

SULFUR AND MERCAPTAN REMOVAL FROM HYDROCARBON STREAMS CONTAINING REACTIVE UNSATURATES

TECHNICAL FIELD

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This invention relates to processes for removal of sulfur from hydrocarbon streams, and more particularly to removal of elemental sulfur and mercaptans (thiols) from hydrocarbon streams containing reactive unsaturates, using metals or compounds of metals from Groups IB, IIB and
10 IIIA of the Periodic Chart of Elements (as denoted in the Merck Index).

INDUSTRIAL APPLICATION

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Removal of elemental sulfur and mercaptan (thiol) contaminants is a frequently encountered problem in the petroleum industries. This invention provides a process in which sulfur and mercaptans in hydrocarbon streams comprising reactive unsaturates are removed by contacting the hydrocarbon stream at mild temperatures with a hydrogen reduced metal oxide, such as copper, zinc and/or aluminum oxide, without the undesirable byproduct
20 reaction of oligomerization or polymerization of the reactive unsaturates. Application of this invention's sulfur and mercaptan removal technique is especially useful in the petrochemical industry where the hydrocarbon streams often contain very high levels of reactive unsaturates and is desired to reduce sulfur levels to very low levels to meet product quality
25 requirements.

BACKGROUND ART

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Elemental sulfur contaminants are difficult to remove. Mercaptan contaminants are very reactive and are often dimerized into disulfides when one tries to remove them. See, e.g. US-A-5,169,516. The resulting disulfides remain in the hydrocarbon stream, failing to achieve the goal of sulfur removal. The problem is even more difficult to solve if the hydrocarbon

stream contains reactive unsaturates such as acetylenes, diolefins, olefins or aromatics.

Metal oxides and metals, including those of Groups IB, IIB and IIIA, have been used in processes seeking to remove sulfur and sulfur containing compounds from hydrocarbons. Metal oxides of copper (Group IB) and zinc (Group IIB) have long been used to remove hydrogen sulfide (e.g. $\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$). See, for example, US-A-2,959,538; US-A-3,660,276; US-A-4,314,902; US-A-4,978,439; US-A-5,106,484; US-A-5,130,109; and US-A-5,157,201.

Metallic copper or zinc has been used in certain circumstances, normally involving elevated temperatures, in sulfur and sulfur compound removal. For example, see: US-A-2,768,932 (contacting a hydrofixed, sulfur-containing petroleum distillate with finely divided metallic copper, copper alloys and copper oxides at elevated temperatures up to about 350°C); US-A-2,897,142 (contacting a hydrodesulfurized petroleum distillate boiling in the range 149°C - 204°C [300°F to 400°F] with free copper or silver in the absence of hydrogen); US-A-3,945,914 (contacting an oxidized sulfur-containing hydrocarbon material with copper or zinc at a temperature from 260°C to 732°C [500°F to 1350°F]); US-A-4,113,606 (contacting a refined hydrocarbon feed with particulate copper, iron or zinc or compounds thereof or composites of them and refractory oxides of Groups II to IV metals supported in a binder of a refractory material and having a surface area of 2 to 700 m²/g); US-A-4,163,708 (contacting a hydrodesulfurized hydrocracked oil in the absence of molecular oxygen and at a temperature of 120°C to 400°C with a composite of a copper or copper compound component and a porous carrier having a surface area of 20 to 1000 m²/g); US-A-4,204,947 (contacting a crude oil based fossil fuel with acetic acid treated metallic copper surfaces at a temperature of 43°C to 49°C [110°F to 120°F]); and US-A-5,173,173 (contacting feedstock containing naphtha or jet fuel with copper components supported on an alumina-containing porous refractory oxide at temperatures from 93°C to 371°C [200°F to 700°F] under sulfur absorption conditions, including absence of free hydrogen).

