United States Patent Office

3,303,124

Patented Feb. 7, 1967



3,303,124

# CATALYTIC HYDROCRACKING OF NAPHTHAS WITH THE USE OF A CATALYST COMPOSITE COMPRISING COPPER ON A SILICEOUS SUPPORT

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No Drawing. Filed Dec. 24, 1964, Ser. No. 421,094

6 Claims. (Cl. 208—111)

This application is a continuation-in-part of applicant's copending U.S. application, Serial No. 325,793, filed November 22, 1963 (now abandoned).

This invention relates to a process for the catalytic conversion of hydrocarbons, particularly paraffinic naphtha fractions to low boiling high octane gasoline components.

In the refining of petroleum, various hydrocarbon fractions boiling in the gasoline boiling range are recovered and are appropriately blended to provide a finished gasoline. Gasoline components include, for example, straight-run gasoline fractions obtained from the distilling of crude oil, cracked fractions obtained from the conversion of hydrocarbon fractions boiling above the gasoline boiling range, and polymer and alkylate fractions derived from reacting low boiling normally gaseous hydrocarbons.

The trend has been to higher octane gasolines to satisfy the demands of modern high compression ratio automotive engines. Aromatic hydrocarbons have quite high octane ratings, therefore, preference has been given to aromatic rich hydrocarbon fractions as a component for finished high octane gasoline. Aromatic rich hydrocarbon fractions are obtained from cracking high boiling fractions and catalytically reforming naphthas—naphthenic straight-run naphthas primarily but cracked naphthas are often included as well. The aromatic content of such aromatic-rich hydrocarbon fractions can be concentrated more by such means as extractive distillation or extraction with selective solvents such as glycols, sulfolane and the like.

Since aromatic hydrocarbons are relatively high boiling gasoline components, low boiling components such as $C_5$ and $C_6$ hydrocarbons are used to provide a finished gasoline of balanced volatility. The $C_5$ and $C_6$ isoparaffins are desired as the octane rating is much better than for the corresponding normal paraffins and octane senssitivity (research octane rating minus motor octane rating) is much better for the corresponding olefins. However, light straight-run $C_5/C_6$ fractions are comprised largely of normal paraffins. To upgrade these light straight-run fractions, resort must be had to isomerization with such catalysts as a Friedel-Crafts catalyst or a supported platinum catalyst. Yet, isomerization processes have a serious disadvantage in that conversion is limited by thermodynamic equilibrium. Thus, isoparaffin to normal paraffin ratios in the product are relatively low, e.g. on the order of 2–3:1. Recovery and recycle of unconverted normal paraffins adds greatly to the cost of an isomerization process.

There remains, then, paraffinic naphthas such as the straight-run naphthas which are less desirable for reforming feed or the raffinates obtained from the extraction of catalytic reformates. These paraffinic naphthas boiling in the range from about 200° F. to 450° F. have low octane rating and are much less desirable as gasoline blending components. A process for upgrading such paraffinic naphthas obviously is desirable.



In accordance with the process of this invention, paraffinic naphthas are selectively converted to low boiling $C_4$–$C_6$ hydrocarbons having a high iso to normal paraffin ratio by means of an active catalyst comprising copper and an acid-acting refractory oxide cracking catalyst at an elevated temperature and pressure and in the presence of hydrogen.

Naphthas which are converted in the process of the invention are the paraffinic naphthas boiling in the range from about 200°–450° F. By paraffinic naphthas it is meant those naphthas which are predominantly, i.e. about 60% by volume and preferably about 70% by volume or more paraffins. Moreover, it is preferred that such naphthas contain less than about 10% by volume of aromatic hydrocarbons. Higher boiling paraffins can be included, if desired.

The catalyst used in the present process is a multifunctional catalyst composition which comprises copper incorporated with an acid-acting refractory oxide cracking catalyst. Acid-acting refractory oxide cracking catalyst are generally the amorphous siliceous materials such as silica in combination with one or more oxides such as alumina, magnesia, zirconia, titania and the like. Silica-alumina is a well know and widely used cracking catalyst and is highly suitable for use in the present invention. In general, silica-content of the cracking component is in the range from about 60% to 90% by weight.

The copper catalyst is prepared by incorporating copper in a hydrogel of the siliceous refractory oxide cracking catalyst such as by ion-exchanging copper cations into the hydrogel. Surprisingly, activity of a copper catalyst prepared by incorporating the copper into a siliceous hydrogel is markedly superior to a catalyst wherein the hydrogel is dried and calcined and copper is deposited thereon by the conventional impregnation technique. The reason for the markedly higher activity is not known. It is possible that the presence of the copper ions in the hydrogel stabilize or help maintain active cracking sites which otherwise are lost during calcination. With silica-alumina, for example, it is the general practice to form a hydrogel from sodium salts, especially sodium silicate. Sodium ions are then washed from the hydrogel by means of ammonium salts or by acidulated water (e.g. water treated with solid ion-exchange resins to remove metallic cations) which leaves volatile cations to maintain the structure. Upon calcination of the hydrogel, the volatile cations and water are removed which presumably allows collapse or reorientation to a less active structure. Incorporation of copper cations into the hydrogel prior to calcination presumably tends to stabilize and maintain a highly active orientation.

