

A Method and System for Treating Hydrocarbon Oil

Technical Field

The present application belongs to the field of petrochemicals, and specifically relates to a method and system for treating hydrocarbon oil to desulfurize it.

Background Art

Refineries produce large amounts of liquefied petroleum gas with high sulfur content. Sulfur compounds in liquefied petroleum gas are converted into sulfur oxides (SO_x) upon combustion, which are emitted into the atmosphere and can lead to acid rain formation, causing serious environmental pollution, therefore, desulfurization treatment thereof is necessary. Sulfides in liquefied petroleum gas are mainly hydrogen sulfide, mercaptans, and thioethers. Among them, organic sulfides such as mercaptans are difficult to remove completely by traditional alkanolamine wet desulfurization. Excessive sulfur content in liquefied petroleum gas will limit its application in downstream processing.

CN105176615A provides a new method for removing mercaptans matters from liquefied petroleum gas, wherein the method comprises the steps of: a) under completely alkali-free conditions, causing alkylation reactions between mercaptans in the liquefied petroleum gas (which has undergone alkanolamine treatment) and olefins under the action of a catalyst in a fixed-bed reactor, generating high-boiling-point thioethers; b) discharging the liquefied petroleum gas containing high-boiling-point thioethers from the fixed-bed reactor and feeding it into a distillation column, where it is separated by distillation into a sulfur-free liquefied petroleum gas component and a sulfur-containing high-boiling-point component, thereby achieving liquefied petroleum gas refining. This method offers advantages of high efficiency and no alkali liquor discharge.

Adsorption methods for removing sulfides from hydrocarbon oils are an emerging technology. These methods utilize adsorbents to selectively adsorb polar sulfides, such as mercaptans, thiophenes, etc., to remove sulfides from gasoline, diesel, or aromatics. The main types of adsorbents reported for hydrocarbon oil desulfurization include: oxide adsorbents (γ -Al₂O₃, TiO₂, ZrO₂, ZnO, SiO₂), oxide adsorbents loaded with metals (Ni, Na, K, Ca, Ba), zeolite adsorbents (A, X, Y, TS-1, SAPO-34, MCM-41), and metal-ion-exchanged zeolite adsorbents. Adsorbents for aromatics desulfurization mainly include metal-loaded (Ni, Pd, Pt, Cu, etc.) oxide adsorbents, as reported in USP2,876,196, USP3,485,884, USP4,419,224 and USP4,592,829, etc.

CN103031150A provides a method using dual reactors to simultaneously remove

sulfides from hydrocarbon oil and liquefied petroleum gas, wherein hydrocarbon oil feedstock and hydrogen enter the first adsorption reactor from the bottom and flow upward, contacting the desulfurization adsorbent in the reactor to adsorb and remove sulfides from the gasoline. At the upper part of the first adsorption reactor, the desulfurized oil-gas and the desulfurization adsorbent are separated. The separated, less active desulfurization adsorbent is introduced into the second adsorption reactor. In the second adsorption reactor, sulfur-containing liquefied petroleum gas contacts hydrogen and the desulfurization adsorbent to remove sulfides from the liquefied petroleum gas. This method maximizes the utilization of the adsorbent's desulfurization activity, using the remaining desulfurization capacity of the adsorbent to remove sulfides from liquefied petroleum gas while adsorbing sulfides from gasoline.

U.S. patent documents US7427581, US6869522, and US6274533, etc., disclose methods for adsorptive desulfurization of light hydrocarbon oils under hydrogen conditions. These methods have characters such as high desulfurization depth, low hydrogen consumption, and low octane number loss, and can produce fuel oil with sulfur content below 30 $\mu\text{g/g}$. The adsorbents used in these methods use zinc oxide, silica, and alumina mixture as carrier and the loaded active components consist of cobalt, nickel, copper, iron, manganese, molybdenum, tungsten, silver, tin, vanadium, etc., or a combination thereof. Under conditions of 0.1-10.3 MPa, 37.7-537.7 $^{\circ}\text{C}$, a weight hourly space velocity (WHSV) of 0.5-50 h^{-1} , and in the presence of hydrogen, sulfur in the oil is captured onto the adsorbent, and hydrocarbons generated from the cracking of sulfides return to the reaction material. The sulfur-containing adsorbent can be recycled through continuous regeneration. In actual industrial application, this process can adsorb and remove sulfur from catalytic cracking gasoline to below 10 $\mu\text{g/g}$, with the product's anti-knock index loss not exceeding 0.6 units.

However, in the prior art, the desulfurizing treatment of hydrocarbon oils containing sulfides and olefins are usually conducted under hydrogen conditions, which can cause saturation loss of olefins.

Chinese patent CN104277877 discloses a process for adsorptive desulfurization of cracked gasoline, which combines a non-hydrogen physical adsorption desulfurization with a hydrogen treatment of the adsorbent to produce clean gasoline. The process uses selectively hydrodesulfurized catalytic gasoline as feedstock, which enters a fixed-bed reactor to contact a desulfurization adsorbent and adsorb thiophene compounds; after the desulfurization adsorbent reaches adsorption saturation, the feed of feedstock oil is stopped, and hydrogen is passed through the desulfurization adsorbent bed to treat the adsorbent under hydrogen conditions. The hydrogen-treated adsorbent can continue to adsorb sulfides from the catalytic gasoline. However, this process is implemented in a fixed bed. Due to the limited adsorption capacity of the desulfurization agent, it quickly reaches adsorption saturation, resulting in low desulfurization efficiency. It can only operate in a batch mode, requiring constant switching between the desulfurization adsorbent and hydrogen, which affects production efficiency and places high demands

on reactor safety. Furthermore, this document does not demonstrate that sulfides can be efficiently and deeply removed in a fluidized bed.

Summary of the Invention

The object of the present invention is to provide a treatment method of hydrocarbon oil that can proceed continuously, this method can avoid loss of olefins due to hydrogenation during desulfurization of hydrocarbon oil and can efficiently and deeply remove sulfides contained in the hydrocarbon oil, especially non-thiophene type sulfides.

To achieve the above object, a first aspect of the present invention provides a method for treating a hydrocarbon oil (particularly liquefied petroleum gas) containing sulfides and optionally olefins. The method comprises step (1): contacting the hydrocarbon oil, preferably hydrocarbon oil in gaseous state, in a desulfurization reactor in the absence of hydrogen, with a desulfurization adsorbent containing a metal active component M to perform a selective desulfurization reaction and generate a metal active component sulfide referred to as a metal sulfide, obtaining an at least partially desulfurized hydrocarbon oil and a spent desulfurization adsorbent containing the metal sulfide; wherein at least a portion, preferably all, of the sulfides in the hydrocarbon oil are non-thiophene type sulfides, and the metal active component M is one or more selected from cobalt, nickel, iron, manganese, copper, molybdenum, tungsten, silver, tin, and vanadium; preferably step (1) is conducted in a continuous manner. For explanation, in this specification, the term "spent desulfurization adsorbent" refers to a desulfurization adsorbent that has at least partially lost activity and needs restoration of activity or regeneration.

According to a preferred technical solution of the first aspect, the desulfurization adsorbent further comprises a carrier, wherein the carrier contains a sulfur-loading component in oxide form, and the metal active component M is supported on the carrier.

According to another preferred technical solution of the first aspect, the method further comprises step (2): transferring the spent desulfurization adsorbent to a sulfur transfer reactor to contact with a hydrogen donor to conduct a sulfur transfer reaction to reduce the metal sulfide into the metal active component M, and converting the sulfur-loading component in oxide form into a sulfide, obtaining at least partially activity-restored desulfurization adsorbent, optionally returning at least a portion of the at least partially activity-restored desulfurization adsorbent to the desulfurization reactor of step (1); preferably step (2) is conducted in a continuous manner.

According to one embodiment of the first aspect, the method for continuously treating a hydrocarbon oil (particularly liquefied petroleum gas) containing sulfides and optionally olefins comprises the steps:

(1) contacting the hydrocarbon oil, preferably gaseous hydrocarbon oil, in the absence

of hydrogen, in a desulfurization reactor, with a desulfurization adsorbent comprising a metal active component and a carrier containing a sulfur-loading component to perform a selective desulfurization reaction to generate a metal sulfide, obtaining at least partially desulfurized, or even almost completely desulfurized, hydrocarbon oil and spent desulfurization adsorbent containing the metal sulfide; wherein at least a portion, preferably at least 50%, more preferably 75%, even more preferably 100%, of the sulfides contained in the hydrocarbon oil are non-thiophene type sulfides;

(2) transferring the spent desulfurization adsorbent to a sulfur transfer reactor to contact with a hydrogen donor to perform a sulfur transfer reaction to reduce the metal sulfide into the metal active component, wherein sulfur element is transferred onto the sulfur-loading component, obtaining at least partially activity-restored desulfurization adsorbent, then returning at least a portion of the at least partially activity-restored desulfurization adsorbent to the desulfurization reactor of step (1).