The use of these prior art methods is acceptable if the feedstream

does not contain reactive unsaturates. However, if the hydrocarbon stream contains reactive unsaturates, these sulfur removal techniques are not acceptable as they require elevated temperatures. The problem of removing elemental sulfur or mercaptans from hydrocarbon streams containing highly reactive unsaturates, such as aromatics, olefins, diolefins or acetylenes, has not been addressed.

Indeed the art contra-indicates possible use of metallic copper or copper oxides for sulfur or mercaptan removal from hydrocarbon streams containing highly reactive unsaturates. The use of copper on a support is taught as a catalyst for selective hydrogenation of acetylenes in the presence of butadienes rather than for sulfur removal; see US-A-4,440,956, US-A-4,493,906. At temperatures from 93°C to 127°C [200°F to 260°F] and in the absence of free hydrogen, copper oxide or silver oxide is employed to crack acetylenes in a hydrocarbon stream in which a polymerization inhibitor is used to also prevent polymerization of butadienes.

Conditions that include elevated temperatures are unsuitable for removal of sulfur and mercaptans from hydrocarbon streams containing reactive unsaturates because at elevated temperatures, the reactive unsaturates tend to oligomerize and polymerize, especially the very labile alkyne and diolefin components such as acetylene and butadiene.

The closest prior art, US-A-4,204,947, teaches a method to remove only thiol (mercaptan) and hydrogen sulfide (column 2, lines 49-56) with the limitation that at least 0.4 ppm of the total sulfur impurity must be thiol. Removal of elemental sulfur is not addressed.

In addition to the limitations regarding type of sulfur removal achievable and the level of thiol impurity that must be present, this patent utilizes high operating temperatures. The operating temperature for contacting the oil feedstream with the copper is from 120°C to 400°C (column 1, line 66). At these temperatures, the reactive unsaturates in the hydrocarbon feedstream will polymerize. This patent does not address sulfur removal for a hydrocarbon stream containing a major portion of reactive unsaturates.

In its gasoline feed example, the feed contained less than 15% olefins

which are unsaturates. Here, the olefins, as unsaturates, are not reactive. Less than 1% of the total olefins present in the gasoline contains olefins with a carbon number of 4 or less as most of the olefins in a typical gasoline feed have a carbon number greater than 5. In this particular environment, the
5 olefins are sufficiently diluted and hence, non-reactive.

In a petro-chemical plant application, with a hydrocarbon stream comprising almost pure olefins, as being a pure component stream, the olefins are reactive. Therefore, a sulfur removal technique which is effective in a non-reactive environment is not necessarily applicable in a reactive
10 environment.

DISCLOSURE OF THE INVENTION

In accordance with the present invention, a process for producing a
15 hydrocarbon stream having reduced sulfur contamination levels from a hydrocarbon stream comprising reactive unsaturates and contaminant sulfur which comprises contacting the stream with a scavenger comprising a Group IB, IIB or IIIA metal obtained by hydrogen reduction of a metal oxide, characterized in that the contaminant sulfur is initially present as elemental
20 sulfur or mercaptan and the stream comprises a major proportion of reactive unsaturates when contaminant mercaptan is present, and in that the contacting is performed under mild temperature conditions such as to reduce the contaminant sulfur level without substantial oligomerization or polymerization of the reactive unsaturates.

In the preferred embodiment, the temperature of contacting is not
25 greater than 35°C. In a more preferred embodiment, the temperature is from 15°C to 30°C, and most preferably 20°C to 25°C. The sulfur contaminant level in the hydrocarbon stream may be less than 500 wppm sulfur. The contacting is performed under conditions to reduce the sulfur
30 level by at least 95%, and preferably at least 99.5%.

In another preferred embodiment, the hydrocarbon stream comprises greater than 70 wt%, and preferably greater than 80 wt%, of the reactive unsaturates.