As the catalyst is multifunctional, it might also be expected that copper bound within the silica-alumina structure would be less available for contact with hydrocarbon and would be, therefore, of reduced activity compared with an impregnated catalyst where the metal is deposited on a preformed silica-alumina support. On the contrary, the impregnated catalysts are much less active. A possible explanation is that the impregnating solution on the catalyst becomes more concentrated as solvent, such as water, gradually is evaporated. Moreover, the remaining solution is drawn within the catalyst pores by capillary action. Thus, when all the solvent has been evaporated from the impregnating solution, the copper compound is deposted in the form of crystallites whose diameters are comparable to the diameters of the catalyst pores. In-

corporating the copper in a hydrogel provides a wide degree of dispersion of the copper most of which at least apparently is retained as the catalyst is dried and calcined.

Any suitable means for preparing a siliceous hydrogel can be used for the present catalyst. For example, the preparation of silica-alumina cracking catalyst is well known and hence need not be discussed here. The copper is incorporated into the hydrogel prior to calcination of the hydrogel. The amount of copper in the final catalyst is in the range from about 0.1–25% by weight, preferably about 1–15% by weight.

It is generally advantageous to incorporated promoters such as fluorine into the catalyst. Incorporation of fluorine into, for example, silica-alumina hydrogel is considered to enhance the effectivness of the copper and of the acidic or cracking function. The presence of fluorine in the hydrogel apparently results in a more complete interaction of the metal ion with silica-alumina gel. The amount of fluorine can vary from about 0.1% to about 5% by weight and preferably is about 1% to 3% by weight, based on the total weight of the catalyst. The fluorine can be incorporated into the catalyst in any suitable manner such as co-precipitation by adding fluoride compounds to the solution from which silica and alumina are precipitated to form silica-alumina hydrogel. Another method is to contact the hydrogel with fluoride compounds.

Incorporation of copper into a siliceous gel such as silica-alumina hydrogel provides a catalyst which is highly active for the selective conversion of the paraffinic naphthas and which appears to be resistant to poisoning by nitrogen compounds. Nitrogen compounds are generally considered to be quite poisonous to acidic catalysts. With most paraffinic naphtha feeds, no pretreatment to remove nitrogen compounds is necessary in the present process and is in contrast to usual hydroprocesses which employ acidic cracking catalysts. Raffinates recovered in the extraction of catalytic reformates, or course, normally will be quite low in nitrogen and sulfur compounds.

In the process of the invention the paraffinic hydrocarbon feed is introduced into a reaction zone with a large excess of hydrogen. The amount of hydrogen employed is expressed in terms of hydrogen to oil mole ratio and is in the range from about 5:1 to about 25:1 or more. The conversion reaction is accompanied by a rather large consumption of hydrogen usually of the order of 500 to about 1500 standard cubic feet of hydrogen per barrel of feed converted. Conversion herein refers to the products obtained which boil below 200° F. Excess hydrogen is generally recovered at least in part from the reaction zone effluent and recycled to the reactor together with additional makeup hydrogen. Pure hydrogen is not necessary as any suitable hydrogen-containing gas which is predominantly hydrogen can be used. Particularly suitable is the hydrogen-rich gas containing on the order of 70–90% hydrogen which is obtained from a catalytic reforming process.

Pressure employed in the selective conversion reaction is in excess of about 500 p.s.i.g. and can range up to as high as about 3000 p.s.i.g. or so, a preferred range being from about 1000 to 2000 p.s.i.g. Average temperature in the reaction zone is in the range from about 450 to 850° F. The conversion reaction is exothermic; therefore, it is generally desired to provide some means of cooling the reaction zone, such as by the injection of relatively cold hydrogen. Liquid hourly space velocity can be in the range from about 0.1 to 25 and preferably from about 1 to 10.

## EXAMPLE I

Silica-alumina which had been prepared in a conventional manner comprising the precipitation of silica from sodium silicate solution, precipitation of alumina onto the silica, removal of sodium ions from the hydrogel, and calcination of the hydrogel, was preformed into pellets and impregnated with a copper nitrate and HF solution. The silica-alumina contained about 25% by weight alumina and the finished catalyst nominally contained 5.0% by weight copper and 2.5% by weight fluorine.

