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DESULFURIZATION OF HYDROCARBON OILS WITH VANADIUM OXIDE CATALYST IN THE PRESENCE OF NAPHTHENES

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The present invention relates to the treatment of sulfur-containing organic materials, in particular, sulfur-bearing hydrocarbon material, to desulfurize the same. More particularly, the present invention relates to the desulfurization of sulfur-containing petroleum fractions, in particular fractions containing ring type sulfur compounds.

The problem of sulfur removal from petroleum fractions and crudes is as old as the petroleum industry. For most purposes, it is undesirable to have an appreciable amount of sulfur in any petroleum products. Gasoline should be relatively sulfur-free to make it compatible with lead. Motor fuels containing sulfur as mercaptans are undesirable because of odor and gum formation characteristics. Sulfur is objectionable in fuel oils of any kind because it burns to form SO_2 which is obnoxious and corrosive.

Sulfur occurs in petroleum stocks, generally in two main forms, as mercaptans and as part of a more or less substituted ring, of which thiophene is the prototype. The former type is generally found in the lower boiling fractions, in the naphtha, kerosene, and light gas oil material, whereas the ring-sulfur compounds form the bulk of the sulfur-bearing material of the higher boiling petroleum fraction. Numerous processes for sulfur removal from relatively low molecular and lower boiling fractions have been suggested, such as "doctor" sweetening, wherein mercaptans are converted to disulfides, caustic treating, solvent extraction, copper chloride treating, etc., all of which give a more or less satisfactory decrease in sulfur or inactivation of mercaptans by their conversion into disulfides. The latter remain in the treated product, and must be removed if it is desired to obtain a sulfur-free product.

Sulfur removal from petroleum fractions containing ring-type sulfur compounds, however, has been a much more difficult operation. Such sulfur is, of course, not susceptible to chemical operations satisfactory with mercaptan sulfur.

One satisfactory method for removing sulfur from products wherein it is present as a ring-type compound has been by hydrogenation in the presence of a so-called sulfative catalyst. Thus, it has been found that certain catalysts, such as cobalt molybdate, tungsten sulfide, nickel sulfide, molybdenum sulfide, etc., are good hydrogenation catalysts and that when these catalyst substances are employed in the hydrogenation of sulfur-containing petroleum stock, these catalysts are not poisoned by sulfur but, on the contrary, tend to reduce the sulfur content of the material being hydrogenated, the sulfur being removed as H_2S . The use of hydrogen, however, is not always feasible nor available, particularly in smaller refinery establishments. For its preparation there is required expensive equipment, as a catalytic methane reforming or a carbon-steam or iron-steam plant, as well as compressors, distribution means and the like. Because of this, hydrogenation of sulfur-containing crudes has added materially to the processing costs and, in many cases, it is more economical to market a lower quality sulfur-containing prod-

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uct at a low price to meet the competition of a crude from an oil field containing little sulfur, than it is to undertake to hydrogenate this crude.

The present invention relates to a novel process for removing catalytically sulfur of the ring type from sulfur-containing crudes and distillates without the necessity of adding extraneous hydrogen, by a process involving a transfer of hydrogen from a hydrogen donor compound to the sulfur compound. It has been discovered that sulfur-containing fractions may be freed of substantial amounts of such sulfur by contacting the sulfur-containing materials in the presence of a compound adapted for use as a hydrogen donor in a hydrogen transfer reaction. Among the hydrogen donors found to be most practicable are the naphthenes.

This invention further differs from conventional hydrogenation reactions in that molecular hydrogen is not supplied to the reaction as such, but is supplied in situ from a hydrogen donor such as a naphthene or an isoparaffin. The invention is especially applicable to catalyzed reactions in which hydrogen is directly transferred from the hydrogen donor to the sulfur being removed from the organic molecule. In general, the sulfur removed from the organic compounds is subsequently converted by the hydrogen transfer reaction to a sulfide, usually hydrogen sulfide. Generally, the hydrogen transfer reaction is carried out in the vapor phase with the use of a catalyst. The use of the selective catalyst results in much greater selectivities in the removal of sulfur to give the desired sulfur-free products and a substantial reduction in undesirable degradation reactions of the starting materials to gaseous products and carbonaceous by-products.

