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CATALYTIC TREATMENT OF HYDROCARBON OILS

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This invention relates to the treatment of distillable hydrocarbon oils containing sulfur compounds, such in particular as unrefined or partially refined gasolines or fractions thereof, with hydrogen in the presence of hydrogenating difficultly reducible compounds of heavy metals to effect a substantial hydrogenation and removal of said sulfur compounds while maintaining the anti-knock properties of the material treated.

Various processes for the catalytic hydrogenation of hydrocarbon distillates of the nature of gasolines to remove sulfur compounds have been suggested. Most of these processes depend upon the use of particular hydrogenation catalysts which are more or less resistant to poisoning by sulfur compounds and/or are capable of being used for relatively long periods of time before regeneration or replacement is necessary. None of the processes disclosed are, however, completely satisfactory. Under conditions for effective removal of sulfur compounds a saturated product having poor anti-knock properties is usually obtained. The usual refinery practice has therefore been to effect a compromise by subjecting the material to be treated to only a limited hydrogenation treatment under mild conditions; that is, the material is subjected to a mild hydrogenation treatment and the hydrogenation is stopped while the material still contains an appreciable amount of unsaturated hydrocarbons. By carefully limiting the severity of the treatment and controlling the extent of hydrogenation most of the more easily removable sulfur compounds and olefinic hydrocarbons are hydrogenated with a comparatively small depreciation of the anti-knock properties. The product is then subjected to a further conventional refining treatment, such as a conventional treatment with sulfuric acid, to complete the refining.

The hydrogenation may be carried out with any one of a large number of sulf-active hydrogenation catalysts. However, some preference has been shown to the use of hydrogenating metals, such as nickel, and hydrogenating metal oxides, such as iron oxide, which tend to react with the sulfur compounds in the feed and gradually converted to the corresponding sulfides. After a period of about 100 hours of use the sulfur is removed from the catalyst by a suitable regeneration treatment which converts the catalyst back to its original state. Metal sulfide catalysts such as nickel sulfide and cobalt-molybdenum sulfide have, however, also been suggested as suitable catalysts. When using such catalysts it is necessary to effect the hydrogenation under mild

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conditions. Thus, for example, temperatures in the order of 450–600° F. are used. Under the mild conditions necessary the desulfurization-hydrogenation is quite slow. The liquid hourly space velocity is usually in the order of 1.5.

The above critique of the previously known and conventional practices is not intended to discredit these processes since they are considerably more effective than the conventional acid refining method for this purpose and have been used for a number of years. It is intended, however, to point out wherein these processes are not completely satisfactory and to show in which respects the process of the present invention is an improvement.

An object of the present invention is to provide a process of the type described which will allow a more complete removal of sulfur compounds and olefins (if present) while substantially maintaining the anti-knock properties of the material treated. Another object is to provide a process of the type described in which high hydrogenation temperatures and higher throughput capacities may be utilized without depreciation of the anti-knock properties of the material treated.

These objects are attained in the process of the present invention by utilizing a catalyst which has been modified in its catalytic properties by a comparatively long period of use under dehydrogenation conditions. It is found that under the usual conditions for effecting hydrogenation and removal of sulfur compounds a wide variety of ill-defined reactions takes place simultaneously, some of which reactions are desirable and some of which are undesirable. It is well known that over a long period of use the over-all activity of the catalyst declines considerably so that in time it becomes necessary to replace the catalyst. It is found, however, that if the catalyst is used for a comparative long period under dehydrogenation conditions the decline in catalytic activity is of such a nature that the ability of the catalyst to catalyze the undesirable reactions decreases at a much faster rate than the ability of the catalyst to catalyze the desired reactions. Thus, by using the catalyst under dehydrogenation conditions for a comparatively long period (say 500–1000 hours) the catalyst is still substantially active for the subsequent desulfurization but is less active in catalyzing the undesirable reactions which in said desulfurization tend to depreciate the anti-knock properties of the material. Also, the catalyst, after preconditioning or pretreating under dehydrogenation conditions, may be used

for the catalytic desulfurization at considerably higher temperatures and at much higher space velocities, and a substantially complete desulfurization may be obtained without detrimentally affecting the anti-knock properties of the material treated. The reason for the improved efficiency of the catalyst for the described desulfurizing hydrogenation after a comparatively long period of use under dehydrogenation conditions is not clearly understood. It does not appear to be due to the deposition of carbonaceous deposits upon the catalyst or to poisoning of the catalyst by sulfur or other organic materials since the effect is noted even if the catalyst, after being used under the dehydrogenation conditions, is regenerated in the conventional manner by burning off carbonaceous deposits and resulfiding. It appears to be due to the long period of heating under reducing conditions at the higher temperatures of the dehydrogenation.