Another catalyst was prepared wherein copper was incorporated into silica-alumina hydrogel before calcination. To a solution of sodium silicate was added a solution of sodium aluminate and sodium fluoride followed by the addition of sulfuric acid to adjust the pH to about 7. The proportions were such as to provide 2.5% w. F. and about 30% w. $Al_2O_3$ in the finished silica-alumina. The hydrogel which formed was recovered by filtration and given repeated washings with ammonium nitrate solution and water to remove substantially all sodium cations from the hydrogel. The washed hydrogel was slurried in an ammoniacal solution of copper nitrate to ion-exchange copper cations into the hydrogel. The ion-exchanged hydrogel was washed with water to remove excess copper nitrate, dried, and calcined at about 1100° F. The finished catalyst contained 4.7% w. copper.

Each catalyst was employed to convert normal decane at 617° F. (325° C.), 1500 p.s.i.g., 10/1 $H_2$/oil mole ratio, and at various liquid hourly space velocities (volumes of oil per volume of catalyst per hour). The results are given in Table I below.

*Table I*

| | Impregnated Copper | | Ion-exchanged Copper | |
|---|---|---|---|---|
| LHSV | 4.0 | 8.4 | 3.9 | 7.7 |
| Conversion, percent w | 48.2 | 36.6 | 90.4 | 70.9 |
| Product analysis, percent w.: | | | | |
| $C_1$–$C_2$ | <0.1 | <0.1 | 0.2 | 0.1 |
| $C_3$ | 3.2 | 2.1 | 8.4 | 7.4 |
| $C_4$ | 12.8 | 9.2 | 27.6 | 23.1 |
| $C_5$ | 12.5 | 9.9 | 27.3 | 20.5 |
| $C_6$ | 12.2 | 8.5 | 23.1 | 15.3 |
| $C_7$–$C_9$ | 4.9 | 4.1 | 3.1 | 3.3 |
| i-$C_{10}$ | 2.4 | 2.6 | 0.6 | 1.1 |
| n-$C_{10}$ | 51.8 | 63.4 | 9.6 | 29.1 |
| $C_{11}$+ | 0.2 | 0.2 | 0.1 | 0.1 |
| Iso/normal paraffin ratio: | | | | |
| $C_4$ | 4.0 | 3.8 | 3.6 | 3.5 |
| $C_5$ | 7.4 | 8.7 | 3.8 | 5.0 |
| $C_6$ | 8.5 | 8.9 | 4.3 | 5.4 |

Based on extrapolated space velocities to provide equivalent conversion the catalyst wherein copper was incorporated into the hydrogel is 4–5 times more active than the catalyst wherein copper was impregnated onto a calcined hydrogel.

It is also to be noted that in general, yield of light gases decreases and the isoparaffin to normal paraffin ratio increases as conversion is decreased.

I claim as my invention:

**1.** A process for converting a paraffinic naphtha having at least 60% by volume paraffins and boiling in the range from about 200° to 450° F. into light gasoline boiling below about 200° F. which comprises contacting said naphtha at a temperature in the range from about 450° to 850° F., a pressure in the range from about 500 to 3000 pounds per square inch and a hydrogen to oil mole ratio in the range from about 5:1 to 25:1; with a catalyst comprising copper intimately associated with an acid-acting siliceous refractory oxide cracking catalyst, said catalyst having been formed by incorporating the copper into a hydrogel of the refractory oxide.

**2.** The process according to claim **1** wherein the naphtha comprises a raffinate from a catalytic reformate.

**3.** The process according to claim **1** wherein the refractory oxide is silica-alumina.

**4.** A process for converting a paraffinic naphtha having at least 60% by volume paraffins and boiling in the range from about 200° to 450° F. into light gasoline boiling below about 200° F. which comprises contacting said naphtha at a temperature in the range from about 450° to 850° F., a pressure in the range from about 500 to 3000 pounds per square inch and a hydrogen to oil mole

ratio in the range from about 5:1 to 25:1, with a catalyst comprising copper intimately associated with an acid-acting siliceous refractory oxide cracking catalyst, said catalyst having been formed by contacting a hydrogel of the refractory oxide with a solution of a copper compound wherein the copper is present as a cation to exchange copper cations into the hydrogel.

5. The process according to claim 4 wherein the refractory oxide is silica-alumina.

6. The process according to claim 5 wherein the naphtha comprises a raffinate from a catalytic reformate.



**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,428,692 | 10/1947 | Voorhies | 208—112 |
| 2,947,683 | 8/1960 | Hennig | 208—96 |
| 3,200,063 | 8/1965 | Wilson | 208—111 |
| 3,224,960 | 12/1965 | Wilson | 208—111 |


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