United States Patent Office

2,885,349
Patented May 5, 1959

2,885,349

HYDROCRACKING PROCESS

Rowland C. Hansford, Fullerton, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

No Drawing. Application July 27, 1956
Serial No. 600,380

5 Claims. (Cl. 208—109)

This invention relates to methods for the catalytic hydrocracking of high-boiling mineral oil fractions to produce therefrom lower boiling fractions such as gasoline. More particularly the invention concerns the use of certain novel catalysts in the hydrocracking process, said catalysts being composed of an adsorbent oxide carrier of the acidic type which in itself displays cracking activity, and distended thereon a minor proportion of a special type of chromium sulfide derived by reduction of chromium sulfate. It has been found that the chromium sulfide composition exhibits a substantially higher activity for promoting the desired hydrocracking reactions than does a corresponding chromium oxide catalyst.

The hydrocracking process itself consists in passing the high boiling feedstock in admixture with hydrogen over the catalyst at suitable temperatures, feed rates, pressures, etc. to effect a substantial conversion of the high boiling hydrocarbons to materials boiling in the gasoline range. Simultaneously, any organic sulfur and nitrogen compounds present in the feed are largely decomposed to hydrogen sulfide, ammonia and hydrocarbon fragments. Such hydrocracking processes are often referred to as destructive hydrogenation, or hydrogenolysis.

It is a principal object of this invention to provide more efficient and selective catalysts for the hydrocracking of mineral oils, which will effect a maximum conversion to high quality gasoline-boiling range hydrocarbons, and a minimum of destructive degradation to products such as methane and coke. Another object is to provide active catalysts which are also thermally stable, and hence may be utilized for long periods of time. Another object is to provide optimum process conditions for the utilization of such catalysts. A further object is to provide hydrocracking catalysts which are more economical than previously utilized catalysts. A still further object is to provide methods for effectively desulfurizing and denitrogenating high boiling feedstocks. A specific object is to provide catalysts which are effective for the hydrocracking of such highly refractory stocks as cycle oils from conventional thermal or catalytic cracking, whereby additional conversion to gasoline may be obtained. Another specific object is to provide catalysts which, in contrast to conventional hydrogenolysis catalysts, will produce gasoline hydrocarbons having even higher antiknock qualities than those produced by conventional catalytic cracking. Other objects and advantages will be apparent from the description which follows.

It is well known that the cracking of petroleum stocks, such as virgin gas oils from any type of crude oil, invariably leads to the production of a considerable proportion of a fraction which boils in the same range as the initial charge stock, but which is much more refractory toward further cracking. This is true whether the cracking process is non-catalytic or catalytic, and as a result there are definite limitations on the degree

to which profitable recycling of this fraction to the cracking operation can be practiced. The effect of increased refractoriness of the "unconverted" portion of a cracking stock is particularly limiting in the case of catalytic cracking, so much so that only small recycle ratios are generally employed, further conversion of the recycle stock often being effected in a subsequent thermal cracking operation. Recycling to extinction invariably results in poor selectivity of the conversion to gasoline, as a result of excessive formation of carbonaceous catalyst deposits and light hydrocarbon gases. This is also true in thermal cracking, except that instead of carbonaceous catalyst deposits a large amount of heavy tar of high carbon content is formed.

The refractoriness of cracked recycle stocks is the result, principally, of the formation of polynuclear aromatic hydrocarbons through reactions of dehydrogenation, hydrogen transfer, cracking, cyclization, or condensation. It is well known, for example, that recycle stocks from catalytic cracking have a high content of methylnaphthalenes. These may be formed by the cracking of long side-chains or of saturated rings attached to a naphthalene nucleus, by the dehydrogenation of polynuclear naphthenes or aromatic-naphthenes such as alkyltetralins, and even by the polymerization and cyclization of olefins produced from saturated hydrocarbons or alkyl side-chains. In thermal cracking, one important mechanism of polynuclear aromatic hydrocarbon formation is the condensation of diolefins with aromatics of lower ring content.

In catalytic cracking, another important factor leading to apparent refractoriness is the accumulation of pyridine- or quinoline-type compounds in the recycle stock. These basic nitrogen compounds exert a temporary poisoning effect on the acidic catalyst centers, and low conversion of the cycle stock results.

