United States Patent Office 2,849,383
Patented Aug. 26, 1958

2,849,383

CATALYTIC COMPOSITION AND HYDROCARBON CONVERSION THEREWITH

Alfred E. Hirschler, Springfield, and Abraham Schneider, Overbrook Hills, Pa., assignors to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

No Drawing. Application October 13, 1955
Serial No. 540,350
18 Claims. (Cl. 196—52)

This invention relates to catalytic compositions effective in processes for converting hydrocarbons. More particularly this invention relates to new catalytic compositions, their preparation, and to a process for converting relatively high molecular weight hydrocarbons to lower molecular weight hydrocarbons employing the new catalyst.

The conversion of petroleum hydrocarbons by processes such as cracking, reforming, destructive hydrogenation, and the like, using a variety of catalysts and reaction conditions has heretofore been described. In cracking processes it is generally desired to produce a good yield of high octane number gasoline and it is known that operation under relatively high temperature conditions improves the octane number of the gasoline fraction from such processes. However, such relatively high temperatures cause an increase in the yield of normally gaseous hydrocarbons and coke, both of which are undesired products. It is also known that catalytic cracking processes should be operated with petroleum stocks having relatively low concentrations of metallic contaminants, such as compounds of chromium, vanadium, nickel and iron, since such contaminants form a deposit, as the metal oxide, on the catalyst and cause a decrease in the gasoline yield and an increase in the formation of normally gaseous hydrocarbons and coke. Thus it has been reported that quantities up to one percent of an oxide of a metal such as chromium or vanadium deposited on a cracking catalyst cause a significant decrease in catalytic activity, an increase in gas formation and an increase in coke deposition (McIntosh, Paper Presented before the Division of Petroleum Chemistry of the Am. Chem. Soc., New York Meeting, September 11–17, 1954).

An object of this invention is to provide a new catalytic composition especially effective for cracking hydrocarbons under relatively high temperature conditions. Another object is to provide a new catalytic composition effective for cracking relatively high boiling petroleum hydrocarbons containing metal compounds as impurities. A further object is to provide a new process for cracking petroleum hydrocarbons wherein high yields of gasoline of high octane number are obtained and only minor quantities of normally gaseous hydrocarbons and coke are formed. 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 cracking relatively high molecular weight petroleum hydrocarbons to lower molecular weight hydrocarbons boiling in the gasoline range. The new catalytic composition consists essentially of a cracking catalyst and an oxide of a metal from group V or VI of the periodic table. While the cracking catalyst portion of the new composition may be prepared by means heretofore known, it is essential that certain steps in preparing the final composition of the invention be performed as hereinafter described. It is also essential that the quantity of metal oxide be within the limits hereinafter defined. It has been found that the new catalytic composition is especially effective in converting relatively high boiling petroleum fractions which contain substantial quantities of contaminating metal compounds to high octane gasoline in good yield, and that in the process only minor quantities of normally gaseous hydrocarbons and coke are formed. It has been further found that the normally gaseous hydrocarbons which are produced are highly unsaturated in character and hence are especially valuable for use in processes such as alkylation and polymerization.

THE CATALYST

The catalyst of the invention consists essentially of a siliceous cracking catalyst, such as a silica-alumina cracking catalyst, and an oxide of a metal from group V A or VI A of the periodic table, the preparation of which includes a specific treatment as hereinafter described. By "siliceous cracking catalyst" is meant a synthetic or natural siliceous composition known to be effective for the cracking of hydrocarbons. The siliceous cracking catalyst, before deposition of the oxide, should contain at least above about 50% silica (calculated as SiO_2). As illustrative of the cracking catalysts which can be used, synthetic silica-alumina, silica-magnesia, silica-zirconia and silica-alumina-zirconia cracking catalysts give good results. Natural cracking catalysts such as the bentonite and kaolin clays, which may have been activated with an acid, give good results. The metal oxide must be incorporated with the cracking catalyst in a quantity of at least 2.9% by weight, and preferably the quantity deposited is in the range of from 2.9% to 11% by weight. When quantities below 2.9% of the metal oxide are used, excessive quantities of normally gaseous hydrocarbons and coke are formed and the yield of gasoline is poor. No advantage accrues from using a quantity of metal oxide greater than 11%, and the use of such larger quantities may have deleterious effects, e. g., in promoting undesired side reactions and decreasing conversion to gasoline. It is preferred to deposit metal oxide on the cracking catalyst. However, if desired, the metal oxide can be incorporated in the composition by coprecipitation, such as by coprecipitation with silica, with another component such as alumina, or both, in which case the quantities of materials in the final composition must be within the stated limits.