Preferably the metal oxide is carried as a porous support. The hydrogen-reduced metal oxide is produced by contacting the supported metal oxide with hydrogen under reducing conditions effective to reduce the metal oxide to elemental metal reactive with elemental sulfur and mercaptans to form sulfides of the metal. Advantageously, the metal oxide is contacted first with a gas consisting of a first predetermined minor amount of hydrogen gas and a major amount of an inert gas at a first temperature in the range from 100°C to 250°C at a pressure in the range from 0.35 to 6.9 MPag (50 to 1000 psig) for a first predetermined period of time effective to reduce a major proportion of the metal oxide to elemental metal, after which the metal oxide is contacted next with a gas consisting of a higher predetermined minor amount of hydrogen gas and a major amount of an inert gas at a higher temperature in the range from 175°C to 300°C at a pressure in the range from 0.35 to 6.9 MPag (50 to 1000 psig) for a second predetermined period of time effective to reduce a major remaining proportion of the metal oxide to elemental metal. Suitably, the metal oxide is an oxide of copper, zinc, aluminum or mixtures thereof.

MODES FOR CARRYING OUT THE INVENTION

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In accordance with the present invention, free (elemental) sulfur and mercaptans (thiols) are removed, preferably to a level less than 0.1 ppm, from a hydrocarbon stream containing reactive unsaturates such as aromatics, olefins, diolefins or acetylenes. The method of this invention is especially suited to removal of sulfur and mercaptans from a hydrocarbon stream containing a major proportion of a reactive diolefin, for example, 1,4-butadiene, or from a fuel rich in aromatics, such as aviation gasoline.

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As employed in this application, the terms "mercaptan" and "thiol" refer to compounds of the general formula R-SH wherein "R" means an alkyl group, normally one of from one to ten carbon atoms, and "SH" means a sulfhydryl group, sometimes called a mercapto group.

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The sulfur contaminant level in the hydrocarbon stream is less than 500 wppm sulfur, preferably less than 400 wppm sulfur, and most preferably

less than 100 wppm.

A hydrogen-reduced metal oxide selected from oxides of Group IB, IIB, and IIIA and mixtures thereof is employed. Especially suitable are reduced metal oxides of copper, zinc and aluminum. The metal oxides are
5 reduced by contacting them with a gas consisting of a major volume percentage of an inert gas and a minor volume percentage of hydrogen gas at a temperature in the range from 100°C to 300°C at a pressure in the range from 0.35 to 6.9 MPag (50 to 1000 psig).

Preferably, the metal oxide reduction is accomplished in at least a two
10 step reduction to control heats of reaction and reduce the oxides efficiently. Accordingly, the metal oxide(s) is contacted first with a gas consisting of a first predetermined minor amount of hydrogen gas and a major amount of an inert gas at a first temperature in the range from 100°C to 250°C at a pressure in the range from 0.35 to 6.9 MPag (50 to 1000 psig) for a first
15 predetermined period of time effective to reduce a major proportion of the metal oxide to elemental metal, after which the metal oxide in mixture with already reduced metal oxide is contacted next with a gas consisting of a higher predetermined minor amount of hydrogen gas and a major amount of an inert gas at a higher temperature in the range from 175°C to 300°C at a
20 pressure in the range from 0.35 to 6.9 MPag (50 to 1000 psig) for a second predetermined period of time effective to reduce a major remaining proportion of the metal oxide to elemental metal. Thus, in a preferred embodiment, mixed metal oxides of copper oxide, zinc oxide and alumina powder are exposed first to an atmosphere of about 99% nitrogen and 1%
25 hydrogen at a temperature of about 160°C and a pressure of 1.400 MPag (200 psig) for about 24 hours, then to an atmosphere of about 98% nitrogen and 2% hydrogen at a temperature of about 200°C and a pressure of about 1.400 MPag (200 psig) for about 24 hours.

After the reduced metal oxides are formed, they are maintained in an
30 oxygen free environment until ready for use.

The hydrogen-reduced metal oxide is produced by contacting the metal oxide with hydrogen under reducing conditions effective to reduce the metal oxide to elemental metal reactive with elemental sulfur and

mercaptans to form sulfides of the metal.