The above-noted difficulties are avoided or minimized by the process herein described. Thus, by preventing complete dehydrogenation of polynuclear naphthenes to polynuclear aromatics, by hydrogenating at least partially the polynuclear aromatics already present in the charge stock, by preventing high olefin or diolefin content with subsequent reactions of polymerization, cyclization, or condensation, and by decomposing basic nitrogen compounds to innocuous ammonia, relatively high partial pressures of hydrogen can permit a maximum theoretical conversion of heavy hydrocarbons of all types to hydrocarbons boiling in the desired gasoline range. A process which, in a single step, employs sufficient hydrogen to cause an appreciably greater conversion of any higher boiling hydrocarbon mixture to gasoline than is possible in one step by conventional catalytic or non-catalytic cracking processes is termed "hydrocracking" for the purposes of this description of invention. In all cases such a process will depend on the use of a suitable catalyst which not only promotes cracking but also activates molecular hydrogen to such an extent that hydrogen will enter into the cracking at some stage, presumably in the very initial stages, though there may not necessarily be a net consumption of hydrogen.

From the above discussion it will be apparent that the catalysts of the present invention may be used advantageously in the hydrocracking of virgin gas oils, whereby greater conversion to gasoline is obtained in a once-through operation than would be obtained in a similar once-through operation in conventional cracking processes, and also the "unconverted" fraction is not greatly degraded with respect to refractoriness, and may hence be recycled substantially to extinction. It will be apparent also that the catalyst may be employed to treat the refractory residues from conventional cracking operations whereby a substantial yield of high quality gasoline is obtained. The residue from this operation may likewise be recycled, either to the hydrocracking step or back to a conventional cracking step in the absence of hydrogen. These results are not obtainable when treating such recycle stocks with a conventional silica-alumina catalyst; hydrogen is practically without effect on the cracking of such stocks with this catalyst.

The hydrocracking conditions employed herein involve passing the vaporized hydrocarbons over the finished catalyst at temperatures ranging between about 750° and 1050° F., hydrogen pressures above about 100 p.s.i.g., preferably between about 500 and 5000 p.s.i.g., and space velocities ranging between about 0.1 and 10.0. The preferred hydrogen ratios may range between about 1000 and 10,000 s.c.f. per barrel of feed. A minimum hydrogen pressure of about 500 p.s.i.g. is critical herein when treating highly refractory, aromatic cycle stocks; at lower pressures dehydrogenation is favored, resulting in increased aromaticity and refractoriness of the stock. The optimum conditions herein defined are adapted to effect partial hydrogenation of fused-ring aromatic hydrocarbons to more highly saturated ring compounds, which are in turn more readily cracked to produce ultimately monocyclic aromatic hydrocarbons, and low-boiling paraffins.

The carriers employed herein consist of the conventional adsorbent oxide type of cracking catalysts, e.g. silica-alumina. It is generally believed that such cracking catalysts owe their cracking activity to the presence of acid centers on the surface, since it is known that active cracking catalysts exhibit acidic properties and that many of the reactions which occur in catalytic cracking are typical of acid catalyzed reactions which proceed through the medium of carbonium ions (Industrial and Engineering Chemistry, vol. 41, pages 2565–73, 1949). The best known examples of such cracking catalysts are silica-alumina, silica-magnesia, silica-zirconia, silica-alumina-zirconia, alumina-boria and titania-boria. In addition, the various natural clays of the montmorillonite type, particularly when subjected to a preliminary acid treatment with a mineral acid such as hydrochloric acid, hydrofluoric acid, sulfuric acid, etc., also possess recognized cracking activity. These natural clays include the various acid-washed bentonites, e.g. Filtrol, Super Filtrol, etc. Such clays usually comprise about 70–90% SiO_2 and 10–30% Al_2O_3 by weight. The preferred group of carriers comprise those cracking catalysts made up of silica and alumina. In particular, synthetic co-precipitated gels of alumina and silica are highly desirable, containing for example between about 5% and 90% by weight of silica and 10% to 95% by weight of alumina.

It is well known in the art that compositions containing the various chromium oxides, e.g. CrO_3 and Cr_2O_3 possess significant hydrogenating-dehydrogenating activity. Such chromium oxide catalysts are usually prepared by impregnating a carrier such as alumina with aqueous solutions of chromic acid, followed by drying and calcining. Usually, for purposes of dehydrogenation, non-acidic carriers have been employed, such as pure alumina.