Especially suitable for deposition on the silica-containing cracking catalyst are the oxides of chromium, vanadium, molybdenum and tungsten. Combinations of such oxides wherein the total quantity thereof is within the stated limits of from 2.9% to 11% by weight can be used if desired.

For simplicity the composition and the process of the invention are hereinafter described in terms of chromia deposited on a silica-alumina cracking catalyst, although the scope of the invention is limited only as herein indicated. To illustrate the preferred catalytic composition of the invention, from 2.9% to 11% chromia is deposited on a synthetic silica-alumina composition containing from 50% to 90% by weight silica and from 50% to 10% alumina. The final catalytic composition thus contains, in percent by weight, from about 45% to 87.5% silica, from about 9% to 48.6% alumina and from about 2.8% to 10% chromia.

PREPARATION OF CATALYST

The preparation of the catalyst of the invention is important and certain steps, as hereinafter described, must be observed in order to obtain the desired catalytic composition. The silica-containing cracking catalyst, however, can be prepared by means heretofore known. For example, the silica-alumina portion of the catalyst can be prepared by impregnating silica with water soluble salts of aluminum, directly combining precipitated hydrated alumina and silica, or by joint precipitation of alumina

and silica from aqueous solutions of their water soluble 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 the catalyst for cracking hydrocarbons and is determined by a method described by Alexander, Proceedings Am. Pet. Inst. 27 (III) 51 (November 1947).

After preparation of the silica-alumina cracking catalyst chromia is deposited thereon. This is accomplished by impregnating the silica-alumina composition with an aqueous solution of a water soluble salt of chromium, such as ammonium dichromate, chromium chloride, chromium nitrate, or the like. The concentration of the selected salt in the aqueous solution, and the quantity of solution used to impregnate the catalyst, should be such that the concentration of the resulting metal oxide is within the defined limits. After impregnation, the silica-alumina composition is drained, if necessary, and dried preferably at a temperature of 100° C. to 200° C. for from 1 to 20 hours, and is then calcined at a temperature of 500° C. to 750° C. If desired, the chromia can be co-precipitated with the alumina, the silica, or both, in which case the composition is dried and calcined as described above.

It is essential to the successful preparation of the catalytic composition of the invention that the calcined composition be subjected to steaming at an elevated temperature. The steaming is performed by maintaining the catalyst in an atmosphere of about 100% steam at a temperature of from about 600° C. to 800° C. for from about 1 hour to 8 hours. It is only through the use of both a relatively large quantity of chromia and steaming the silica-alumina-chromia composition that the highly advantageous results of the invention are obtained. It is essential that the chromia be incorporated with the silica-alumina prior to the steaming step, since steaming the silica-alumina composition prior to the incorporation of metal oxide does not give a composition comparable, for cracking, to the catalyst of the invention.

The catalytic composition of the invention, and the preparation thereof, is above illustrated by a silica-alumina-chromia catalyst. Other catalysts within the scope of the invention are prepared in a similar manner. For example, a silica-containing cracking catalyst such as silica-magnesia or the like can be prepared by means known in the art, and an oxide of chromium, vanadium, molybdenum or tungsten deposited thereon as above described for chromia. In each event, however, it is essential that the cracking catalyst having the metal oxide incorporated therewith be subjected to the steaming step as described for the silica-alumina-chromia catalyst. It is not known with certainty why the steaming step is essential in preparing the catalyst of the invention and it is not desired to be limited by theoretical considerations, but it is believed that the steaming causes some modification in the physical structure of the composition which gives the highly beneficial results in accordance with the invention.