According to a second aspect, the present invention also provides a system for treating hydrocarbon oil, characterized in that the system comprises a non-hydrogen desulfurization reactor (2), wherein a bottom of the non-hydrogen desulfurization reactor (2) is provided with a hydrocarbon oil inlet for feeding the hydrocarbon oil, a lower part is provided with a desulfurization adsorbent inlet, a top is provided with a desulfurized oil-gas outlet, and an upper part is provided with a spent desulfurization adsorbent outlet.

According to an embodiment of the second aspect, the system for treating hydrocarbon oil according to the present invention comprises a non-hydrogen desulfurization reactor (2) and a hydrogen-condition sulfur transfer reactor (7), wherein a bottom of the non-hydrogen desulfurization reactor (2) is provided with a hydrocarbon oil inlet for feeding the hydrocarbon oil, a lower part is provided with a desulfurization adsorbent inlet, a top is provided with a desulfurized oil-gas outlet, and an upper part is provided with a spent desulfurization adsorbent outlet; a bottom of the hydrogen-condition sulfur transfer reactor (7) is provided with a hydrogen donor inlet, a lower part is provided with a spent desulfurization adsorbent inlet and an optional regenerated desulfurization adsorbent inlet, an upper part is provided with an outlet for at least partially activity-restored desulfurization adsorbent, and a top is provided with a gas outlet; the spent desulfurization adsorbent outlet of the non-hydrogen desulfurization reactor (2) is connected via a pipeline to the spent desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7), and the activity-restored desulfurization adsorbent outlet of the hydrogen-condition sulfur transfer reactor (7) is connected via a pipeline to the desulfurization adsorbent inlet of the non-hydrogen desulfurization reactor (2); wherein the pipelines (6, 20) are provided with a device for respectively conveying the spent desulfurization adsorbent and the at least partially activity-restored desulfurization adsorbent into the hydrogen-condition sulfur transfer reactor (7) and the non-hydrogen desulfurization reactor (2) and a device for preventing gas from flowing between the non-hydrogen desulfurization reactor (2) and the hydrogen-condition sulfur transfer reactor (7).

Through in-depth research, the inventors surprisingly found that when treating a hydrocarbon oil containing non-thiophene type sulfides and a large amount of olefins, reactive adsorption of sulfides can be achieved even in the absence of hydrogen. More specifically, contacting this hydrocarbon oil in the absence of hydrogen with a desulfurization adsorbent containing a metal active component, a carrier, and optionally a sulfur-loading component in a desulfurization reactor can rapidly and deeply remove non-thiophene type sulfides, especially mercaptans, thioethers, hydrogen sulfide, etc., contained in the hydrocarbon oil through chemical reaction between sulfur in the sulfides and the metal active component, without causing hydrogenation reactions of the contained olefins. Moreover, contrary to physical adsorption methods in the prior art, since this desulfurization reaction causes sulfides formed by sulfur and the metal active component to be firmly contained in the desulfurization adsorbent, thus this desulfurization reaction can be continuously implemented in a fluidized bed under conditions of high temperature and high gas flow rate, and the metal sulfide is continuously carried out of the desulfurization reactor with the spent desulfurization adsorbent. Then, the spent desulfurization adsorbent containing the metal sulfide can be reduced to the metal active component M by reaction with the sulfur-loading component contained in the carrier under hydrogen conditions in the sulfur transfer reactor, in which case, the spent desulfurization adsorbent is converted into at least partially activity-restored desulfurization adsorbent; then at least a portion of the obtained at least partially activity-restored desulfurization adsorbent can be circulated to the desulfurization reactor. Since the sulfur transfer reaction can also be carried out in a fluidized bed, the method of the present invention can be implemented continuously as a whole without requiring intermittent feeding or replacement of the desulfurization adsorbent, thereby saving operating costs and operating time; additionally, it can reduce the amount of metal active component used in the desulfurization adsorbent. Based on research, the inventors believe, without being bound by any theory, that the principle of this hydrogen-condition sulfur transfer process may be as follows: under the action of hydrogen, the metal active component sulfide (e.g., nickel sulfide) in the spent desulfurization adsorbent undergoes a reduction reaction to generate the metal active component (e.g., nickel). Under the catalytic action of this metal active component (e.g., nickel), sulfur combines with the sulfur-loading component (e.g., zinc oxide) in the desulfurization adsorbent to form a sulfide and is transferred into the adsorbent interior. As the metal active component on the adsorbent surface is released, it can repeat the non-hydrogen chemical reaction adsorption process of step (1).

More specifically, without being bound by any theory and without any limitation to the present invention, based on detection results of products from the non-hydrogen adsorptive desulfurization reaction and the hydrogen-condition sulfur transfer reaction, the inventors believe that when the desulfurization adsorbent of the present invention is applied to the desulfurization of sulfides such as methyl mercaptan, the following reactions may occur in the desulfurization reactor and sulfur transfer reactor, respectively:

non-hydrogen adsorptive desulfurization reaction: $\text{CH}_3\text{-SH} + \text{Ni} \rightarrow \text{CH}_4 + \text{NiS}$;

hydrogen-condition sulfur transfer reaction: $\text{NiS} + \text{ZnO} + \text{H}_2 \rightarrow \text{Ni} + \text{ZnS} + \text{H}_2\text{O}$.

From the above reactions, it can be seen that the chemical reaction adsorption of the method of the present invention only replaces the sulfur element from non-thiophene type sulfides in the hydrocarbon oil, and the sulfur element is carried out of the desulfurization reactor with the desulfurization adsorbent, rather than the entire sulfide (e.g., mercaptan) being carried out. By causing rapid and sufficient reaction between the sulfide in the hydrocarbon oil and the metal active component, sulfur is deeply removed. Therefore, this desulfurization method does not cause loss of carbon and hydrogen elements in the hydrocarbon oil. In contrast, physical adsorption in the absence of hydrogen in the prior art can only carry out entire organic sulfides such as thiophene with the adsorbent, causing the hydrocarbon oil to lose a portion of carbon and hydrogen elements.

According to a preferred embodiment, in the method according to the present invention, the desulfurization reactor is a fluidized bed reactor or moving bed, and/or the sulfur transfer reactor is a fluidized bed reactor or moving bed; preferably, the desulfurization reactor is a fluidized bed reactor, and/or the sulfur transfer reactor is a fluidized bed reactor.

According to a preferred embodiment, in the method according to the present invention, conditions for the selective desulfurization reaction include: a temperature of 150-550°C, preferably 300-450°C, for example 350°C or 400°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa, for example 2.0 MPa, 2.5 MPa, 3.0 MPa, or 3.5 MPa; a weight hourly space velocity (WHSV) of the hydrocarbon oil containing sulfides and olefins of 0.1-30 h⁻¹, preferably 1-20 h⁻¹, for example 2 h⁻¹, 4 h⁻¹, 6 h⁻¹, 8 h⁻¹, 10 h⁻¹, 12 h⁻¹, 14 h⁻¹, 16 h⁻¹, and 18 h⁻¹.

According to a preferred embodiment, in the method according to the present invention, the sulfur content in the hydrocarbon oil containing sulfides and olefins, calculated as sulfur element, is 10-5000 µg/g, preferably 30-3000 µg/g, and the mass percentage content of olefins is 2-100%, preferably 5-85%.

According to a preferred embodiment, in the method according to the present invention, the hydrocarbon oil containing sulfides and olefins is one or more selected from dry gas, liquefied petroleum gas (liquefied petroleum gas), and catalytic gasoline; preferably, the hydrocarbon oil containing sulfides and olefins is one or more selected from catalytic cracking dry gas, catalytic cracking liquefied petroleum gas, dry gas from deep catalytic cracking, liquefied petroleum gas from deep catalytic cracking, ethylene and/or propylene products from steam cracking, or one or more selected from light fractions of C7 and below from catalytic cracking gasoline, catalytic pyrolysis gasoline, and steam pyrolysis gasoline. If the hydrocarbon oil is liquid at room temperature, it can be preheated before entering the desulfurization reactor to convert it into a gaseous state.

According to a preferred embodiment, in the method according to the present invention, conditions for the sulfur transfer reaction include: a temperature of 300-550°C, preferably 350-450°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa.

According to a preferred embodiment, in the method according to the present invention, the hydrogen donor is one or more selected from hydrogen, a mixed gas containing hydrogen, and a hydrogen donor; preferably, in the mixed gas containing hydrogen, the volume fraction of hydrogen is 10-99%, preferably 30-90%; or the hydrogen donor is one or more selected from cyclohexane, methylcyclohexane, tetralin, and decalin; preferably, the volume ratio of hydrogen in the hydrogen donor to the spent desulfurization adsorbent is (10-3000):1, preferably 100-2500:1, for example 300:1, 500:1, 800:1, 1200:1, 1500:1, or 2000:1.

