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HYDROCRACKING OF HYDROCARBONS WITH A CATALYST COMPOSITE COMPRISING PRE-SULFIDED PALLADIUM COMPOSITED WITH A CRACKING SUPPORT

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This invention relates to procedure for hydrocracking of hydrocarbons which contain relatively small amounts of nitrogenous impurities and which are substantially free of asphaltic materials utilizing a hydrocracking catalyst which contains palladium.

The hydrocracking of various hydrocarbons into gasoline utilizing palladium catalysts is well known. (See for instance Ciapetta et al. U.S. 2,845,805.) Practically all research work which has been done in connection with a palladium type catalyst for hydrocracking has been carried out using the free metal. It is known that the free metal gives relatively low ratio of isomeric hydrocarbons to normal hydrocarbons. Furthermore it is known that free palladium is highly active for hydrogenation of aromatic hydrocarbons. For these reasons the hydrocracked product produced with this catalyst invariably contains little or no aromatics even when the feed stock is rich in aromatic hydrocarbons.

This invention has for its object to provide improved procedure for hydrocracking hydrocarbons into gasoline utilizing a palladium containing catalyst. Another object is to provide improved procedure for hydrocracking of hydrocarbons whereby higher ratios of iso-to-normal hydrocarbons can be obtained. A still further object is to provide improved hydrocracking procedure utilizing a palladium containing catalyst in which aromatic hydrocarbons present in the feed stock are hydrogenated to a lesser extent than heretofore. Another object is to improve the state of the art. Other objects will appear hereinafter.

These and other objects are accomplished by our invention, which includes subjecting a hydrocarbon feed stock which contains a relatively small amount of nitrogenous impurities and which is substantially free of asphaltic materials to treatment with hydrogen in the presence of a pre-sulfided palladium catalyst composited with an active cracking support. We have found by operating in this manner that relatively high ratios of isomeric hydrocarbons to normal hydrocarbons are obtained during the hydrocracking operation.

The catalyst utilized in our process may contain between about 0.1 to 5 percent by weight of palladium and preferably between about 0.5 and 1.0 percent palladium. The catalyst may be deposited upon any siliceous support having high cracking activity. These supports are well-known in the catlytic cracking art. They usually have a high surface acidity. Suitable supports comprise active cracking such as synthetic silica-alumina, silica-magnesia, silica - alumina - magnesia, silica - alumina-zirconia cracking catalysts or synthetic cracking catalysts prepared from natural clays by acid treating such as "Super Filtrol." Any catalyst support may be employed as long as it has the characteristics of a cracking catalyst. Especially useful materials are the high alumina synthetic

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silica-alumina cracking catalysts containing about 25 percent alumina such as "Triple A" silica-alumina cracking catalyst. An A.I. above 25 and preferably about 50 is advantageous.

The catalyst employed in our invention may be prepared using any known procedure for manufacture of two component catalysts of this general type. Thus the palladium may be deposited upon the pre-formed cracking carrier. Thus the palladium sulfide may be either impregnated in or on the silica-alumina carrier or the palladium sulfide may be deposited thereon by precipitation. Alternatively the cracking carrier and the palladium or palladium sulfide may be co-precipitated. In the event that the palladium is deposited as a metal or in another form than the sulfide, the palladium may be converted into the sulfide by suitable treatment such as by treatment with a hydrogen-hydrogen sulfide mixture at elevated temperature. These various procedures for preparing palladium sulfide or similar sulfide catalysts are well-known in the art. They do not form a part of our invention and therefore will not be described in greater detail.

Our invention is applicable to the hydrocracking of any feed stock which is substantially free of asphaltic materials, which is relatively low in nitrogenous impurities, i.e., below about 5 p.p.m. nitrogen and which has a boiling point higher than the desired product. Thus our invention is applicable to the hydrocracking of residual stocks which have been deasphalted and denitrogenated or which naturally have the necessary low nitrogen content. Our invention is also applicable to the treatment of hydrocarbon distillates such as hydrocarbons boiling between about 350° and 800° F. Such distillate feed stocks includes straight-run light or heavy furnace oil, cycle stock from catalytic cracking and/or aromatic extracts of various petroleum fractions such as a sulfur dioxide extract of a cycle stock. As indicated above, one advantageous aspect of our invention is the treatment of a feed stock which contains a substantial amount of aromatic hydrocarbons such as above 20 percent by volume of aromatics. Our invention is particularly advantageous in connection with feed stocks containing more than about 30 percent aromatics. Our invention, however, is applicable to feeds which are substantially free of aromatic hydrocarbons since with such feeds a relatively high iso-to-normal ratio is obtained in the hydrocracked product.

In the event that the feed stock in question does not have the required low content of nitrogenous impurities, i.e., below about 5 p.p.m. nitrogen, it will be necessary to pre-treat the feed stock to lower the nitrogen content to the required level. This can be accomplished utilizing any known procedure for removing nitrogenous compounds from hydrocarbon mixtures. One advantageous method for nitrogen removal is catalytic hydrogenation. Nitrogen content can also be lowered by treatment with an acid or an adsorbent having a high surface area, etc. Procedures for the removal or lowering of the nitrogen content are well-known in the art and do not constitute a part of our invention. Therefore, this procedure will not be described in greater detail.

