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CRACKING A HYDROCARBON OIL WITH A SILICA - ALUMINA - CHROMIUM OXIDE-BERYLLIUM OXIDE CATALYST COMPOSITE

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This invention relates to a catalytic composition effective in catalytic processes for converting hydrocarbons. More particularly, this invention relates to new and improved catalytic compositions, 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 beryllium oxide, chromia, silica and alumina in defined quantities, 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 normally gaseous hydrocarbons produced in the process are remarkably high in olefinic content, so that such normally gaseous hydrocarbons are especially suitable for subsequent processing in reactions such as polymerization and alkylation.

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, the general techniques of which are known in the art. 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 be observed as hereinafter discussed.

The catalyst

As above stated, the catalytic composition of the present invention contains beryllium oxide, chromia, alumina and silica. It is important that the weight percent, based on the final composition, of each component be within the following ranges: beryllium oxide=0.2 to 7, chromia=1 to 12, alumina=6 to 20, silica=61 to 93.

When the quantity of beryllium oxide in the catalytic composition is below 0.2% by weight, a substantial loss of octane rating of the gasoline hydrocarbons is observed, whereas in quantities above 7% by weight, excessive coke formation on the catalyst is observed. When the quantity of chromia is below 1% by weight, a substantial loss in octane number of the gasoline product is observed, whereas at concentrations above 12% by weight, conversion of higher boiling hydrocarbons to hydrocarbons boiling within the gasoline range is low. 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.

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 components 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 precipitation of alumina and silica from aqueous solutions of their salts, and by washing, drying, and heating the resulting composition. The resulting silica-alumina catalyst 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 remaining components in the catalytic composition may be deposited on the silica-alumina composition by means known to the art. Impregnation may be accomplished by using solutions of soluble compounds of the metals and is advantageously performed by using aqueous solutions of water soluble salts. Impregnation may be with the beryllium salt followed by the chromium salt, by the chromium salt followed by the beryllium salt, or simultaneously with the same aqueous solution. It is preferred to first impregnate silica-alumina with an aqueous solution of a water soluble beryllium salt, calcine the impregnated composition in contact with an oxidizing gas at a temperature of from about 500° C. to about 750° C., impregnate the calcined composition with an aqueous solution of a water soluble chromium compound, and again calcine, in contact with an oxidizing gas, the impregnated composition at a temperature of from about 500° C. to about 750° C., to prepare the final composition, since this procedure yields a catalyst of exceptionally high activity in producing gasoline hydrocarbons of high octane rating from higher boiling hydrocarbons.

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. 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.

Example

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:

355 parts of a synthetic silica-alumina cracking catalyst prepared by coprecipitation containing about 13% by weight alumina and having an activity index of about 46, was impregnated with an aqueous solution containing about 92.3 parts of beryllium nitrate trihydrate. A small amount of excess liquid was drained from the composition. The impregnating composition was dried for about 16 hours at 97° C. and calcined at about 504° C. for 2 hours. The calcined composition was cooled and impregnated with an aqueous solution containing about 25.8 parts of ammonium dichromate. A small amount of excess liquid was drained from the composition. The impregnated composition was again dried, as described above, and calcined at a temperature of about 650° C. for about 1 hour, a stream of air being passed through the catalyst during the calcination. The resulting composition constitutes a preferred catalytic composition in accordance with the invention and contained in parts by weight, 2.6 parts beryllium oxide, 3.7 parts chromia, 12.2 parts alumina and 81.5 parts silica.

In order to illustrate the efficacy of this new catalytic composition 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., and 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=520° C., space velocity=0.97, 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 14 cycles of operation and regeneration.

A yield of gasoline hydrocarbons, i. e., hydrocarbons from pentane to those boiling at 350° F. of 23.8% by volume was obtained. There were also obtained 6.2% by volume percent hydrocarbons having 4 carbon atoms and 2.15% by weight of hydrocarbons having 3 carbon atoms. The bottoms fractions, i. e., hydrocarbons boiling over 350° F. constituted 61.9% by volume of the charge. Where desired, a gasoline fraction having a higher end point can be separated from the reaction mixture thereby increasing the observed yield of gasoline. However, it is preferred to maintain the boiling range of the gasoline product below the boiling range of the charge stock.

The gasoline fraction had an octane number of 99 (ASTM Method D908–53) and an aromatic content of 60% by volume. The hydrocarbons having 3 carbon atoms contained 78.2% by weight propylene and the hydrocarbons containing 4 carbon atoms contained 55.3% by weight olefins, principally isobutylene.

If the above example is repeated using, as the catalyst, silica-alumina composition on which was deposited beryllium oxide and chromia in the above example, the octane number of the gasoline product is substantially lower and the olefinic content of the normally gaseous hydrocarbons is lower. For example, in a comparable procedure using the silica-alumina composition as the catalyst, the olefinic content of the butane fraction was found to be only 30.5% by weight, as compared to 57.9% by weight obtained in the above example.

The foregoing example illustrates a preferred embodiment of the invention, including a preferred catalytic composition and its preferred use in dehydrocracking a refractory, relatively high boiling hydrocarbon fraction to gasoline having a remarkably high octane number in good yield. The catalyst is also effective to dehydrocrack other relatively high boiling fractions, such as gas oils boiling from about 400° F. to 750° F. or higher, to gasoline.

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:

Process of cracking which comprises contacting a straight run petroleum hydrocarbon fraction boiling in the range of from 375° F. to 500° F. with a catalyst consisting essentially of from 61 to 93% by weight silica, from 6 to 20% by weight alumina, from 1 to 12% by weight chromium oxide and from 0.2 to 7% by weight beryllium oxide 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.

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