According to a preferred embodiment, in the method according to the present invention, the sulfur content of the at least partially activity-restored desulfurization adsorbent, calculated as sulfur element, is 0.5-12%, preferably 1-10%, relative to the total weight of the desulfurization adsorbent.

According to a preferred embodiment, in the method according to the present invention, the method further comprises step (3): subjecting a remaining portion of the at least partially activity-restored desulfurization adsorbent obtained in step (2) that is not returned to the desulfurization reactor of step (1) to oxygen-containing coke burning regeneration to obtain regenerated desulfurization adsorbent, and subjecting the regenerated desulfurization adsorbent to reduction treatment in a reducing gas atmosphere to obtain reduced desulfurization adsorbent, then returning the reduced desulfurization adsorbent to the desulfurization reactor of step (1).

According to a preferred embodiment, in the method according to the present invention, the oxygen-containing coke burning is conducted in the presence of an oxygen-containing gas, the oxygen-containing gas having an oxygen volume fraction of 5-50 vol%; preferably, the oxygen-containing gas is one selected from air, a mixture of oxygen and nitrogen, a mixture of air and nitrogen; preferably, reaction conditions for the oxygen-containing coke burning include: a temperature of 300-800°C, preferably 350-600°C; a pressure of 0.1-3.0 MPa, preferably 0.1-1.0 MPa.

According to a preferred embodiment, in the method according to the present invention, conditions for the reduction treatment of the regenerated desulfurization adsorbent include: a temperature of 300-550°C, preferably 350-450°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa; a volume hourly space velocity of hydrogen in the reducing gas of 10-3000 h⁻¹; preferably, the reducing gas is one or more selected from hydrogen, a mixed gas containing hydrogen, and a precursor compound capable of producing hydrogen; preferably, in the mixed gas containing hydrogen, the volume fraction of hydrogen is 10-99%, preferably 30-95%; preferably, the reduction treatment of the

regenerated desulfurization adsorbent is also conducted in the sulfur transfer reactor.

According to a preferred embodiment, in the method according to the present invention, the metal active component is one or more selected from cobalt, nickel, iron, manganese, copper, molybdenum, tungsten, silver, tin, and vanadium, preferably cobalt and nickel, and/or the sulfur-loading component is mainly selected from oxides of Group IVB, VIIB, VIIIB, IB, IIB, IIA, and IVA metal elements, preferably selected from ZnO, TiO₂, ZrO₂, MnO₂, Fe₂O₃, CuO, MgO, CaO, SrO, GeO, SnO and PbO; more preferably, selected from ZnO.

According to a preferred embodiment, in the method according to the present invention, the carrier containing a sulfur-loading component comprises, based on the weight of the carrier, 20-85 wt%, preferably 25-75 wt% of the sulfur-loading component, 10-75 wt%, preferably 15-60 wt% of alumina, and 5-70 wt%, preferably 15-60 wt% of silica.

According to a preferred embodiment, in the method according to the present invention, based on the total weight of the desulfurization adsorbent, the content of the metal active component is 2-30 wt%, and the content of the carrier containing a sulfur-loading component is 70-98 wt%.

According to a preferred embodiment, in the method according to the present invention, the sulfides are one or more selected from mercaptans, thioethers, carbonyl sulfide, and hydrogen sulfide.

According to the second aspect, the present invention also provides a system for treating hydrocarbon oil, characterized in that the system comprises a non-hydrogen desulfurization reactor (2), wherein a bottom of the non-hydrogen desulfurization reactor (2) is provided with a hydrocarbon oil inlet for feeding the hydrocarbon oil, a lower part is provided with a desulfurization adsorbent inlet, a top is provided with a desulfurized oil-gas outlet, and an upper part is provided with a spent desulfurization adsorbent outlet.

According to an embodiment of the second aspect, the system for treating hydrocarbon oil according to the present invention comprises a non-hydrogen desulfurization reactor (2) and a hydrogen-condition sulfur transfer reactor (7), wherein a bottom of the non-hydrogen desulfurization reactor (2) is provided with a hydrocarbon oil inlet for feeding the hydrocarbon oil, a lower part is provided with a desulfurization adsorbent inlet, a top is provided with a desulfurized oil-gas outlet, and an upper part is provided with a spent desulfurization adsorbent outlet; a bottom of the hydrogen-condition sulfur transfer reactor (7) is provided with a hydrogen donor inlet, a lower part is provided with a spent desulfurization adsorbent inlet and an optional regenerated desulfurization adsorbent inlet, an upper part is provided with an outlet for at least partially activity-restored desulfurization adsorbent, and a top is provided with a gas outlet; the spent desulfurization adsorbent outlet of the non-hydrogen desulfurization reactor (2) is

connected to the spent desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7) via a pipeline, and the activity-restored desulfurization adsorbent outlet of the hydrogen-condition sulfur transfer reactor (7) is connected to the desulfurization adsorbent inlet of the non-hydrogen desulfurization reactor (2) via a pipeline; wherein the pipelines (6, 20) are provided with a device for respectively forcing the spent desulfurization adsorbent and the at least partially activity-restored desulfurization adsorbent into the hydrogen-condition sulfur transfer reactor (7) and the non-hydrogen desulfurization reactor (2) and a device for preventing gas from flowing between the non-hydrogen desulfurization reactor (2) and the hydrogen-condition sulfur transfer reactor (7).

According to a preferred embodiment, the system for treating hydrocarbon oil of the present invention further comprises a first receiver (5) and a second receiver (19), the first receiver (5) having a first material inlet and a first material outlet, the second receiver (19) having a second material inlet and a second material outlet; wherein the spent desulfurization adsorbent outlet of the non-hydrogen desulfurization reactor (2) is connected to the first material inlet of the first receiver (5), the first material outlet of the first receiver (5) is connected to the spent desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7); and the activity-restored desulfurization adsorbent outlet of the hydrogen-condition sulfur transfer reactor (7) is connected to the second material inlet of the second receiver (19), the second material outlet of the second receiver (19) is switchably connected to the desulfurization adsorbent inlet of the non-hydrogen desulfurization reactor (2).

According to a preferred embodiment, the system for treating hydrocarbon oil of the present invention further comprises a lock hopper (11) and a regenerator (14); wherein a bottom of the regenerator (14) is provided with an oxygen-containing gas inlet, a lower part is provided with a regenerated desulfurization adsorbent outlet, an upper part is provided with a desulfurization adsorbent inlet, and a top is provided with a flue gas outlet; the lock hopper (11) has a third material inlet, a third material outlet, and a regenerated desulfurization adsorbent inlet; the second material outlet of the second receiver (19) is further switchably connected to the third material inlet of the lock hopper (11), the third material outlet of the lock hopper (11) is switchably connected to the desulfurization adsorbent inlet of the regenerator (14), the regenerated desulfurization adsorbent outlet of the regenerator (14) is connected to the regenerated desulfurization adsorbent inlet of the lock hopper (11), and the third material outlet of the lock hopper (11) is further switchably connected to the regenerated desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7).

According to a preferred embodiment, the above system for treating hydrocarbon oil according to the present invention is used to implement the above treatment method of hydrocarbon oil according to the present invention.

According to a preferred embodiment, in the system of the present invention, the

regenerator (14) is a fluidized bed reactor or moving bed reactor, preferably a fluidized bed reactor.

Through the above technical solutions, the present invention contacts a hydrocarbon oil containing sulfides and olefins with a desulfurization agent in the absence of hydrogen to perform desulfurization reaction. This not only achieves deep desulfurization of the hydrocarbon oil but also avoids loss of olefins and octane number caused by hydrogenation saturation of unsaturated olefins under hydrogen-condition reaction, improving the selectivity of the desulfurization reaction.

Other characters and advantages of the present invention will be described in detail in the subsequent specific embodiments.

Brief Description of the Figures

The figures are provided for further understanding of the present invention and constitute a part of the specification. Together with the following specific embodiments, they are used to explain the present invention but do not limit it. In the figures:

FIG. 1 shows a schematic flow diagram of a system for treating hydrocarbon oil according to one embodiment of the present invention.

FIG. 2 shows a schematic flow diagram of a system for treating hydrocarbon oil according to a preferred embodiment of the present invention.

The reference numbers in FIG. 1 and FIG. 2 are explained as follows:

- 1: Hydrocarbon oil-gas inlet
- 2: Desulfurization reactor
- 3: Desulfurized hydrocarbon oil-gas outlet
- 4: Spent desulfurization adsorbent outlet
- 5: First receiver
- 6: Pipeline
- 7: Hydrogen-condition sulfur transfer reactor
- 8: Hydrogen inlet
- 9: Circulating hydrogen outlet
- 10: Pipeline
- 11: Lock hopper
- 12: Pipeline
- 13: Pipeline
- 14: Regenerator
- 15: Gas inlet
- 16: Regeneration flue gas outlet
- 17: Pipeline
- 18: Activity-restored desulfurization adsorbent outlet
- 19: Second receiver
- 20: Pipeline

Specific Embodiments

Specific embodiments of the present application are described in detail below with reference to the figures. It should be understood that the specific embodiments described herein are only for illustrating and explaining the present application and are not intended to limit it.