Naphthenes can be defined as saturated compounds of the general formula C_nH_{2n} having closed links composed of methylene groups. The naphthenic hydrocarbons which can be employed as hydrogen donors may be those having six cyclic carbon atoms or more, that is, cyclohexane and its derivatives. Naphthenic rings having four or less carbon atoms are too unstable to function satisfactorily. Alkylated derivatives of these naphthenes such as methylcyclohexane can also be employed. During the course of the reaction, the naphthenes are dehydrogenated to produce aromatic type products. For instance, when cyclohexane is used, it is converted to benzene and when methylcyclohexane is used, it is converted to toluene. The hydrogen atoms which are thus removed from the naphthenes are catalytically utilized in the presence of the catalyst to combine with the sulfur present as organically bound sulfur in the feed stock, thereby removing the sulfur from the feed stock and converting it into an easily separable form. Cyclohexane and its higher homologues are particularly adapted for use in the role of hydrogen donors because the removal of six hydrogen atoms from cyclohexane converts it to the completely aromatized benzene.

The reaction is carried out in vapor phase in the presence of the catalyst and under conditions of temperature, pressure, feed rates, and the like, so chosen as to produce the maximum possible removal of sulfur from the feed stock and at the same time to obtain high selectivity and relatively pure final sulfur-free products. The equipment employed for this process may be of any type known to those skilled in the art for effecting a vapor phase catalytic reaction. Thus, for example, liquid feed is charged to a vaporizer from which the resulting feed vapors pass through a preheating zone and thence into the catalytic reaction zone in which the vapors are contacted with the catalyst. The effluent vapors from the reaction zone are subsequently cooled and condensed to produce a liquid reaction product and non-condensable gases.

The catalyst which has been found to be particularly

useful in carrying out the reaction to remove organically bound sulfur is a specially prepared vanadium oxide catalyst supported on alumina. The use of vanadium catalysts for certain specific refinery operations has previously been suggested, for instance, hydroforming and isomerization and the like. In these operations it has been the general equivalent of related compounds such as molybdenum, chromium and the like. These processes are generally ones involving added hydrogen, and the catalysts generally have behavior and activities of a comparable nature. In the present invention, however, involving a hydrogen transfer from a naphthene to a thiophene, probably to form an unstable tetrahydrothiophene which is then cracked with the evolution of H_2S , not only is the catalytic action specific to the vanadium, but also to the nature of the carrier; furthermore, the reaction is specific to the manner whereby the catalyst is prepared, for two catalysts having the same composition, but differing only in the manner of preparation have quite different properties as hydrogen transfer catalysts, as will be made more clear below.

In order to reactivate the catalyst, carbonaceous deposits are removed and the catalyst regenerated by a stripping process as with steam, nitrogen, flue gas and the like, at elevated temperatures of about 1300° – 1600° F. Also, the organic matter may be burned off directly with air. In its ease of regeneration, the catalyst has a decided advantage over such materials as activated carbon, or catalysts supported on activated carbon.

The desulfurized reaction mixture is taken from the catalytic reaction zone and preferably condensed to a liquid comprising the reaction products and non-condensable gases. The liquid reaction product so obtained can be worked up in any suitable manner, for example, by fractionation, adsorption, or crystallization, to recover both the desulfurized feed and the aromatized hydrogen donor, as well as any hydrogenated product present as the result of the use of unsaturates in the reaction. Any hydrogen sulfide present in the liquid may be removed by extraction, caustic washing, or by other conventional methods for removal of hydrogen sulfide. Unchanged or incompletely desulfurized reactants can be recycled, together with fresh sulfur-containing feed and fresh hydrogen donor material. If desired, an inert diluent such as, for example, a portion of the non-condensable gaseous products can be employed. It is also possible to recycle a part of the product as a diluent. Although there is no necessity for a diluent in order to obtain the desired features of the reaction, the use of some such inert material may at times be desirable to effect more efficient and simpler control of the reaction.

It will be understood that the exact conditions employed in carrying out the desulfurization reaction will be determined by the nature of the feed constituents, the desired extent of removal of sulfur per pass, and the exact catalyst being employed. The reaction may be carried out under pressures ranging from atmospheric to superatmospheric with the restriction that the reaction must be carried out in the vapor phase. The range of pressures may vary from 0 to 200 p. s. i. g. and higher.

In general, the range of temperatures for carrying out the desulfurization reaction is of the order of 600° – 1100° F. Optimum temperatures for the reaction are considered to be about 750° – 950° F. At temperatures below this range, the rate of reaction tends to fall off and become somewhat slow and the removal of sulfur is substantially incomplete, even after adequate contact with the catalyst. At temperatures higher than this limit, there is noticed an increased tendency towards the occurrence of side reactions such as thermal cracking, gas formation, polymerization, and other undesirable reactions. The total feed rates employed generally lie in the range of 0.3 to 5 liquid volumes per volume of catalyst per hour. It is considered that the contact time may

be relatively short, such as 0.1 to 1 second, to achieve optimum selectivity and satisfactory removal of sulfur. In general, it is best to have a substantial excess of the hydrogen donor present in the material to be desulfurized. This may be determined by ascertaining the naphthene content of the feed and, if necessary, augmenting this with extraneous naphthenes, such as cyclohexane, etc.

