The following conditions were employed during the contacting: temperature of catalyst=512° C., space velocity=0.99 to 1.03, pressure=atmospheric. The catalyst bed was regenerated after operation for 20 minutes by burning carbonaceous materials therefrom with a stream of air as above described. Products were collected over 9 cycles of operation and regeneration, and results obtained are shown in the following table. In the table, a mixture of hydrocarbons, each having a certain number of carbon atoms, is designated simply by indicating such number of carbon atoms. For example, "C_4" designates a mixture of hydrocarbons each of which has 4 carbon atoms.

Table

Catalyst	A	B
Liquid recovery (volume percent):		
Total	101.6	102.1
C_4	14.3	14.1
C_5—350° F. (gasoline)	29.9	31.1
Bottoms	57.4	56.9
Gas (weight percent):		
C_2 and lighter	1.01	0.80
C_3	1.24	1.36
Coke (weight percent)	0.90	0.96
Octane number of C_5—350° F. (A. S. T. M. D908-53)	96.8	96.2
Conversion (volume percent)	42.6	43.1
Olefins in C_4 (weight percent)	54.8	42.5
Olefins in C_3 (weight percent)	66.4	75.9
Gasoline yield/conversion	70.2	72.2

As shown in the foregoing table, both Catalyst A and Catalyst B gave excellent results. Coke formation was negligible. Formation of normally gaseous hydrocarbons was also practically negligible and the normally gaseous hydrocarbons produced contained large quantities of unsaturated hydrocarbons. A good yield of high octane gasoline was also obtained. An even larger yield of gasoline can be obtained by using a higher end point therefor.

In order to emphasize the necessity for using the catalyst having the quantities of components within the defined ranges and having physical properties within the defined ranges, another catalyst was prepared in a manner as above described. This catalyst contained 2.2% by weight chromium fluoride deposited on the synthetic silica-alumina composition above described. The resulting catalyst had a surface area of 109 m.²/g. and a pore radius of 73.9 A. When this catalyst was used in a process otherwise identical to the process described for Catalyst A and Catalyst B, the quantity of coke obtained was 3.28 weight percent, the quantity of gas containing C_2 hydrocarbons and lighter materials was 2.57 weight percent, and the quantity of hydrocarbons having 3 carbon atoms was 2.55 weight percent. It will be noted that these values of undesirable products are far greater than obtained with Catalyst A or Catalyst B. A further disadvantage in using this composition containing less than 4% by weight chromium fluoride was the relatively small quantities of unsaturated hydrocarbons obtained in normal gaseous hydrocarbons. Thus the hydrocarbons having 4 carbon atoms contained only 21.8 weight percent unsaturated hydrocarbons. The gasoline/yield conversion using this catalyst was only 59.5.

For illustrative purposes, the synthetic silica-alumina catalyst, on which was deposited chromium fluoride in the above examples, was used without such deposition in a process otherwise identical to the process described for Catalyst A and Catalyst B. In this process, coke formation was 4.24 weight percent, the formation of C_2 and lighter materials was 3.57 weight percent and the formation of hydrocarbons having 3 carbon atoms was 5.99 weight percent, all of which values are far in excess of those obtained for the catalytic compositions of the invention. The silica-alumina composition had the further disadvantage of supplying, in the normally gaseous hydrocarbons formed, only a relatively small amount of unsaturated hydrocarbons. Thus, the quantity of unsaturated hydrocarbons having 4 carbon atoms was 33 weight percent and the quantity of unsaturated hydrocarbons having 3 carbon atoms was only 32 weight percent. The gasoline/yield conversion was only 55.8.

In order to demonstrate the failure of other catalytic compositions in the process of the invention, a comparable catalyst wherein ceric fluoride was substituted for chromium fluoride was prepared. The final composition contained 6.3% ceric fluoride deposited on the above-described silica-alumina composition, and had a surface area of 160 m.²/g. and a pore radius of 62.8 A. This catalyst was used in a process otherwise identical for proc-

ess used for Catalyst A and Catalyst B. The quantity of coke formed was 3.35 weight percent. The quantity of C_2 and lighter materials was 1.92% and the quantity of hydrocarbons having 3 carbon atoms was 3.68 weight percent. The gasoline/conversion was only 59.1 weight percent.