Any specific numerical values disclosed herein (including endpoints of numerical ranges) are not limited to the precise value but should be understood to also encompass values close to that precise value, such as all possible numerical values within the range of that precise value $\pm 5\%$. Furthermore, for the disclosed numerical ranges, one or more new numerical ranges may be arbitrarily combined between the endpoint values of the range, between an endpoint value and a specific point value within the range, and between each specific point value within the range, and these new numerical ranges should also be considered specifically disclosed herein.

Unless otherwise stated, terms used herein have the same meaning as generally understood by those skilled in the art. If a term is defined herein and its definition differs from the general understanding in the art, the definition herein prevails.

In this application, unless explicitly stated otherwise, any matter or item not mentioned directly applies to those known in the art without making any modification. Moreover, any embodiment described herein may be freely combined with one or more other embodiments described herein, and the technical solutions or technical ideas thus formed are considered as part of the original disclosure or original description of the present invention and should not be considered as new content not disclosed or anticipated herein, unless those skilled in the art consider such combination clearly unreasonable.

Unless otherwise clearly indicated, throughout the specification and claims, the term "comprise" or variations such as "include" or "contain" will be understood to include the stated element or component, but not to exclude other elements or components.

In this specification, terms "first", "second", etc., are used to distinguish two different elements or parts and are not intended to limit a specific position or relative relationship. In other words, in some examples, terms "first", "second", etc., may also be interchangeable with each other.

In this application, the term "olefin" has the meaning generally understood in the art, i.e., unsaturated hydrocarbon compounds having carbon-carbon double bonds. The olefins may be chain olefins or cyclic olefins, the number of carbon-carbon double bonds may be one, two, or more, and the carbon-carbon double bonds may be at the end of the carbon chain or in the middle of the carbon chain (i.e., internal olefins). In

addition, olefins may contain other functional groups, such as hydroxyl, aromatic rings, etc. In the method of the present application, the olefins are preferably monoolefins, more preferably linear or branched monoolefins.

"Upper part", "lower part", "top" or "bottom" of a reactor mentioned in this specification refers to the relative position of different areas of the reactor in terms of horizontal height. The "top" position may be above or below the "upper part" position. The "upper part" position is above the "lower part" position. The "lower part" position may be above or below the "bottom" position. The "top" and "upper part" positions are generally within the upper 1/2, even the upper 1/3, of the total height of the reactor. The "bottom" and "lower part" positions are generally within the lower 1/2, even the lower 1/3, of the total height of the reactor.

All patents and non-patent literature mentioned herein, including but not limited to textbooks and journal articles, are incorporated herein by reference in their entirety.

According to a preferred embodiment, the present invention provides a method for treating hydrocarbon oil, particularly liquefied petroleum gas, especially a method for desulfurizing the hydrocarbon oil, which comprises the following steps:

(1) in the absence of hydrogen, in a desulfurization reactor, contacting a hydrocarbon oil containing sulfides and optionally olefins with a desulfurization adsorbent comprising a metal active component and a carrier containing a sulfur-loading component to perform a selective desulfurization reaction and generate a metal sulfide to obtain at least partially desulfurized hydrocarbon oil and spent desulfurization adsorbent containing the metal sulfide; wherein the sulfides are non-thiophene compounds;

(2) directly contacting the spent desulfurization adsorbent in a sulfur transfer reactor with a hydrogen donor to perform a sulfur transfer reaction to reduce the metal sulfide into the metal active component to obtain at least partially activity-restored desulfurization adsorbent, then returning at least a portion of the at least partially activity-restored desulfurization adsorbent to the desulfurization reactor of step (1).

The present invention contacts a hydrocarbon oil, particularly liquefied petroleum gas, containing sulfides and optionally olefins, with a desulfurization adsorbent comprising a metal active component and a carrier containing a sulfur-loading component in the absence of hydrogen to perform desulfurization reaction. It modifies the one-step desulfurization reaction under hydrogen conditions in the prior art into two separate steps: non-hydrogen desulfurization and hydrogen-condition sulfur transfer reaction, avoiding the problem of hydrogenation saturation of olefins in the feedstock during desulfurization reaction under hydrogen conditions, thereby avoiding loss of olefins.

The desulfurization adsorbent after desulfurization reaction in the absence of hydrogen contacts hydrogen to perform a sulfur transfer reaction, releasing the metal active center, at least partially restoring the desulfurization activity of the desulfurization adsorbent,

increasing the sulfur-holding capacity of the desulfurization adsorbent, so that this at least partially activity-restored desulfurization adsorbent can be partially recycled back to the desulfurization reactor, and reducing the intensity of sulfur burning regeneration of the desulfurization adsorbent in the regenerator.

When applying the method of the present invention to desulfurization of light fractions of catalytic gasoline, it can avoid octane number loss caused by existing hydrodesulfurization processes; when applying the method of the present invention to desulfurization of liquefied petroleum gas, it can avoid loss of unsaturated olefins due to hydrogenation saturation during hydrodesulfurization, which is beneficial for improving the quality of hydrocarbon oil. Compared with traditional alkali washing desulfurization, the desulfurization method of the present invention avoids the problem of alkali liquor discharge and offers higher desulfurization depth.

In the context of the present invention, "at least a portion" means part or all. For example, in one specific embodiment of the present invention, all of the at least partially activity-restored desulfurization adsorbent may be returned to the desulfurization reactor of step (1) to continue the desulfurization reaction; in another specific embodiment of the present invention, a portion of the at least partially activity-restored desulfurization adsorbent may be returned to step (1) to perform desulfurization reaction, and the remaining portion of the at least partially activity-restored desulfurization adsorbent may be subjected to oxygen-containing regeneration and reduction in sequence before returning to the desulfurization reactor in step (1).

In the context of the present invention, "at least partially activity-restored desulfurization adsorbent" refers to a desulfurization adsorbent whose metal active component has restored its desulfurization activity. Contacting the spent desulfurization adsorbent with a hydrogen donor to perform a sulfur transfer reaction achieves transfer of sulfur from the metal active component to the sulfur-loading component under hydrogen conditions, releasing the metal active center, and restoring at least part of the desulfurization activity of this desulfurization adsorbent. Therefore, the spent desulfurization adsorbent after the sulfur transfer reaction can be recycled back to the desulfurization reactor to continue participating in desulfurization reaction, significantly increasing the sulfur-holding capacity of the desulfurization adsorbent, notably extending the time the desulfurization adsorbent can be used for desulfurization reaction, reducing the frequency of sulfur and carbon burning regeneration of the desulfurization adsorbent, and thereby reducing loss of the desulfurization adsorbent during the regeneration process.

Preferably, conditions for performing the selective desulfurization reaction in the desulfurization reactor allow the reactor to operate as a fluidized bed; preferably, the reaction conditions include: a temperature of 150-550°C, preferably 200-450°C, for example, 250°C, 300°C, 350°C, or 400°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa, for example 2.0 MPa, 2.5 MPa, 3.0 MPa, or 3.5 MPa; a weight hourly space

velocity of the hydrocarbon oil containing sulfides and olefins of 0.1-30 h⁻¹, preferably 1-20 h⁻¹, for example 2 h⁻¹, 4 h⁻¹, 6 h⁻¹, 8 h⁻¹, 10 h⁻¹, 12 h⁻¹, 14 h⁻¹, 16 h⁻¹, or 18 h⁻¹. Under the above reaction conditions, the catalytic efficiency for the contact desulfurization reaction between the hydrocarbon oil containing sulfides and olefins and the desulfurization adsorbent is higher. Preferably, the flow rate of the hydrocarbon oil allows the desulfurization reactor to operate in a fluidized bed mode.

In the present invention, the hydrocarbon oil containing sulfides and olefins contains C2-C7 olefins and sulfides, wherein at least a portion, preferably all, of the sulfides in the hydrocarbon oil are not thiophene-type sulfides. the sulfides mainly include hydrogen sulfide, mercaptans, thioethers, disulfides, or a mixture of one or more thereof.

Wherein, the sulfur content in the hydrocarbon oil containing sulfides and olefins is 10 µg/g or above, preferably 15-5000 µg/g, more preferably 20-45000 µg/g; the mass percentage content of olefins is 2-100%; preferably, the sulfur content in the hydrocarbon oil containing sulfides and olefins is 30-3000 µg/g, and the mass percentage content of olefins is 5-85%.