Ordinarily the hydrocracking catalyst will be employed in the form of a fixed bed. However, our invention is applicable to the utilization of the catalyst in the form of a fluidized or similar bed in which catalyst pieces or

particles are completely or partially suspended in the hydrogen gas and/or hydrocarbon vapors.

Ordinarily the temperature employed in our hydrocracking process will be between about 450° and 800° F. and preferably between about 550° and 750° F. The pressure is advantageously between about 500 and 2000 p.s.i. (hydrogen partial pressure) and preferably between about 750 and 1500 p.s.i. A space velocity (liquid volume of feed per volume of catalyst per hour) of 0.1 to 10 and preferably between about 0.5 and 3 may be used. The hydrogen circulation rate (cubic feet per barrel of feed) is advantageously between about 2000 and 20,000 and preferably between about 6000 and 10,000. The hydrogen purity may be between about 70 and 100 percent and preferably between 80 and 100 percent based on the gas present in the reactor.

In accordance with a specific embodiment of our invention we maintain sulfur or sulfur compounds in the hydrocracking reactor. We have found that this improves the iso-to-normal hydrocarbon ratio and also reduces aromatic saturation if aromatic hydrocarbons are present in the feed stock. If the feed stock contains sulfur compounds, this should be taken into consideration in determining the amount of sulfur which is added. Furthermore, the recirculated hydrogen containing gas will as a general rule contain hydrogen sulfide, and this should be considered in determining the amount of sulfur to be added. It is desirable in accordance with this aspect of our invention to have sufficient sulfur present in the reactor to result in at least 20 p.p.m. of sulfur in the reactor. It is advantageous to have between about 50 and 2500 p.p.m. or more of sulfur present. Any organic or inorganic sulfur compound having a hydrocarbon-to-sulfur or a carbon-to-sulfur linkage as well as elemental sulfur can be used to supply the necessary sulfur content in the reactor. Examples of suitable substances are butyl mercaptan, thiopene, hydrogen sulfide and carbon disulfide. These substances may be added to the feed and/or hydrogen or introduced directly into the reactor. Halogens are known to be useful in hydrocracking. If desired, a halogen may be added during the process of our invention. The halogen may be introduced into the reactor, with the feed and/or hydrogen and/or it may be added to the catalyst. The sulfur and halogen, when it is also employed, are advantageously added continuously. However, discontinuous addition may be practiced as long as the desired amounts are maintained in the reaction system.

Example I

A PdS on silica-alumina catalyst was prepared by impregnating a commercial cracking catalyst consisting of about 13 percent Al_2O_3 and 87 percent SiO_2 with a solution of $PdCl_2$ to incorporate Pd in the catalyst structure. The wet catalyst then was treated with H_2S gas to convert $PdCl_2$ to PdS. Subsequently, the catalyst was dried and calcined in a nitrogen atmosphere. The finished catalyst contained 1.18 percent PdS. A second catalyst which contained unsulfided Pd on silica-alumina was prepared by impregnating the same support with a sufficient amount of $PdCl_2$ solution to incorporate 1 percent Pd in the catalyst structure. Following the impregnation step the catalyst was dried at 250 F. and calcined for two hours at 900° F. The analyses of this catalyst indicated that it contained 1.04 percent Pd and less than 0.05 percent S. These catalysts were compared for hydrocracking a denitrogenated South Louisiana No. 2 fuel oil into gasoline, and the results are presented in Table I. In columns 1 and 2 the unsulfided palladium catalyst was used without sulfur addition. In column 3 the run was with the presulfided catalyst, but without sulfur addition. In column 4 the run was with the presulfided catalyst and with 38 p.p.m. of sulfur added to the feed. The pretreated feed contained 12 p.p.m. of sulfur, therefore total sulfur was 50 p.p.m. in this run. The hydrocracking conditions were 750 p.s.i.g., 1.0 LHSV

(volume of oil/volume of catalyst/hour), 10,000 SCF of H_2/bbl., and temperatures as indicated in Table I.

TABLE I

	Column No.			
	1	2	3	4
	Pd—No Sulfur Added	Pd—No Sulfur Added	PdS—No Sulfur Added	PdS 50 p.p.m. Sulfur
Temperature, ° F	602	653	631	626
Iso/n-Pentane, Wt./Wt	2.3	2.8	7.1	8.6
Iso/n-Hexane, Wt./Wt	3.3	2.5	4.5	6.8
Retention of Aromatics, Percent by Vol. of Aromatics in Charge	0.0	0.0	0.0	14.3
Octane Rating of Gasoline Fraction (Hexane-210° F.) Motor Octane Number (+3 cc. TEL)	----------	85.5	89.2	91.1

From the data in Table I it will be seen that utilizing a pre-sulfided catalyst results in considerable improvement in regard to iso-to-normal ratios as compared with an unsulfided catalyst. However, a further and larger improvement is obtained by not only utilizing a pre-sulfied catalyst but by addition of sulfur during the onstream reaction. Also sulfur addition markedly improves retention of aromatics.