CRACKING

The cracking process of the invention employing the new catalyst composition, as above described, is especially valuable for converting hydrocarbons boiling above the gasoline range to gasoline hydrocarbons in good yield without the formation of substantial quantities of gaseous hydrocarbons or coke. Especially suitable charge stocks are gas oils boiling within the range of from about 200° C. to about 600° C., such as the gas oil fraction boiling within the range from about 207° C. to 370° C., but other gas oils boiling within other ranges within the described limits are suitable. Especially advantageous results are obtained with charge stocks having relatively high concentrations of metal compounds, as impurities, which are known to deleteriously affect the cracking activity of heretofore used catalysts, such as compounds of vanadium, chromium, molybdenum or tungsten. Good results are obtained, for example, with charge stocks having from less than 1 p. p. m. (parts per million based on the metal) up to 10 p. p. m. or more, say up to 200 p. p. m. It is not known why good results are obtained with such charge stocks but it is believed that the catalytic composition of the invention, which already contains a substantial quantity of the same or a similar metal oxide, is not poisoned by the addition of minor quantities of such oxides during the cracking process.

As above stated the catalytic composition of the invention gives especially beneficial results when used for cracking under relatively high temperature conditions, say at temperatures from 450° C. to 540° C., and preferably at temperatures within the range of from about 480° C. to 540° C. Such high temperatures result in a gasoline product having a relatively high octane number so that the gasoline fraction can be used, without further processing, as motor fuel or as a component of motor fuels blended with other suitable materials. The cracking process is preferably operated at atmospheric pressure, but superatmospheric pressure, say up to about 50 p. s. i. g. (pounds per square inch gauge), can be used with good results. Hydrogen may be added to the process if desired, and good results are obtained therewith. The space rate (v./v./hr.), which is the volume of hydrocarbons charged per volume of catalyst per hour, should be maintained within the range from 0.5 to 6 in continuous operations such as in fixed bed or moving bed processes. Although such continuous processes are preferred, batch operation can be used under conditions substantially equivalent to the conditions described above.

After operation for a substantial time catalytic activity of the catalyst may decrease due to coke deposition, but such decrease is much slower than is observed with processes heretofore described. When the activity of the catalyst is decreased to an extent so that the operation therewith is uneconomical, the catalyst can be regenerated by the usual means for regenerating a silica-alumina cracking catalyst, i. e. by burning coke therefrom. Such regeneration has been found to substantially restore the activity of the catalyst.

EXAMPLES

Example 1

A synthetic silica-alumina cracking catalyst containing about 87% silica and about 13% alumina and having an activity index of about 46 was impregnated with an aqueous solution of ammonium dichromate, dried and calcined. The calcined composition was then subjected to an atmosphere of 100% steam at about 732° C. for 4 hours. The resulting composition consisted essentially of about 83.5% silica, about 12.5% alumina, and about 4% chromia.

A gas oil boiling from about 207° C. to about 371° C. was contacted with the silica-alumina-chromia catalyst at a temperature of about 510° C. using a space rate of 1 and substantially atmospheric pressure. In a single pass 51.5% of the charge was converted. For comparison, the procedure was repeated using the silica-alumina cracking catalyst, above-described, which had been steamed also as above described, but which did not contain chromia. In a single pass 57.9% of the charge was converted. Results obtained were as follows:

	Silica-alumina-chromia	Silica-alumina
Gasoline fraction (volume percent)	36.7	35.5
Butanes (volume percent)	11.3	16.9
Dry gas (weight percent)	5.6	8.1
Coke (weight percent)	2.6	3.1
Olefin content of butanes (volume percent)	55.4	45.7
Olefin content of propanes (weight percent)	79.4	75.4

The gasoline fractions consisted of the hydrocarbons boiling above the butanes up to about 207° C. It will be noted that, while the silica-alumina catalyst gave a somewhat greater conversion than the silica-alumina-chromia catalyst, the latter catalyst gave a higher yield of gasoline. Thus, the "gasoline/conversion," which is the gasoline produced divided by the conversion obtained (calculated as 100×gasoline produced/conversion), and which shows the selectivity of the catalyst for producing gasoline, was 71.3 for the catalyst of the invention and only 61.3 for the silica-alumina catalyst.