Said hydrocarbon oil containing sulfides and olefins can be those coming from any source. Preferably, the hydrocarbon oil containing sulfides and olefins is one or more selected from dry gas, liquefied petroleum gas, and catalytic gasoline; preferably, the hydrocarbon oil containing sulfides and olefins is one or more selected from catalytic cracking dry gas, catalytic cracking liquefied petroleum gas, dry gas from deep catalytic cracking, liquefied petroleum gas from deep catalytic cracking, ethylene and/or propylene products from steam cracking, or one or more selected from light fractions of C7 and below from catalytic cracking gasoline, catalytic pyrolysis gasoline, and steam pyrolysis gasoline.

The sulfur transfer reaction performed in the sulfur transfer reactor involves reaction between the metal sulfide, the hydrogen donor, and the sulfur-loading component; preferably, the conditions for performing the reaction in this reactor allow the reactor to operate as a fluidized bed; preferably, conditions for the sulfur transfer reaction include: a temperature of 300-550°C, preferably 350-450°C, for example, 370°C, 400°C, or 420°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa, for example 2.0 MPa, 2.5 MPa, 3.0 MPa, or 3.5 MPa. The hydrogen donor may be one or more selected from hydrogen, a mixed gas containing hydrogen, and a precursor compound capable of producing hydrogen; the mixed gas containing hydrogen has a hydrogen volume fraction of 10-99%, preferably 30-90%, for example 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, or 85%; the precursor compound capable of producing hydrogen is one or more selected from cyclohexane, methylcyclohexane, tetralin, and decalin; the volume ratio of hydrogen in the hydrogen donor to the spent desulfurization adsorbent is (10-3000):1, preferably 50-2000:1, for example 100:1, 200:1, 300:1, 400:1, 500:1, 600:1, 700:1, 800:1, 900:1, 1000:1, 1100:1, 1200:1, 1300:1, or 1400:1.

The at least partially activity-restored desulfurization adsorbent obtained from the sulfur transfer reaction in the sulfur transfer reactor has a sulfur content of 0.5-12%, preferably 0.6-8%, for example 2%, 3%, 4%, 5%, 6%, or 7%.

To further restore the activity of the at least partially activity-restored desulfurization adsorbent, the method for treating hydrocarbon oil according to the present invention further comprises: subjecting a remaining portion of the at least partially activity-restored desulfurization adsorbent to oxygen-containing coke burning regeneration, obtaining regenerated desulfurization adsorbent, subjecting the regenerated desulfurization adsorbent to reduction treatment in a reducing gas atmosphere to obtain reduced desulfurization adsorbent, then returning the reduced desulfurization adsorbent to the desulfurization reactor of step (1).

According to a specific embodiment, the at least partially activity-restored desulfurization adsorbent may also undergo oxygen-containing coke burning regeneration with an oxygen-containing gas to burn off sulfur and carbon adsorbed on the desulfurization adsorbent to obtain fully regenerated desulfurization adsorbent, then subjecting the regenerated desulfurization adsorbent to reduction under hydrogen conditions, and returning The regenerated reduced desulfurization adsorbent to the desulfurization reactor to contact the hydrocarbon oil containing sulfides and olefins to perform desulfurization reaction.

According to a specific embodiment, the oxygen-containing coke burning performed in the regenerator is conducted in the presence of an oxygen-containing gas, wherein the oxygen-containing gas has an oxygen volume fraction of 5-50 vol%, preferably 10-45 vol%; the oxygen-containing gas is one selected from air, a mixture of oxygen and nitrogen, a mixture of air and nitrogen; preferably, reaction conditions for the oxygen-containing coke burning include: a temperature of 300-800°C, preferably 350-600°C; a pressure of 0.1-3.0 MPa, preferably 0.1-1.0 MPa. The flue gas discharged from the top of the regenerator mainly contains carbon dioxide, sulfur oxides, etc., and needs to be treated to meet environmental protection requirements before being discharged into the atmosphere.

According to a specific embodiment, conditions for the reduction treatment of the regenerated desulfurization adsorbent include: a temperature of 300-550°C, preferably 350-450°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa; sulfur content of the reduced desulfurization adsorbent is 0.3-10%, preferably 0.3-6%; the volume ratio of hydrogen in the reducing gas to the regenerated desulfurization adsorbent is (10-3000):1, preferably (50-2000):1; the reducing gas is one or more selected from hydrogen, a mixed gas containing hydrogen, and a precursor compound capable of producing hydrogen; the mixed gas containing hydrogen has a hydrogen volume fraction of 10-99%, preferably 30-90%; the precursor compound capable of producing hydrogen may be one or more selected from cyclohexane, methylcyclohexane, tetralin, and decalin.

According to a specific embodiment, the desulfurization adsorbent comprises a metal active component and a carrier containing a sulfur-loading component, wherein the sulfur-loading component is selected from zinc oxide; based on the weight of the carrier, the carrier comprises 20-85 wt% of zinc oxide, 10-75 wt% of alumina, and 5-70 wt% of silica, preferably 25-75 wt% of zinc oxide, 15-65 wt% of alumina, and 10-60 wt% of silica; based on the total weight of the desulfurization adsorbent, the content of the metal active component is 2-30 wt%, preferably 10-25 wt%, for example 15 wt% or 20 wt%; the metal active component is one or more selected from cobalt, nickel, iron, manganese, copper, molybdenum, tungsten, silver, tin, and vanadium, preferably one or more of cobalt, nickel, molybdenum.

The desulfurization adsorbent of the present invention can be prepared according to general methods known in the art, wherein the carrier is prepared by slurring and mixing zinc oxide, alumina, and silica, followed by shaping, drying, and calcination. The metal active component is loaded onto the carrier by impregnation, spraying, etc., then dried, calcined, and reduced with hydrogen before use, to obtain the above desulfurization adsorbent for desulfurization reaction.

In the present invention, the desulfurization adsorbent can be in any shape such as microspheres, ellipsoids, strips, tablets, rings, etc. The specific shape can be determined based on the type of desulfurization reactor, preferably microsphere shape.

In the present invention, the type of desulfurization reactor can be fluidized bed, moving bed, etc. The specific type can be determined based on the properties of the hydrocarbon oil to be treated and operational economics; preferably, it is a fluidized bed type reactor.

A second aspect of the present invention provides a system for treating hydrocarbon oil, wherein the system comprises a non-hydrogen desulfurization reactor 2, a hydrogen-condition sulfur transfer reactor 7, wherein a bottom of the non-hydrogen desulfurization reactor 2 is provided with a hydrocarbon oil inlet for feeding the hydrocarbon oil, a lower part is provided with a desulfurization adsorbent inlet, a top is provided with a desulfurized oil-gas outlet, and an upper part is provided with a spent desulfurization adsorbent outlet; a bottom of the hydrogen-condition sulfur transfer reactor 7 is provided with a hydrogen donor inlet, a lower part is provided with a spent desulfurization adsorbent inlet and a regenerated desulfurization adsorbent inlet, an upper part is provided with an outlet for at least partially activity-restored desulfurization adsorbent, and a top is provided with a gas outlet; the spent desulfurization adsorbent outlet of the non-hydrogen desulfurization reactor (2) is connected to the spent desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7) via a pipeline, and the activity-restored desulfurization adsorbent outlet of the hydrogen-condition sulfur transfer reactor (7) is connected to the desulfurization adsorbent inlet of the non-hydrogen desulfurization reactor (2) via a pipeline; wherein the pipelines (6, 20) are provided with a device for respectively

forcing the spent desulfurization adsorbent and the at least partially activity-restored desulfurization adsorbent into the hydrogen-condition sulfur transfer reactor (7) and the non-hydrogen desulfurization reactor (2) and/or a device for preventing gas from flowing between the non-hydrogen desulfurization reactor (2) and the hydrogen-condition sulfur transfer reactor (7) (not shown).

According to a preferred embodiment, as shown in FIG. 1, the system according to the present invention comprises a non-hydrogen desulfurization reactor 2, a hydrogen-condition sulfur transfer reactor 7, a first receiver 5, and a second receiver 19, wherein a bottom of the non-hydrogen desulfurization reactor 2 is provided with a hydrocarbon oil inlet for feeding the hydrocarbon oil, a lower part is provided with a desulfurization adsorbent inlet, a top is provided with a desulfurized oil-gas outlet, and an upper part is provided with a spent desulfurization adsorbent outlet; a bottom of the hydrogen-condition sulfur transfer reactor 7 is provided with a hydrogen donor inlet, a lower part is provided with a spent desulfurization adsorbent inlet and a regenerated desulfurization adsorbent inlet, an upper part is provided with an outlet for at least partially activity-restored desulfurization adsorbent, and a top is provided with a gas outlet; the first receiver 5 has a first material inlet and a first material outlet, and the second receiver 19 has a second material inlet and a second material outlet; wherein the spent desulfurization adsorbent outlet of the non-hydrogen desulfurization reactor 2 is connected to the first material inlet of the first receiver 5, the first material outlet of the first receiver 5 is connected to the spent desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor 7 via pipeline 6; and the activity-restored desulfurization adsorbent outlet of the hydrogen-condition sulfur transfer reactor 7 is connected to the second material inlet of the second receiver 19, the second material outlet of the second receiver 19 is switchably connected to the desulfurization adsorbent inlet of the non-hydrogen desulfurization reactor 2 via pipeline 20; wherein the pipelines (6, 20) are provided with a device for respectively forcing the spent desulfurization adsorbent and the at least partially activity-restored desulfurization adsorbent into the non-hydrogen desulfurization reactor (2) and the hydrogen-condition sulfur transfer reactor (7) and/or a device for preventing gas from flowing between the non-hydrogen desulfurization reactor (2) and the hydrogen-condition sulfur transfer reactor (7) (not shown).