It is to be particularly pointed out that the catalyst used for the present desulfurization-hydrogenation treatment is not one which has been deactivated by previous use. Thus, the pretreated or preconditioned catalyst, after regeneration, if necessary, is substantially as active as the freshly prepared catalyst when tested under either dehydrogenating or hydrogenating conditions. The catalyst is changed, however, during the preconditioning and this is particularly evident from the differences in the rates of decline of fresh and preconditioned catalysts under dehydrogenation conditions. Under hydrogenation conditions both catalysts show substantially the same very slow rate of decline.

The process of the present invention is applicable for the desulfurization of various distillable hydrocarbon oils and fractions thereof including straight run gasolines from high sulfur petroleum. It is, however, particularly advantageous for the desulfurization of such materials as catalytically cracked gasolines, thermally cracked gasolines, thermally reformed gasolines, coal tar distillates, and various fractions thereof. Thus, it is particularly advantageous for the desulfurization of distillates containing appreciable concentrations of olefins and/or aromatic hydrocarbons, which distillates normally have excellent initial anti-knock properties (for example, A. S. T. M. octane numbers of 76 or above), since the depreciation of the anti-knock properties of such materials is considered particularly undesirable.

The catalyst used is a preformed heavy metal sulfide dehydrogenation catalyst and is preferably one prepared by precipitation methods. Examples of such catalytic materials are the sulfides of iron, nickel, cobalt, molybdenum and tungsten. These materials may be used per se but are usually used in combination with a suitable relatively inert carrier or diluent material such as alumina, magnesia, silica, zirconia or the like.

One preferred catalyst for the process of the invention is, for example, a preformed compound catalyst comprising as the predominant active constituent a combination of a major mol amount of a metal of the iron group and a minor mol amount of tungsten combined with sulfur in amounts to approximately satisfy the general formula $WS_2 \cdot 2FeS_3$. This catalyst is preferably prepared by forming an intimate mixture as by precipitation methods, of a sulfide of a metal of the iron group and tungsten sulfide and then further sulfiding the material with hydrogen sulfide or a mixture of hydrogen sulfide and hydrogen

at a temperature between about 700 and 850° F. until the prescribed sulfur concentration is obtained. Of the metals of the iron group, nickel is preferred. The mol proportion of nickel (or iron or cobalt) to tungsten may range from below 1:1 up to about 2:1. However, a ratio between about 1.5:1 and 1.8:1 is preferred. While the above described catalyst is preferred for the reasons that it is very selective and affords a particularly long catalyst life without regeneration, cobalt thiomolybdate catalysts such for instance as described in United States Patent 2,325,033 and other preformed sulf-active metal sulfide hydrogenation catalysts may also be employed.

The catalyst prior to being used for the selective hydrogenation of sulfur compounds is used for a period of time under dehydrogenation conditions. Such conditions are characterized by the production of hydrogen and hydrocarbons poorer in hydrogen as net reaction products. In general dehydrogenation is effected with these catalysts at higher temperatures than those normally used for the hydrogenation of sulfur compounds, for instance temperatures between about 850° F. and 950° F. The dehydrogenation is preferably carried out substantially continuously with a feed containing 0.15% sulfur or less and in the presence of a considerable excess of recycled product gases consisting largely of hydrogen. Suitable preconditioning of the catalyst, for example, may be had by using the freshly prepared catalyst for a period of about 500-1000 hours and at a temperature of about 880° F. for the dehydrogenation of a straight run gasoline fraction containing about 0.1% sulfur. The preconditioning should be continued for at least about 100-200 hours and is preferably carried out for about 1000 hours or more, for example, for a time corresponding to between one-quarter and one-half of the normal life of the catalyst under such conditions.

The catalyst after being preconditioned by use under dehydrogenation conditions may be simply transferred to the hydrogenation reactor (or the same reactor may be used) and used therein under desulfurizing hydrogenation conditions without any intermediate treatment. In general, however, the catalyst becomes contaminated to a small extent with carbonaceous deposits during use under dehydrogenation conditions, particularly if the amount of hydrogen recycled is not sufficiently large. It is therefore advantageous to first regenerate the preconditioned catalyst by removing carbonaceous deposits prior to using it for the desulfurizing hydrogenation. This may be accomplished by any one of the known conventional regeneration treatments.

After preconditioning as above described, the catalyst is employed for the desulfurizing hydrogenation. The desulfurizing hydrogenation may be carried out at temperatures in the order of 400-650° F. at relatively low space velocities as heretofore practiced with ordinary catalysts which have not been preconditioned. However, an important advantage of the present process is that the desulfurizing hydrogenation may be carried out at high temperatures in the order of 860-880° F. and at high liquid hourly space velocities even up to 30 while substantially maintaining the anti-knock properties of the original feed.

As mentioned above, if the desulfurization of olefinic stocks such as cracked and reformed gasolines is carried out with catalysts which have not been so pretreated, the hydrogenation must

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be stopped long before the desulfurization is complete in order to avoid an appreciable and undesirable depreciation of the anti-knock properties. An advantage of the present process is that the desulfurizing hydrogenation may be carried out more nearly to completion without suffering any appreciable loss of anti-knock properties.