To illustrate other uses for the catalytic compositions of the invention, Catalyst A of Example 1 was used in the process for cracking a gas oil having a boiling range of from 405 to 700° F. The reaction conditions were similar to the process as described for Catalyst A and Catalyst B. Specifically, the catalyst temperature was 500° C., the space velocity was 1.01 and the pressure was atmospheric. The catalyst was regenerated after operation for 20 minutes as above described. The products were collected over 9 cycles of operation and regeneration. The following results were obtained—

Liquid recovery (vol. percent):	
Total	99.2
C_4	10.3
C_5—350° F.	32.3
Bottoms	51.3
Gas (weight percent):	
C_2 and lighter	1.27
C_3	3.3
Coke (weight percent)	1.08
Octane Number of C_5—350° F. (A. S. T. M. D908–53)	94.2
Conversion (volume percent)	48.7
Olefins in C_4 (weight percent)	48.5
Olefins in C_3 (weight percent)	80.6
Gasoline yield/conversion	77.1

When other catalytic compositions within the scope of the present invention are employed, substantially equivalent results are obtained, and when other operating conditions are employed within the ranges herein described, substantially equivalent results are obtained. The process may also be operated batchwise or as a moving bed or fluidized process by maintaining the reaction conditions equivalent to those herein described.

The catalyst of the invention can be used in other reactions involving the conversion of hydrocarbons, such as destructive hydrogenation using elevated pressures in an atmosphere of hydrogen, reforming, and the like, in which catalytic conversion conditions known to be effective in such processes give good results.

The invention claimed is:

1. A catalyst for the conversion of hydrocarbons consisting essentially of a synthetic silica-alumina composition impregnated with from 4 to 19% by weight, based on the final composition, of chromium fluoride, the radius of the pores of said catalyst being from 135 to 300 A., and the surface area of said catalyst being from 20 to 90 square meters per gram.

2. A catalyst according to claim 1 wherein the quantity of silica is from 75 to 90% by weight, based on the final composition, and the quantity of alumina is from 6 to 21% by weight, based on the final composition.

3. Process for the preparation of a catalyst for use in the conversion of hydrocarbons which comprises impregnating a synthetic silica-alumina composition having an activity index of from 30 to 50 with an aqueous solution of a water soluble chelate compound of chromium fluoride, drying the resulting composition and calcining the dried composition in contact with air at a temperature of from about 500° C. to about 750° C., wherein the concentration of the chelate compound of chromium fluoride in said aqueous solution is sufficient to give a concentration of chromium fluoride of from 4 to 19% by weight in the final composition.

4. Process for converting a hydrocarbon fraction boiling above the gasoline range which comprises contacting said fraction with a catalyst consisting essentially of from 75 to 90% silica, from 6 to 21% by weight alumina and from 4 to 19% by weight chromium fluoride under catalytic conversion conditions whereby said hydrocarbon fraction is converted to gasoline of high octane rating, the radius of the pores of said catalyst being from 135 to 300 A. and the surface area of said catalyst being from 20 to 90 square meters per gram.

5. Process according to claim 4 wherein said hydrocarbon fraction boiling above the gasoline range boils within the range of from 375° F. to 500° F.

6. Process of dehydrocracking which comprises contacting a petroleum hydrocarbon fraction boiling in the range of from 375° F. to 500° F. with a catalyst consisting essentially of from 75 to 90% by weight silica, from 6 to 21% by weight alumina and from 4 to 19% by weight chromium fluoride, at a temperature within the range of 450° C. to 540° C., a space velocity of from 0.5 to 3 and at substantially atmospheric pressure, and recovering gasoline of high octane rating from the reaction mixture.

7. Process for cracking a gas oil having a boiling range of from about 405° F. to about 700° F. which comprises contacting said gas oil with a catalyst consisting essentially of from 75 to 90% by weight silica, from 6 to 21% by weight alumina, and from 4 to 19% by weight chromium fluoride under catalytic cracking conditions, and recovering gasoline of high octane rating from the reaction mixture.

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