Example 2

A silica-alumina-chromia catalyst containing 4.4% chromia, 12.4% alumina and 83.2% silica was prepared substantially as described in Example 1, including maintaining the silica-alumina-chromia composition in an atmosphere of 100% steam at about 732° C. for 4 hours. This catalyst was used to crack the same gas oil used in Example 1. In the cracking, the temperature was maintained at about 510° C., and the space rate at 1. Atmospheric pressure was used and the catalyst was regenerated, by burning, after operation for 20 minute periods. The following results were obtained, the data presented being obtained over the indicated number of catalyst regenerations, designated "cycles" in the table:

Cycles	3–8 and 10–17	56–67	99–104 and 106–11
Conversion (volume percent)	55.0	54.3	54.6
Gasoline (volume percent)	34.1	35.3	36.0
Butanes (volume percent)	18.4	18.7	20.1
Dry gas (weight percent)	5.88	6.41	4.09
Coke (weight percent)	2.5	2.5	2.5
Gasoline/conversion	62.0	65.1	65.9
Octane number of gasoline (ASTM method D908–53)	97.2	95.5	96.2
Olefins in C_4 fraction (volume percent)	57	55	74
Olefins in C_3 fraction (weight percent)	78	78	80

Example 3

Example 2 was repeated using the same catalyst and reaction conditions, a gas oil boiling from about 202° C. to about 516° C. being used as the charge stock. Results were comparable to those obtained in Example 2, the conversion being 54.1 vol. percent, and the selectivity for producing gasoline (100×gasoline produced/conversion) being 64.8. The octane number of the gasoline product was 96.0 (ASTM method D908–53).

Example 4

Example 1 was repeated using, as the catalyst, the silica-alumina-chromia composition of Example 1 prior to the steaming operation, i. e., the catalyst was identical to the catalyst of Example 1 except that it was not contacted with steam prior to use. In cracking the gas oil of Example 1 under the same conditions as there used, coke formation was excessive, the actual value being 6.2 wt. percent. Also, the olefinic contents of the C_4 (butane) fraction and the C_3 (propane) fraction were small, the values being 36.4 vol. percent and 65.8 wt. percent, respectively. The gasoline produced/conversion was only 57.0.

When other catalysts within the limits above-defined are used, and when other relatively high boiling petroleum fractions, especially those containing relatively large amounts of compounds of metals known to be catalyst poisons, are used results substantially equivalent to those above-described are obtained.

The invention claimed is:

1. Process for converting the hydrocarbons of a relatively high boiling petroleum fraction to lower boiling hydrocarbons which comprises contacting said high boiling hydrocarbons, at a cracking temperature of from 450° C. to 540° C., with a catalytic composition prepared by incorporating from 2.9% by weight to 11% by weight of an oxide selected from the group consisting of chromium oxide, vanadium oxide, molybdenum oxide and tungsten oxide on a synthetic siliceous cracking catalyst and subjecting the resulting composition to contact with steam at a temperature of from about 600° C. to 800° C. for from about 1 hour to 8 hours, whereby the hydrocarbons of the relatively high boiling petroleum fraction are converted to lower boiling hydrocarbons.