The removal mechanism is believed to involve the formation of metal sulfide. The reduction of metal oxides provides fresh metal surface which is much more reactive toward sulfur than plain metal, which is usually protected by a thin layer of surface oxides. Another advantage of the reduced metal oxides is their porosity. Metal oxide could be made porous via the addition of a porous binder such as alumina, silica, and clay. The porosity increases the scavengers' surface area which improves the removal efficiency.

The resulting scavenger has a specific surface area of from 50 to 750 m²/g, preferably 50 to 600 m²/g, and most preferably 50 to 500 m²/g. Preferably the reduced metal oxide has a specific surface area sufficient for reducing the sulfur and mercaptans in the hydrocarbon stream to a level less than 0.1 ppm.

In the method of this invention, elemental sulfur and mercaptans in a hydrocarbon stream containing reactive unsaturates, are removed by contacting the stream with a hydrogen-reduced metal oxide (suitably prepared as just described) under mild sulfur and mercaptan removing conditions, preferably at ambient temperature, and preferably for a time sufficient to reduce the sulfur or mercaptan content of the hydrocarbon stream to less than 0.1 ppm.

The temperature of contacting must be above the freezing point of the hydrocarbon stream and can be as low as 0°C, but not greater than 35°C, preferably from 15°C to 30°C, and most preferably 20°C to 25°C. It is important that the temperature of contacting for sulfur removal is done below the temperature at which oligomerization or polymerization of the reactive unsaturates occurs. The contacting is performed under conditions which reduce the contaminant sulfur level to the desired level, while oligomerizing or polymerizing less than 0.01 wt% of the reactive unsaturates in the hydrocarbon stream.

The contacting is performed under conditions to reduce the sulfur level by at least 95%, preferably at least 99%, and most preferably at least 99.5%.

EXAMPLE 1 [Preparation of reduced metal oxide]

This example illustrates the preparation of the sulfur and mercaptan removing scavengers (reduced metal oxides) which may be used in the process of this invention. A mixed metal oxides containing 33% copper oxide, 33% zinc oxide, and 34% alumina in the form of pellets (Katalco Corp, Houston, Texas) were ground to 0.1425 cm / 0.025 cm (40/60 mesh) particles and reduced first in an atmosphere of 99% nitrogen/1% hydrogen by volume, at 163°C (325°F) and 1.38 MPag (200 psig) for 24 hours, followed by an atmosphere of 98% nitrogen/2% hydrogen at 204°C (400°F) and 1.38 MPag (200 psig) for another 24 hours. The reduced metal oxides so produced were used in the following Examples.

EXAMPLE 2 [Process of invention]

This example illustrates the effectiveness of the scavenger produced in Example 1 in removing elemental sulfur from aviation gasoline. The aviation gasoline used in this test was of typical aviation grade and contained 3.3 ppm by weight of elemental sulfur. Five grams of the reduced metal oxides produced in Example 1 were mixed with 50 cc of the aviation gasoline in a sealed bottle at ambient temperature (22°C) and atmospheric pressure for two hours. The liquid phase from the bottle was then sampled and analyzed by polarograph, which showed that the elemental sulfur concentration was reduced from 3.3 ppm to less than 0.1 ppm.

EXAMPLE 3 [Comparative process using causticized lime]

One of the commonly used mercaptan scavengers is caustic-treated lime. The basic lime absorbs the acidic mercaptans through an acid-base reaction which removes them from hydrocarbons. The problem is that basic materials catalyze the dimerization of mercaptans. To illustrate this point, a caustic-treated lime ("Sofnolime" from Molecular Products Ltd., Houston, Texas) was used to treat a butadiene stream comprising greater than 99.9

wt.% butadiene and containing 45 ppm by weight methyl mercaptan. Ten grams of the causticized lime was allowed to equilibrate with 65 grams of butadiene in a dosed stainless steel cylinder at ambient temperature (22°C) and 0.69 MPag (100 psig) overnight. After the equilibration, analysis of the butadiene showed that it contained less than 0.1 ppm methyl mercaptan. However, as much as 2 ppm dimethyl disulfide, which was not originally present in the feed, was detected. The presence of dimethyl disulfide could be accounted for only by the dimerization of methyl mercaptan. The goal of sulfur removal therefore was not accomplished.