It has now been found that chromium sulfides of unknown composition, when prepared by reduction of chromium sulfate previously impregnated upon an acid type cracking catalyst, display a substantially greater activity for hydrocracking, and for desulfurization and denitrogenation, than do corresponding catalysts composed of chromium oxide. Chromium sulfide catalysts cannot normally be prepared by the usual method of sulfiding a chromium oxide catalyst because the oxides of chromium cannot readily be converted to sulfides by reaction with hydrogen sulfide or other sulfur compounds. However, at high temperatures, the reaction:

$$2CrO_3+6H_2S \rightarrow Cr_2S_3+6H_2O+3S \qquad (1)$$

has been reported (Ann. 37, 350 (1841). But, chromium

sulfide is readily convertible to the oxide by treatment with water or oxygen. Hence the sulfide catalyst must be employed in the substantial absence of oxygen compounds. If any oxygen compounds are present in the feed it is preferable to remove such components prior to the hydrocracking treatment. It is possible however to tolerate small amounts of oxygen if there is present in the feed a large mol excess of total sulfur. This sulfur is converted to hydrogen sulfide, and will tend to prevent to some extent the deleterious effects of small mol proportions of oxygen compounds by shifting the equilibrium of Equation 1 to the right.

The preferred method of preparing the catalyst comprises first preparing the adsorbent carrier in the form of pellets or granules, then impregnating with an aqueous solution of chromium sulfate. However, other methods of preparation may be employed. For example, a wet gel of the carrier components may be slurried with a concentrated chromium sulfate solution and the mixture then dried and calcined. Alternatively the powdered, dry carrier may be wetted with a concentrated chromium sulfate solution and then dried, calcined and pressed into pellets or tablets. Normally, the impregnation of the dry, adsorbent carrier is the preferred method, both from the standpoint of convenience and activity. The proportion of chromium sulfate added should be sufficient to provide, in the finished catalyst, between about 1% and 20% by weight of Cr, preferably between about 3% and 10%.

The sulfide form of the catalyst is prepared normally by subjecting the composite of chromium sulfate on the carrier to reduction with hydrogen at elevated temperatures. For this purpose, temperatures between about 300° and 600° C. may be employed, while continuously passing hydrogen over the catalyst and removing the water, hydrogen sulfide, sulfur dioxide and free sulfur formed during the reaction. Normally, the reduction may be completed in about 1 to 5 hours, as evidenced by the absence of H_2O, H_2S and SO_2 in the exhaust gases. Instead of subjecting the chromium sulfate composite to a pre-reduction, the sulfate catalyst may be employed directly in the hydrocracking process, and reduction is accomplished during the processing by virtue of the hydrogen present therein. For the latter mode of operation, the chromium sulfate catalyst need only be dried at a low temperature, e.g. 200 to 400° F., or preferably it may be calcined in air at 400 to 1000° F., and is then ready for use. The calcining treatment normally does not effect decomposition of the sulfate. In the preferred method of operation, the sulfate catalyst is pre-reduced in hydrogen as described.

The following examples are cited to illustrate the comparative activity of the chromium sulfide catalyst as compared to a corresponding oxide catalyst. These examples however should not be construed as limiting in scope.

EXAMPLE I

An alumina-silica gel containing an estimated 95% Al_2O_3 and 5% SiO_2 by weight was prepared by co-precipitation of an aqueous mixture of sodium aluminate and sodium silicate with carbon dioxide. The precipitate was washed until substantially free of sodium ions, dried at 200° to 230° F., and activated by heating for two hours at 1000° F.

A portion of the foregoing carrier was then impregnated with an aqueous solution of chromium sulfate, $Cr_2(SO_4)_3 \cdot 9H_2O$, of sufficient concentration to give a final catalyst containing 4.7% Cr. The catalyst was then drained and dried at a low temperature, and was then subjected to reduction in hydrogen at 475° C. to give a chromium sulfide of unknown structure. The evolution of SO_2 and H_2S during the reduction was noted. This catalyst is designated as catalyst No. 1.

Another portion of the above carrier was then impregnated with an aqueous solution of chromic acid. The excess solution was drained, and the catalyst was dried and reduced in hydrogen as above described to give a final catalyst comprising 8.6% by weight Cr_2O_3 (5.9% Cr). This catalyst is designated as catalyst No. 2.