As to the types of sulfur-containing feed stocks which may be desulfurized by this novel hydrogen transfer reaction, these include various types of organic materials having organically bound sulfur such as thiophene, alkylated thiophenes, and other thiophene derivatives, diethyl sulfide, diethyl disulfide, dipropyl sulfide, dibutyl sulfide, diamyl sulfide, mercaptans, various types of sulfur acids, etc. The process is especially useful for desulfurizing petroleum fractions, as for instance, naphtha fractions containing organically bound sulfur which must be removed before the fractions can be used for many purposes. In general, compounds must be used whose desulfurized products are sufficiently stable to withstand the relatively high temperatures and yet emerge from the reaction zone as intact molecules.

The process may be executed in a batch or continuous manner. Generally, better conversions are obtained with multipass processes. The catalyst may be employed in a fixed bed, moving bed, or in a fluidized manner, depending on the type of operation desired.

This invention will be better understood with reference to the following examples and tables indicating the results obtained in the desulfurization reaction of thiophene in the presence of a hydrogen donor. Results reported were obtained after a single pass operation unless otherwise specified.

The catalyst of the present process, which consists of about 5 to 20% vanadia on alumina, is preferably prepared by impregnation of dry alumina gel with ammonium meta vanadate followed by subsequent conversion of the ammonium vanadate to vanadium oxide by heat. A good way of preparing the catalyst is as follows:

Aluminum amylate was hydrolyzed by the addition of water to give an aqueous slurry containing about 5 weight percent alumina. Glacial acetic acid was added to this slurry to the extent of 6 weight percent based on alumina and the resulting slurry was dried for twenty-four hours in a steam oven (250° F.). The recovered dry gel was ground to a powder. 1000 grams of dry alumina was treated with 85.2 grams of ammonium meta vanadate dissolved in 1400 grams of hot water. The resulting paste was well mixed and dried in a steam oven. After drying, the powder was reimpregnated with another 85.2 grams of ammonium meta vanadate as above and again dried to give a final composition of 10% V_2O_5 on alumina. The catalyst was activated by heating at 850° F. overnight prior to use.

Similarly, catalysts can be prepared from alumina obtained from other sources, such as by precipitation from aqueous solutions of alumina nitrate, chloride, etc., by the addition of ammonium hydroxide.

The impregnation of the hydrous gel (see Example II) was carried out in an analogous manner except that the gel was not dried prior to impregnation.

Example I

That high sulfur removal by hydrogen transfer is apparently specific to the vanadia-alumina system and is not shown by vanadia supported on other carriers, or alumina alone, is demonstrated by the following data. A mixture of 10 volume percent thiophene in methyl cyclohexane was passed through a vaporizer and preheater and the vapors passed over the respective catalyst bed at a temperature of 800° F. and a pressure of 200 p. s. i. g. at a feed rate of 0.5 v./v./hr. The resulting products were condensed (400° F.), scrubbed with caustic to remove H_2S and mercaptans, and the resulting liquid

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analyzed for sulfur. The catalyst compositions in these runs were all prepared by impregnation of the hydrous gels.

Catalyst	Wt. Percent Sulfur		Percent Sulfur Decrease
	Feed	Product	
10% V ₂ O ₅ on Al ₂ O ₃	4.9	1.2	75
10% V ₂ O ₅ on SiO ₂	4.2	3.3	21
10% V ₂ O ₅ on 50/50 SiO ₂ /Al ₂ O ₃	4.9	1.4	71
10% V ₂ O ₅ on 25/75 MgO/SiO ₂	4.2	2.3	45
10% V ₂ O ₅ on MgO.....	4.2	3.9	7
100% Al ₂ O ₃	4.1	3.9	5

Example II

That the method of preparation of the catalyst is a very important factor in its activity as a hydrogen transfer desulfurizing catalyst is shown by the following data. The catalyst produced by the dry impregnation of the gel was considerably more active than that prepared by impregnation of the hydrous gel. The reaction conditions of Example I were employed.