According to a specific embodiment, the method for treating hydrocarbon oil according to the present invention in the system shown in FIG. 1 can be implemented as follows: preheated hydrocarbon oil containing sulfides and olefins in gaseous form enters the non-hydrogen desulfurization reactor 2 via hydrocarbon oil inlet 1 at the bottom of the non-hydrogen desulfurization reactor 2, flows upward through reactor 2, and contacts with desulfurization adsorbent A in fluidized bed form, to perform desulfurization reaction in the absence of hydrogen, obtaining desulfurized hydrocarbon oil-gas and spent desulfurization adsorbent with reduced activity. The desulfurized hydrocarbon oil-gas and the spent desulfurization adsorbent are separated at the top of reactor 2, then the desulfurized hydrocarbon oil-gas is sent via desulfurized hydrocarbon oil-gas outlet

3 to a stabilization system to perform subsequent treatment. The spent desulfurization adsorbent is sent to the first receiver 5 via spent desulfurization adsorbent outlet 4, then conveyed to the hydrogen-condition sulfur transfer reactor 7 via pipeline 6, where it is contacted with hydrogen entering from the bottom of the hydrogen-condition sulfur transfer reactor 7 via hydrogen inlet 8 to perform a sulfur transfer reaction, obtaining at least partially activity-restored desulfurization adsorbent B and hydrogen-containing gas. The hydrogen-containing gas is sent via circulating hydrogen outlet 9 to a hydrogen circulation system. The at least partially activity-restored desulfurization adsorbent B enters the second receiver 19 via activity-restored desulfurization adsorbent outlet 18. Then, all of the at least partially activity-restored desulfurization adsorbent B is returned to the non-hydrogen desulfurization reactor 2 via pipeline 20 to continue participating in the desulfurization reaction.

According to a preferred embodiment, as shown in FIG. 2, the system for treating hydrocarbon oil of the present invention further comprises a lock hopper 11 and a regenerator 14; wherein a bottom of the regenerator 14 is provided with an oxygen-containing gas inlet, a lower part is provided with a regenerated desulfurization adsorbent outlet, an upper part is provided with a desulfurization adsorbent inlet, and a top is provided with a flue gas outlet; lock hopper 11 has a third material inlet, a third material outlet, and a regenerated desulfurization adsorbent inlet; the second material outlet of the second receiver 19 is further switchably connected to the third material inlet of lock hopper 11, the third material outlet of lock hopper 11 is switchably connected to the desulfurization adsorbent inlet of the regenerator 14, the regenerated desulfurization adsorbent outlet of the regenerator 14 is connected to the regenerated desulfurization adsorbent inlet of lock hopper 11, and the third material outlet of lock hopper 11 is further switchably connected to the regenerated desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor 7.

According to a specific embodiment, the method for treating hydrocarbon oil according to the present invention can be implemented in the above system according to the present invention as follows: as shown in FIG. 2, preheated hydrocarbon oil containing sulfides and olefins in gaseous form enters the non-hydrogen desulfurization reactor 2 via hydrocarbon oil inlet 1 at the bottom of the non-hydrogen desulfurization reactor 2, flows upward through the non-hydrogen desulfurization reactor 2, and contacts desulfurization adsorbent A in fluidized bed form to perform desulfurization reaction in the absence of hydrogen and to obtain desulfurized hydrocarbon oil-gas and spent desulfurization adsorbent with reduced activity. The desulfurized hydrocarbon oil-gas and the spent desulfurization adsorbent are separated at the top of reactor 2, then the desulfurized hydrocarbon oil-gas is sent via outlet 3 to a stabilization system to perform subsequent treatment. The spent desulfurization adsorbent is sent via spent desulfurization adsorbent outlet 4 to the first receiver 5, then conveyed via pipeline 6 to the hydrogen-condition sulfur transfer reactor 7, where it is contacted with hydrogen entering from the bottom of the hydrogen-condition sulfur transfer reactor 7 via hydrogen inlet 8 to perform sulfur transfer reaction, obtaining at least partially activity-

restored desulfurization adsorbent B and hydrogen-containing gas. The hydrogen-containing gas is sent via circulating hydrogen outlet 9 to a hydrogen circulation system. The at least partially activity-restored desulfurization adsorbent B enters the second receiver 19 via activity-restored desulfurization adsorbent outlet 18. Then, a portion of the at least partially activity-restored desulfurization adsorbent B is returned via pipeline 20 to the non-hydrogen desulfurization reactor 2 to continue participating in the desulfurization reaction.

The remaining portion of desulfurization adsorbent B is conveyed via pipeline 10 to lock hopper 11 to adjust pressure and change the hydrogen atmosphere to nitrogen atmosphere, then conveyed via pipeline 13 to the regenerator 14, where it contacts an oxygen-containing gas entering from the bottom of the regenerator 14 via gas inlet 15 to perform an oxygen-containing coke burning reaction to burn off sulfur and carbon loaded on desulfurization adsorbent B, obtaining desulfurization regenerated adsorbent with deeply restored activity. The regenerated desulfurization adsorbent is sent via pipeline 17 to lock hopper 11 to adjust pressure and change the oxygen atmosphere to hydrogen atmosphere, then conveyed via pipeline 12 to the hydrogen-condition sulfur transfer reactor 7, where it is contacted with hydrogen in hydrogen-condition sulfur transfer reactor 7 to perform reduction, to obtain reduced desulfurization adsorbent. The reduced desulfurization adsorbent enters the second receiver 19 via activity-restored desulfurization adsorbent outlet 18, then returns via pipeline 20 to the non-hydrogen desulfurization reactor 2 to continue participating in the reaction.

In the above method, the sulfur transfer reaction of the spent desulfurization adsorbent in reactor 7 and the reduction reaction of the regenerated desulfurization adsorbent in reactor 7 are preferably operated in a continuous manner.

FIG. 1 and FIG. 2 only schematically show the composition and connection mode of the system for treating hydrocarbon oil according to two preferred embodiments of the present invention. It should be noted that the systems shown in the figures can be used to implement a method for treating hydrocarbon oil according to the present invention, which does not mean that the method according to the present invention cannot be implemented using other systems or devices.

Examples

The technical solution of the present invention is further illustrated by the following examples. Raw materials used in the examples and comparative examples can be obtained through commercial channels or prepared by conventional techniques in the art. Wherein, liquefied petroleum gas feedstock A used in the examples and comparative examples comes from the 2 million tons/year catalytic cracking unit of Sinopec Cangzhou Refining & Chemical Co., Ltd. (Cangzhou LPG), and liquefied petroleum gas feedstock B comes from the 3 million tons/year catalytic cracking unit of Sinopec Shijiazhuang Refining & Chemical Co., Ltd. (Shijiazhuang LPG). The

compositions of liquefied petroleum gas feedstock A and liquefied petroleum gas feedstock B are shown in Table 1-1, and the compositions of sulfides in liquefied petroleum gas feedstock A and liquefied petroleum gas feedstock B are shown in Table 1-2. Measurements conducted in the examples are implemented according to the most conventional methods in the art, for example, metal sulfides on the adsorbent surface are measured by X-ray photoelectron spectroscopy (XPS).

The preparation of desulfurization adsorbents used in the examples of the present invention and comparative examples is implemented in Examples 1-4.