EXAMPLE 4 [Process of Invention]

This example illustrates the effectiveness of the reduced metal oxide scavengers from Example 1 in removing methyl mercaptan from butadiene as opposed to converting the mercaptan to a disulfide still resident in the butadiene. The reduced metal oxide scavenger was loaded into a 0.635 x 7.62 cm (0.25 x 3 inch) stainless steel column. A butadiene stream with a purity of greater than 99.9 wt.% butadiene and containing 45 ppm by weight of methyl mercaptan was pumped through the column at a liquid hourly space velocity of 1 hr⁻¹ at ambient temperature and 0.41 MPag (60 psig). Column effluent was sampled periodically and analyzed for sulfur. It was found that even after being on stream for five days, the effluent still contained less than 0.1 ppm methyl mercaptan and less than 0.1 ppm dimethyl disulfide, indicating the superior performance of the hydrogen reduced mixed copper, zinc and aluminum metal oxide sulfur scavengers, compared with the causticized lime of Example 3.

CLAIMS

1. A process for producing a hydrocarbon stream having reduced sulfur contamination levels from a hydrocarbon stream comprising reactive
5 unsaturates and contaminant sulfur which comprises contacting the stream with a scavenger comprising a Group IB, IIB or IIIA metal obtained by hydrogen reduction of a metal oxide, characterized in that the contaminant sulfur is initially present as elemental sulfur or mercaptan and the stream comprises a major proportion of reactive
10 unsaturates when contaminant mercaptan is present, and in that the contacting is performed under mild temperature conditions such as to reduce the contaminant sulfur level without substantial oligomerization or polymerization of the reactive unsaturates.
- 15 2. The process of Claim 1, wherein the temperature of contacting is not greater than 35°C.
3. The process of Claim 2, wherein the temperature is from 15 to 30°C, preferably 20 to 25°C.
- 20 4. The process of any of the preceding claims, wherein the sulfur contaminant level in the hydrocarbon stream is less than 500 wppm sulfur.
- 25 5. The process of any of the preceding claims, wherein contacting is performed under conditions to reduce the sulfur level by at least 95%.
6. The process of any of the preceding claims, wherein the hydrocarbon stream comprises greater than 70 wt%, and preferably greater than 80
30 wt%, of the reactive unsaturates.
7. The process of any of the preceding claims, wherein the metal oxide is carried on a porous binder.



8. The process of any of the preceding claims, wherein the metal oxide is an oxide of copper, zinc, or aluminum or a mixture of two or more thereof.
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9. The process of any of the preceding claims wherein the metal oxide is hydrogen-reduced by
- (a) in a first step, contacting the metal oxide with a gas comprising inert gas and a first minor proportion of hydrogen gas; and
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- (b) in a second step, contacting the treated metal oxide of step (a) with a gas comprising inert gas and a second minor proportion of hydrogen gas, which is greater than the first minor proportion, to reduce the remaining
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- metal oxide to elemental metal.
10. The process of any of the preceding claims, wherein the scavenger has a specific surface area of from 50 to 750 m²/g.
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11. The process of any of the preceding claims, wherein the reactive unsaturates comprise an olefin, diene or acetylene.
12. The process of Claim 11, wherein the diene is 1,4-butadiene.
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13. The process of any of the preceding claims wherein the contacting is performed under conditions which reduce the contaminant sulfur level while oligomerizing or polymerizing less than 0.01 wt% of the reactive unsaturates in the hydrocarbon stream.