Catalyst (10% V ₂ O ₅ on Al ₂ O ₃)	Product Dist., Wt. Percent			Wt. Percent Sulfur		Percent Sulfur Reduction
	Gas	Coke	Oil	Feed	Prod.	
Impregnated Dry Gel.....	2.7	1.0	96.3	4.2	0.5	88
Impregnated Hydrous Gel.....	11.7	0.7	87.6	4.9	1.2	75

These data show clearly the superior results obtained by the dry impregnation method, though the two catalysts had substantially the same chemical composition and physical properties. These data not only demonstrate the superior desulfurizing characteristics of the impregnated dry gel, but also show that the latter gives a much superior oil yield, with less coking and gas formation, than that associated with the impregnated hydrous gel.

Example III

The following data show the superiority of the V₂O₅—Al₂O₃ catalyst over activated carbon, which is also a hydrogen transfer catalyst, and over a molybdena-alumina catalyst, which is a known efficient hydrogenation-dehydrogenation catalyst. The feeds and the reaction conditions are the same as those previously employed. The vanadia-chromia and molybdena catalysts were prepared by impregnation of the dry gel.

Catalyst	Prod. Dist., Wt. percent			Wt. percent Sulfur		Percent Sulfur Reduction
	Gas	Coke	Oil	Feed	Prod.	
10% V ₂ O ₅ on Al ₂ O ₃	2.7	1.0	96.3	4.2	0.5	88
10% MoO ₃ on Al ₂ O ₃	19.0	2.0	79.0	4.2	1.2	71
10% Cr ₂ O ₃ on Al ₂ O ₃	7.4	1.3	91.3	4.2	1.8	57
Activated Carbon.....	---	---	---	4.2	1.1	74

The superior results obtained not only in desulfurization, but in product yield and low coke and gas formation, by the vanadia catalyst as opposed to the results obtained with molybdena and chromia, coupled with the known dehydrogenation-hydrogenation properties of the latter, serve to point out that the reaction with V₂O₅ is not merely a catalytic dehydrogenation followed by hydrogenation, but an actual hydrogen transfer reaction.

Example IV

To determine the effectiveness of this method of desulfurizing upon refinery streams, a heavy naphtha containing 0.66 wt. percent thiophene sulfur and a naphthene

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content of 40 vol. percent was passed over a catalyst consisting of 10% V₂O₅ on Al₂O₃ at 0.5 v./v./hr. under a pressure of 200 p. s. i. g. at 800° F. After caustic washing, the oil product had a sulfur content of 0.17, equivalent to a 74% reduction in sulfur.

Similarly, a kerosene cut containing 5.2% of thiophene type sulfur was treated as above, and an oil product containing 1.7% residual sulfur, equivalent to a 70% reduction, was obtained. Both examples were once-through operations and recycling would have substantially further decreased the sulfur content.

The process of the invention admits of many modifications obvious to those skilled in the art. Thus, the hydrogen donating naphthene may be present initially in the stream being treated. In these cases, it is not necessary to add extraneous naphthenes. Where there is only a relatively small amount of naphthenes present, it is desirable to add extraneous naphthenes, such as cyclohexane and cyclopentane, and their homologues and analogues.

What is claimed is:

1. A process for catalytic desulfurization of hydrocarbons containing ring sulfur which comprises reacting in the vapor phase, a gaseous mixture containing added naphthenes and hydrocarbons containing ring sulfur in the presence of a hydrogen transfer gel type catalyst consisting essentially of vanadium oxide supported on alumina, prepared by impregnating dry alumina gel with a water soluble vanadium compound followed by thermal conversion of said compound to vanadium oxide and thereafter activating the catalyst by heating at elevated temperatures, at temperatures of between about 750° to about 950° F.

2. A process for the catalytic removal of ring sulfur from sulfur-containing hydrocarbons which comprises vaporizing said hydrocarbons, forming a gaseous stream containing said vapors in the presence of a vaporized naphthenic hydrocarbon and in the substantial absence of added free hydrogen, passing said gaseous stream at a temperature of between 750° to about 950° F. in contact with a hydrodesulfurization catalyst prepared by impregnating dry alumina gel with a vanadium-containing compound followed by the thermal conversion of said vanadium compound to vanadium oxide and thereafter activating the catalyst by a heat treatment, transferring hydrogen from said naphthenic compound to said hydrocarbons containing ring sulfur by the catalytic action of said vanadium catalyst whereby said ring sulfur is removed from said hydrocarbons and said naphthenic hydrocarbon is converted at least partly to aromatic hydrocarbons.

3. The process of claim 2 wherein said catalyst contains about 10% V₂O₅.

4. The process of claim 2 wherein said sulfur removal is carried out at superatmospheric pressures.

5. The process of claim 2 wherein additional naphthenic compounds are extraneously added to said naphtha.

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