Table 1-1. Composition of liquefied petroleum gas feedstock

	liquefied petroleum gas feedstock A	liquefied petroleum gas feedstock B
Composition (vol%)		
propane	8.71	18.75
propylene	28.97	28.82
iso-butane	27.32	20.58
n-butane	6.88	12.89
trans-butene	7.94	5.12
n-butene	7.32	5.3
iso-butene	6.33	5.03
cis-butene	6.46	3.47
1,3-butadiene	0.05	0.040
Total sulfur (mg/m ³)	192.18	906.79

Table 1-2. Composition of Sulfides in Liquefied Petroleum Gas Feedstock

liquefied petroleum gas feedstock A		liquefied petroleum gas feedstock B	
Sulfides (mg/m ³)	content	Sulfides (mg/m ³)	content
Methanethiol	153.79	Hydrogen sulfide	0.89
Ethanethiol	3.87	Carbonyl sulfide	23.33
Isopropyl methyl sulfide	0.24	Methanethiol	641.95
Dimethyl disulfide	24.27	Ethanethiol	92.02
n-Butylmethyl sulfide	1.19	Dimethyl sulfide	0.69
Isopropyl propyl sulfide	0.64	Methyl ethyl sulfide	0.44

Diallyl sulfide	0.96	sec-Butylthiol	0.75
Diethyl disulfide	2.38	Isopropyl methyl sulfide	1.61
Dimethyl trisulfide	1.56	Isobutylthiol	0.21
Other unknown sulfides	3.28	Dimethyl disulfide	101.76
P (S) / (mg/m ³)	192.18	Methyl ethyl disulfide	9.18
		Diethyl disulfide	0.53
		Dimethyl trisulfide	27.39
		Methyl ethyl trisulfide	3.45
		Diethyl trisulfide	0.39
		Other unknown sulfides	1.76
		P (S) / (mg/m ³)	906.79

The following Examples 1-4 illustrate the preparation of desulfurization adsorbents according to conventional methods in the art:

Example 1

40g of perlite and 200g of zinc oxide were mixed and ground for 30 minutes to obtain mixture A1. Then, 100g of dispersed aluminum sol, 230g of deionized water, and 120g of 5% dilute nitric acid were mixed with mixture A1 to obtain mixture A2. After stirring uniformly, a CCX130AT spray drying system was used to obtain carrier A3 with an average particle size of 60-80 μm . Carrier A3 was calcined at 650°C for 90 minutes. 93.24g of nickel nitrate hexahydrate was mixed with 110g of deionized water and dissolved, to obtain an impregnation solution. 100g of the above carrier A3 was impregnated with this impregnation solution. The obtained product was dried at 120°C for 60 minutes, then calcined at 650°C for 90 minutes to obtain desulfurization adsorbent **a**.

Example 2

40g of perlite and 200g of zinc oxide were mixed and ground for 30 minutes to obtain mixture A1; then, 100g of dispersed aluminum sol, 230g of deionized water, and 120g of 5% dilute nitric acid were mixed with mixture A1 to obtain mixture A2. After stirring uniformly, a CCX130AT spray drying system was used to obtain carrier A3 with an average particle size of 60-80 μm . Carrier A3 was calcined at 650°C for 90 minutes. 93.24g of nickel nitrate hexahydrate and 12.8g of copper nitrate trihydrate were mixed with 110g of deionized water and dissolved, to obtain an impregnation solution. The above carrier A3 was impregnated with this impregnation solution. The obtained product was dried at 120°C for 60 minutes, then calcined at 650°C for 90 minutes to

obtain desulfurization adsorbent **b**.

Example 3

This example was operated in the same manner as Example 1, except that the impregnation solution used was a mixture of 57.54g of cobalt nitrate and 110g of deionized water. Desulfurization adsorbent **c** was obtained.

Example 4

This example was operated in the same manner as Example 1, except that the impregnation solution used was a mixture of 73.50g of molybdenum nitrate and 110g of deionized water. Desulfurization adsorbent **d** was obtained.

The following Examples 5-10 are used to illustrate desulfurization treatment on liquefied petroleum gas feedstocks in the absence of hydrogen by using the desulfurization adsorbent of the present invention. Before implementing the following examples and comparative examples, the above desulfurization adsorbents were reduced under a hydrogen atmosphere by using techniques known to those skilled in the art.

Example 5

This example performed desulfurization treatment on liquefied petroleum gas feedstock A in the absence of hydrogen, specifically comprising the following steps:

(1) 800g of desulfurization adsorbent **a** and liquefied petroleum gas feedstock A were subjected to desulfurization reaction in a medium-scale unit fluidized bed desulfurization reactor 2, with reaction pressure of 1.5 MPa, reaction temperature of 350°C, liquefied petroleum gas feed rate of 4 kg/h. The reaction was conducted for 1 hour, obtaining desulfurized liquefied petroleum gas and spent desulfurization adsorbent. The desulfurized liquefied petroleum gas was discharged from desulfurized liquefied petroleum gas outlet 3; its sulfur content and hydrocarbon component content were measured by chromatography (results are shown in Table 2). Spent desulfurization adsorbent was discharged from the reactor, and the metal sulfide content of spent desulfurization adsorbent was measured. Sampling analysis showed that more than 15% of nickel in the spent desulfurization adsorbent was converted to nickel sulfide, and trace amount of zinc sulfide was contained (less than 0.01% of the surface zinc oxide was converted to zinc sulfide relative to the total weight of surface zinc oxide).

Example 6

This example performed a desulfurization treatment on the liquefied petroleum gas feedstock A in the absence of hydrogen and the sulfur transfer and oxidative regeneration of the spent desulfurization adsorbent under hydrogen conditions,

specifically comprising the following steps:

(1) 800g of desulfurization adsorbent a and liquefied petroleum gas feedstock A were subjected to desulfurization reaction in a medium-scale unit fluidized bed desulfurization reactor 2, with reaction pressure of 1.5 MPa, reaction temperature of 350°C, liquefied petroleum gas feed rate of 4 kg/h. The reaction was conducted for 1 hour, obtaining desulfurized liquefied petroleum gas and spent desulfurization adsorbent. The desulfurized liquefied petroleum gas was discharged from desulfurized liquefied petroleum gas outlet 3, its sulfur content and hydrocarbon component content were measured by chromatography (results are shown in Table 2). The content of metal sulfides in the spent desulfurization adsorbent was measured by sampling. The analysis and calculation showed that more than 10% of nickel on the surface of the spent desulfurization adsorbent was converted to nickel sulfide, and trace amount of zinc sulfide was contained (less than 0.01% of the surface zinc oxide was converted to zinc sulfide relative to the total weight of surface zinc oxide).

(2) The spent desulfurization adsorbent was transferred from spent desulfurization adsorbent outlet 4 at a rate of 10 g/min via the first receiver 5 and pipeline 6 to a medium-scale unit fluidized bed sulfur transfer reactor 7, where it was contacted with hydrogen to perform sulfur transfer reaction at a temperature of 350°C, a pressure of 1.5 MPa, a volume ratio of hydrogen to spent adsorbent in the reactor of 500, and average sulfur transfer reaction time of about 0.5 h, to obtain at least partially activity-restored desulfurization adsorbent. By sampling, analysis and calculation showed that nickel sulfide on the surface of the at least partially activity-restored desulfurization adsorbent was almost completely reduced to nickel, while over 1% of zinc oxide on the desulfurization adsorbent surface was converted to zinc sulfide.

(3) A portion of the at least partially activity-restored desulfurization adsorbent was sent from activity-restored desulfurization adsorbent outlet 18 to the fluidized bed desulfurization reactor 2 via the second receiver 19 and pipeline 20 to continue the desulfurization reaction. The proportion of this portion of at least partially activity-restored desulfurization adsorbent fed to the fluidized bed desulfurization reactor 2 was 90% of the total desulfurization adsorbent circulation amount.

(4) The remaining portion of the at least partially activity-restored desulfurization adsorbent was sent to regenerator 14 via pipeline 10, lock hopper 11, and pipeline 13 to be contacted with air to perform regeneration, obtaining regenerated desulfurization adsorbent, wherein the regeneration temperature was 500°C and the pressure was an atmospheric pressure. The proportion of this portion of at least partially activity-restored desulfurization adsorbent sent to the fluidized bed regenerator was 10% of the total desulfurization adsorbent circulation amount.

(5) The regenerated desulfurization adsorbent was sent via pipeline 17, lock hopper 11, and pipeline 12 to the fluidized bed sulfur transfer reactor 7 of step (1), where it was contacted with hydrogen to perform reduction treatment. The regenerated reduced desulfurization adsorbent, together with a portion of the at least partially activity-restored desulfurization adsorbent obtained in step (3), was returned to step (1) to continue the desulfurization reaction in the absence of hydrogen. Product properties are shown in Table 2.