Example

A tungsten nickel sulfide catalyst is prepared by precipitation (645 pounds of tungstic acid to 1050 pounds of nickel nitrate hexahydrate). The precipitate is treated at about 750° F. with a mixture of hydrogen sulfide and hydrogen until the sulfur content is between about 27% and 28%. The material is then mixed with about ½% of a binder and formed into pellets.

This catalyst is very active for desulfurization and hydrogenation and also catalyzes other reactions such as isomerization. Prior to using the catalyst for the desired desulfurization-hydrogenation it is used for a period of about 2000 hours under dehydrogenation conditions as follows:

Feed	A straight run gasoline fraction containing about 0.1% S
Temperature	°F. 860-880
Pressure	p. s. i. 750
Liquid hourly space velocity	1.5
Recycle H ₂ ratio	7:1

The catalyst after the treatment contains a small amount of carbonaceous deposits. It is, however, not spent and can be used for the desulfurization without further pretreatment. It is, however, regenerated by first burning off the carbonaceous deposits with a mixture of air and steam while maintaining the temperature below about 1100° F. and then treating with hydrogen sulfide. This regeneration removes any loss of activity or efficiency due to the above-mentioned deposits. The regenerated catalyst if used again under the above-described dehydrogenation treatment is found to be substantially as active and effective as the freshly prepared catalyst. The catalyst is, however, now employed for the described desulfurization-hydrogenation of a fraction of catalytically cracked aviation base stock containing about 36% by volume aromatic hydrocarbons, about 0.31% sulfur and having a bromine number (Rosenmund) of about 76 and a 1-C octane No. +4.6 cc. T. E. L. of about 86.1. When operating the desulfurization-hydrogenation under the following conditions:

Temperature	°F. 506-710
Pressure	p. s. i. 769-792
Liquid hourly space velocity	3.0-4.7
Recycle H ₂ ratio	6.5-9.0

over 99% of the sulfur is removed (sulfur content 0.002%) and the bromine number is reduced to about 8. The aromatics are substantially unaffected (aromatic content of the product about 35%) and the 1-C octane No. +4.6 cc. T. E. L. is increased to 95.8. The catalyst may be used continuously under these conditions for a long time without showing any noticeable decline in activity, selectivity or efficiency.

The desulfurization may also be carried out at higher temperatures and/or at higher space velocities. For instance the catalyst may be used to treat a catalytically cracked base stock frac-

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tion containing about 0.09% sulfur and under the following conditions:

Temperature	°F. 880-890
Pressure	p. s. i. 720
Liquid hourly space velocity	6
Recycle H ₂ ratio	7:1

Under these conditions the sulfur is reduced to below 0.01% for a period of over 1000 hours while substantially maintaining the anti-knock properties. When the catalyst finally loses its desired effectiveness it may be regenerated and reused for further extended periods of time.

I claim as my invention:

1. In the substantially continuous catalytic hydrogenation of sulfur-containing hydrocarbon oils of the nature of gasoline to effect removal of sulfur while substantially maintaining the anti-knock properties, the improvement which comprises effecting the hydrogenation with an active preformed heavy metal sulfide hydrogenation catalyst which has been preconditioned by its continuous employment for at least two hundred hours for the catalytic dehydrogenation of a relatively sulfur free hydrocarbon fraction prior to its application in said hydrogenation.

2. In the continuous catalytic hydrogenation of sulfur-containing hydrocarbon oils of the nature of gasoline having an A. S. T. M. octane number of at least 76 while substantially maintaining the anti-knock properties, the improvement which comprises effecting the hydrogenation with an active preformed heavy metal sulfide hydrogenation catalyst which has been preconditioned by its continuous employment for at least two hundred hours for the dehydrogenation of a hydrocarbon oil containing less than 0.15% sulfur prior to its application in said hydrogenation.

3. In the substantially continuous catalytic hydrogenation of sulfur-containing hydrocarbon oils of the nature of gasoline to effect removal of sulfur while substantially maintaining the anti-knock properties, the improvement which comprises effecting the hydrogenation with an active preformed heavy metal sulfide hydrogenation catalyst which has been preconditioned by its continuous employment under hydrogenation pressure at a temperature within the range of about 850° F. and 950° F. for at least two hundred hours for the dehydrogenation of a hydrocarbon oil containing less than 0.15% sulfur prior to its application in said hydrogenation.

4. In the substantially continuous catalytic hydrogenation of sulfur-containing hydrocarbon oils of the nature of gasoline to effect removal of sulfur while substantially maintaining the anti-knock properties, the improvement which comprises effecting the hydrogenation with an active preformed heavy metal sulfide hydrogenation catalyst consisting essentially of a preformed composite comprising a major mol amount of a sulfide of a metal of the iron group and a minor mol amount of tungsten sulfide, which catalyst has been preconditioned by its continuous employment under hydrogen pressure at a temperature within the range of about 850° F. and 950° F. for at least two hundred hours for the dehydrogenation of a hydrocarbon oil containing less than 0.15% sulfur prior to its application in said hydrogenation.

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