Example II

A Pd on silica-alumina catalyst was prepared following the same procedure as in Example I. However, the silica-alumina support in this case was a commercial cracking catalyst which contained 25 percent Al_2O_3 and 75 percent SiO_2. The finished catalyst contained 1.0 percent Pd and was evaluated in hydrocracking. The same charge stock and the same reaction conditions were used as in Example I, excepting that a temperature of 625° F. was employed here in all of the runs. The effect of sulfur was studied by addition to the feed at several concentration levels as well as with a substantially sulfur-free feed. The results of this study are shown in Table II.

TABLE II

	Column No.			
	1	2	3	4
Sulfur Added to Charge Stock, p.p.m	None	30	50	2,500
Iso/n-Pentane	3.5	6.5	10.0	13.5
Iso/n-Hexane	2.3	4.2	5.5	8.5
Aromatics Retention, Percent by Vol. of Aromatics in Charge	0.0	0.0	0.0	0.0

The data in Table II show that with or without sulfur addition there is no retention of aromatics when an unpresulfided palladium catalyst is used.

Example III

A PdS catalyst was prepared employing a commercial silica-alumina cracking catalyst support that contained 25 percent Al_2O_3 and 75 percent SiO_2. The support was impreganted with a $PdCl_2$ followed by drying and calcination. A portion of this catalyst was reduced with hydrogen at atmospheric pressure and 580° F. for one-half hour while passing hydrogen over the catalyst. The reduced catalyst was sulfided with a gas containing 18 percent H_2S and 82 percent H_2. The sulfiding was carried out at 580° F., 1200 p.s.i.g., for a total period of three hours. The catalyst was cooled in the H_2 and H_2S gas atmosphere. The finished catalyst contained 1.1 percent PdS. This catalyst was evaluated for hydrocracking denitrogenated FCC furnace oil without addition of sulfur and at several sulfur levels. The hydrocracking was carried out at 1000 p.s.i.g., 2 LHSV, 10,000 s.c.f.

of H_2/bbl., and 635° to 640° F. The charge stock prior to sulfur addition contained 1 p.p.m. S, 0.4 p.p.m. N, 36.6 percent by volume aromatics, 1.7 percent by volume olefins, 61.7 percent paraffins. The results are given in Table III.

TABLE III

	Column No.			
	1	2	3	4
	PdS No S Added	PdS 33.0 p.p.m. S Added	PdS 63.0 p.p.m. S Added	PdS 500 p.p.m. S Added
Iso/n-Pentane Wt./Wt.	4.1	5.4	6.9	7.8
Retention of Aromatics, Percent by Volume of Aromatics in Charge	0.0	5.2	5.6	25.0

The data in Table III establish that by using a pre-sulfided catalyst together with addition of sulfur, excellent results are obtained with respect to both iso-to-normal ratios and aromatics retention.

We claim:

1. In a hydrocracking process in which a hydrocarbon feed stock which is low in nitrogen and substantially free of asphaltic materials is contacted with hydrogen in the presence of a hydrogenation catalyst composited with an active cracking support, that improvement which comprises contacting the feed stock with a catalyst comprising essentially pre-sulfided palladium composited with the cracking support.

2. In a hydrocracking process in which a hydrocarbon feed stock which contains below about 5 p.p.m nitrogen and which is substantially free of asphaltic materials, is contacted with hydrogen in the presence of a hydrogenation catalyst composited with an active cracking siliceous support, that improvement which comprises contacting the feed stock with a catalyst comprising essentially pre-sulfided palladium composited with the siliceous support.

3. In a hydrocracking process in which a hydrocarbon feed stock which is low in nitrogen and substantially free of asphaltic materials is contacted with hydrogen in the presence of a hydrogenation catalyst composited with an active cracking siliceous support, that improvement which comprises contacting the feed stock with pre-sulfided palladium composited with the siliceous support, said contacting being carried out in the presence of at least 20 p.p.m. of sulfur.

4. In a hydrocracking process in which a hydrocarbon feed stock which is low in nitrogen and substantially free of asphaltic materials is contacted with hydrogen in the presence of a hydrogenation catalyst composited with an active cracking siliceous support, that improvement which comprises contacting a feed stock which contains a substantial amount of aromatic hydrocarbons with pre-sulfided palladium composited with the siliceous support, said contacting being carried out in the presence of between about 50 and 2500 p.p.m. of sulfur.

5. In a hydrocracking process in which a hydrocarbon feed stock which is low in nitrogen is contacted with hydrogen in the presence of a hydrogenation catalyst composited with an active cracking siliceous support, that improvement which comprises contacting a feed stock which boils in a range between about 350° and 800° F. and which contains above about 30 percent of aromatic hydrocarbons with pre-sulfided palladium composited with the siliceous support, said contacting being carried out in the presence of between about 50 and 2500 p.p.m. of sulfur and a halogen.

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