2. Process for preparing gasoline from a relatively high boiling petroleum fraction which comprises contacting, under cracking conditions including a temperature of from 450° C. to 540° C., a petroleum fraction boiling within the range of from about 200° C. to about 500° C. with a catalytic composition prepared by depositing from 2.9% by weight to 11% by weight an oxide selected from the group consisting of chromium oxide, vanadium oxide, molybdenum oxide and tungsten oxide on a synthetic siliceous cracking catalyst and subjecting the resulting composition to contact with steam at a temperature of from about 600° C. to 800° C. for from about 1 hour to 8 hours, and separating a gasoline fraction from the reaction mixture.

3. Process according to claim 2 wherein the metal oxide selected is chromium oxide.

4. Process according to claim 2 wherein the metal oxide selected is vanadium oxide.

5. Process according to claim 2 wherein the metal oxide selected is molybdenum oxide.

6. Process according to claim 2 wherein the metal oxide selected is tungsten oxide.

7. A new catalytic composition for use in the conversion of hydrocarbons prepared by incorporating from 2.9% by weight to 11% by weight of an oxide of a metal selected from the group consisting of chromium oxide, vanadium oxide, molybdenum oxide and tungsten oxide with a synthetic siliceous cracking catalyst and contacting the resulting composition with steam at a temperature of from about 600° C. to 800° C. for from about 1 hour to 8 hours.

8. A new catalytic composition according to claim 7 wherein the metal oxide selected is chromium oxide.

9. A new catalytic composition according to claim 7 wherein the metal oxide selected is vanadium oxide.

10. A new catalytic composition according to claim 7 wherein the metal oxide selected is tungsten oxide.

11. A new catalytic composition according to claim 7 wherein the metal oxide selected is molybdenum oxide.

12. A new catalytic composition according to claim 7 wherein the synthetic siliceous cracking catalyst is a synthetic silica-alumina cracking catalyst.

13. A new catalytic composition according to claim 7 wherein the synthetic siliceous cracking catalyst is a synthetic silica-magnesia cracking catalyst.

14. A new catalytic composition according to claim 7 wherein the synthetic siliceous cracking catalyst is a synthetic silica-zirconia cracking catalyst.

15. Process for the preparation of a catalytic composition which comprises depositing of 2.9% by weight to 11% by weight of a metal oxide selected from the group consisting of chromium oxide, vanadium oxide, tungsten oxide and molybdenum oxide on a synthetic siliceous cracking catalyst, and contacting the resulting composition with steam at a temperature of from about 600° C. to 800° C. for from about 1 hour to 8 hours.

16. Process according to claim 15 wherein said synthetic siliceous cracking catalyst is a synthetic silica-alumina cracking catalyst.

17. Process for the preparation of gasoline from a petroleum fraction boiling in the range of from about 200° C. to about 500° C. having metal compounds as impurities which comprises contacting said fraction, under cracking conditions, with a catalytic composition prepared by incorporating from 2.9% by weight to 11% by weight of an oxide selected from the group consisting of chromium oxide, vanadium oxide, molybdenum oxide

and tungsten oxide on a synthetic siliceous cracking catalyst and subjecting the resulting composition to contact with steam at a temperature of from about 600° C. to 800° C. for from about 1 hour to 8 hours, and separating a gasoline fraction from the reaction mixture.

18. Process for the preparation of gasoline from a petroleum fraction boiling in the range of from about 200° C. to about 500° C. having metal compounds as impurities which comprises contacting said fraction, under cracking conditions, with a catalytic composition prepared by incorporating from 2.9% by weight to 11% by weight of an oxide selected from the group consisting of chromium oxide, vanadium oxide, molybdenum oxide and tungsten oxide on a natural clay cracking catalyst

and subjecting the resulting composition to contact with steam at a temperature of from about 600° C. to 800° C. for from about 1 hour to 8 hours, and separating a gasoline fraction from the reaction mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,375,757	Bates	May 15, 1945
2,381,820	Grosse et al.	Aug. 7, 1945
2,437,531	Huffman	Mar. 9, 1948
2,489,334	Shabaker	Nov. 29, 1949
2,698,305	Plank	Dec. 28, 1954
2,700,013	Oblad	Jan. 18, 1955
2,734,874	Drake	Feb. 14, 1956