Each of the above catalysts was then employed for hydrocracking a cycle oil boiling above 400° F. derived from a commercial catalytic cracking operation, and containing about 65% by volume of aromatic hydrocarbons, 1.0% by weight sulfur, 0.14% by weight of nitrogen. The conditions of hydrocracking were: temperature 900° F., pressure 1000 p.s.i.g., liquid hourly space velocity 0.5, and hydrogen/feed ratio of 8000 cubic feet per barrel. Analysis of the respective products gave the following data:

Table 1

Catalyst	Vol. Percent Gasoline Yield, C_5—400° F.	Wt. Percent S in Total Product	Wt. Percent N in Total Product
1. Cr Sulfide	39	0.14	0.03
2. Cr Oxide	33	0.26	0.06

The above data show that the chromium sulfide catalyst prepared by reduction of the sulfate gave a substantially higher yield of gasoline, and substantially better desulfurization and denitrogenation than did the chromium oxide catalyst. Moreover, this result was obtained in spite of the fact that the oxide catalyst contained a significantly higher proportion of chromium. Similar differential results are obtained under other conditions of hydrocracking varying within the scope of the specification.

EXAMPLE II

When the test procedure of Example I is repeated employing a commercial synthetic silica-alumina cracking catalyst containing about 85% by weight SiO_2 and 15% Al_2O_3 as carrier, higher gasoline yields and better desulfurization and denitrogenation are obtained with each catalyst, but the chromium sulfide catalyst still displays a higher activity in all respects than the chomium oxide catalyst.

EXAMPLE III

When the procedure of Example I is repeated using as carried a 50/50 mixture of co-precipitated silica-zirconia, the gasoline yield, desulfurization, and denitrogenation obtained are each substantially better for the chromium sulfide catalyst than for the chromium oxide catalyst.

From the above it will be apparent that the catalysts described herein exhibit surprisingly higher activity for the hydrocracking of refractory cycle stocks than do the corresponding chromium oxide catalysts. Similarly improved results are obtained when treating other feedstocks within the scope of the invention. It is not intended that the invention should be restricted to the details disclosed in the examples or elsewhere since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A process for hydrocracking and desulfurizing a mineral oil feedstock boiling above the gasoline range and containing at least about 0.1% sulfur to produce gasoline-boiling-range hydrocarbons of reduced sulfur content, which comprises contacting said feedstock with a hydrocracking catalyst substantially in the absence of water and oxygen and in the presence of between about 1,000 and 10,000 s.c.f. of hydrogen per barrel of feed, said hydrocracking catalyst consisting essentially of a major proportion of an adsorbent acidic oxide carrier having cracking activity, and a minor proportion of mixed chromium sulfides derived by the reduction of chromium sulfate as defined in claim 4, the conditions of hydrocracking comprising a temperature between about 750° and 1050° F., hydrogen pressure between about 500 and 5,000 p.s.i.g., and space velocity between about 0.1 and 10 volumes of liquid feed per volume of catalyst per hour.

2. A process as defined in claim 1, wherein said feedstock is a residual oil rich in fused-ring aromatic hydrocarbons obtained from a catalytic cracking operation conducted in the absence of added hydrogen at a temperature between about 800° F. and 1000° F.

3. A process as defined in claim 1 wherein said carrier is a silica-alumina composite containing between about 10% and 95% Al_2O_3 and about 5% to 90% of SiO_2 by weight.

4. A method for preparing a hydrocracking catalyst, wherein the hydrogenating component consists of a highly active form of chromium sulfide, which comprises impregnating an adsorbent, acidic oxide carrier having cracking activity with sufficient of an aqueous solution of chromium sulfate to deposit on said carrier a minor proportion of chromium sulfate, draining and drying the impregnated catalyst and then subjecting the dried catalyst to reduction in a stream of hydrogen at 300° to 600° C. for 1 to 5 hours while continuously removing water, hydrogen sulfide, sulfur dioxide and free sulfur from the contacting zone.

5. A process as defined in claim 4 wherein said carrier is a silica-alumina composite containing between about 10% and 95% Al_2O_3 and about 5% to 90% of SiO_2 by weight.

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