Example 7

This example performed desulfurization treatment on liquefied petroleum gas feedstock B in the absence of hydrogen and performed sulfur transfer and oxidative regeneration of the spent desulfurization adsorbent under hydrogen conditions, specifically comprising the following steps:

- (1) 800g of desulfurization adsorbent b and liquefied petroleum gas feedstock B were subjected to desulfurization reaction in a medium-scale unit fluidized bed desulfurization reactor 2, with reaction pressure of 1.5 MPa, reaction temperature of 430°C, liquefied petroleum gas feed rate of 2 kg/h, obtaining desulfurized liquefied petroleum gas and spent desulfurization adsorbent. The desulfurized liquefied petroleum gas was discharged from the desulfurized hydrocarbon oil-gas outlet 3, and the sulfur content and hydrocarbon component content in the desulfurized liquefied petroleum gas were measured by chromatography (results are shown in Table 2). The metal sulfide content in the spent desulfurization adsorbent was measured. Sampling analysis and calculation showed that more than 6% of nickel and more than 5% of copper on the surface of the spent desulfurization adsorbent were converted to nickel sulfide and copper sulfide, respectively, and trace amount of zinc sulfide was contained.
- (2) The spent desulfurization adsorbent was transferred from the spent desulfurization adsorbent outlet 4 at a rate of 40 g/min via a first receiver 5 and pipeline 6 to a medium-scale unit fluidized bed sulfur transfer reactor 7, where it was contacted with hydrogen to conduct a sulfur transfer reaction, to obtain at least partially activity-restored desulfurization adsorbent, wherein the sulfur transfer reaction temperature was 400°C, the pressure was 1.5 MPa, the volume ratio of hydrogen to spent desulfurization adsorbent in the reactor was 300, and the average sulfur transfer reaction time was about 2.0 h. Sampling analysis of this at least partially activity-restored desulfurization adsorbent and calculation showed that the nickel sulfide in the at least partially activity-restored desulfurization adsorbent was almost completely reduced to nickel, the copper sulfide was almost completely reduced to copper, and meanwhile more than 0.6% of zinc oxide on the surface of the desulfurization adsorbent was converted to zinc sulfide;
- (3) a portion of the at least partially activity-restored desulfurization adsorbent was sent from the activity-restored desulfurization adsorbent outlet 18 to the fluidized bed desulfurization reactor 2 via a second receiver 19 and pipeline 20 to continue the desulfurization reaction, wherein the proportion of this portion of at least partially activity-restored desulfurization adsorbent sent to the fluidized bed desulfurization reactor 2 accounts for 80% of the total desulfurization adsorbent circulation amount;
- (4) The remaining portion of the at least partially activity-restored desulfurization adsorbent was sent into a regenerator 14 via pipeline 10, a lock hopper 11, and pipeline 13 to be contacted with air to conduct regeneration, obtaining regenerated desulfurization adsorbent, wherein the temperature for performing the regeneration was 500°C, and the pressure was atmospheric pressure. The proportion of this portion of at

least partially activity-restored desulfurization adsorbent sent to the fluidized bed regenerator was 20% of the total desulfurization adsorbent circulation amount;

(5) The regenerated desulfurization adsorbent was sent via pipeline 17, lock hopper 11, and pipeline 12 into the fluidized bed sulfur transfer reactor 7 of step (1), where it was contacted with hydrogen to perform reduction treatment. The regenerated desulfurization adsorbent after the reduction, together with a portion of the at least partially activity-restored desulfurization adsorbent obtained in step (3), was returned to step (1) to continue the desulfurization reaction under non-hydrogenation conditions. The properties of product are shown in Table 2.

Example 8

This example performed desulfurization treatment on liquefied petroleum gas feedstock B under non-hydrogenation conditions and performed sulfur transfer and oxidation regeneration of the spent desulfurization adsorbent under hydrogenation conditions, specifically comprising the following steps:

(1) 800 g of desulfurization adsorbent c and liquefied petroleum gas feedstock B were subjected to a desulfurization reaction in a medium-scale unit fluidized bed desulfurization reactor, to obtain desulfurized liquefied petroleum gas and spent desulfurization adsorbent, wherein the reaction pressure was 2.5 MPa, the reaction temperature was 430°C, and the liquefied petroleum gas feed rate was 2 kg/h. The

desulfurized liquefied petroleum gas was discharged from the desulfurized hydrocarbon oil-gas outlet 3, and the sulfur content and hydrocarbon component content therein were measured by chromatography (results are shown in Table 2). The metal sulfide content in the spent desulfurization adsorbent was measured. Sampling analysis and calculation showed that more than 6% of cobalt on the surface of the spent desulfurization adsorbent was converted to cobalt sulfide and trace amount of zinc sulfide was contained;

(2) The spent desulfurization adsorbent was transferred from the spent desulfurization adsorbent outlet 4 at a rate of 30 g/min via the first receiver 5 and pipeline 6 to a medium-scale unit fluidized bed sulfur transfer reactor 7, where it was contacted with hydrogen to perform sulfur transfer reaction, wherein the sulfur transfer reaction temperature was 410°C, the pressure was 2.5 MPa, the volume ratio of hydrogen to

spent desulfurization adsorbent in the reactor was 500, and the average sulfur transfer reaction time was about 0.5 h, to obtain at least partially activity-restored desulfurization adsorbent. Sampling analysis and calculation showed that the cobalt sulfide in the at least partially activity-restored desulfurization adsorbent was almost completely reduced to cobalt, and meanwhile more than 0.6% of zinc oxide on the surface of the desulfurization adsorbent was converted to zinc sulfide;

(3) a portion of the at least partially activity-restored desulfurization adsorbent was sent from the activity-restored desulfurization adsorbent outlet 18 via the second receiver 19 and pipeline 20 to the fluidized bed desulfurization reactor to continue the desulfurization reaction, wherein the proportion of this portion of at least partially

activity-restored desulfurization adsorbent sent to the fluidized bed desulfurization reactor 2 accounts for 70% of the total desulfurization adsorbent circulation amount;

(4) the remaining portion of the at least partially activity-restored desulfurization adsorbent was sent via pipeline 10, lock hopper 11, and pipeline 13 into a regenerator 14 to be contacted with air to perform regeneration, obtaining regenerated desulfurization adsorbent, wherein the temperature for performing this regeneration was 500°C, and the pressure was atmospheric pressure. The proportion of this portion of at least partially activity-restored desulfurization adsorbent sent to the fluidized bed regenerator was 30% of the total desulfurization adsorbent circulation amount;

(5) the regenerated desulfurization adsorbent was sent via pipeline 17, lock hopper 11, and pipeline 12 into the fluidized bed sulfur transfer reactor 7 of step (1), where it was contacted with hydrogen to perform reduction treatment. The regenerated reduced desulfurization adsorbent, together with a portion of the at least partially activity-restored desulfurization adsorbent obtained in step (3), was returned to step (1) to continue the desulfurization reaction under non-hydrogenation conditions. The properties of product are shown in Table 2.

Example 9

This example performed desulfurization treatment on liquefied petroleum gas feedstock A under non-hydrogenation conditions and performed sulfur transfer and oxidation regeneration of the spent desulfurization adsorbent under hydrogenation conditions, specifically comprising the following steps:

(1) 800 g of desulfurization adsorbent d and liquefied petroleum gas feedstock A were subjected to a desulfurization reaction in a medium-scale unit fluidized bed desulfurization reactor, wherein the reaction pressure was 2.5 MPa, the reaction temperature was 400°C, and the liquefied petroleum gas feed rate was 3 kg/h, to obtain

desulfurized liquefied petroleum gas and spent desulfurization adsorbent. The desulfurized liquefied petroleum gas was discharged from the desulfurized hydrocarbon oil-gas outlet 3, and the sulfur content and hydrocarbon component content therein were measured by chromatography (results are shown in Table 2). The metal sulfide content in the spent desulfurization adsorbent was measured. Sampling analysis and calculation showed that more than 9% of molybdenum on the surface of the spent desulfurization adsorbent was converted to molybdenum sulfide and trace amount of zinc sulfide was contained;

(2) The spent desulfurization adsorbent was transferred from the spent desulfurization adsorbent outlet 4 at a rate of 5 g/min via the first receiver 5 and pipeline 6 to a medium-scale unit fluidized bed sulfur transfer reactor 7, where it was contacted with hydrogen to perform sulfur transfer reaction, to obtain at least partially activity-restored desulfurization adsorbent, wherein the sulfur transfer reaction temperature was 430°C, the pressure was 2.5 MPa, the volume ratio of hydrogen to spent desulfurization adsorbent in the reactor was 500, and the average sulfur transfer reaction time was about

0.5 h. Sampling analysis and calculation showed that the molybdenum sulfide in the at least partially activity-restored desulfurization adsorbent was almost completely reduced to molybdenum, and meanwhile more than 0.8% of zinc oxide on the surface of the desulfurization adsorbent was converted to zinc sulfide;

(3) a portion of the at least partially activity-restored desulfurization adsorbent was sent from the activity-restored desulfurization adsorbent outlet 18 via the second receiver 19 and pipeline 20 to the fluidized bed desulfurization reactor to continue the desulfurization reaction, wherein the proportion of this portion of at least partially activity-restored desulfurization adsorbent sent to the fluidized bed desulfurization reactor 2 accounts for 50% of the total desulfurization adsorbent circulation amount;

(4) The remaining portion of the at least partially activity-restored desulfurization adsorbent was sent via pipeline 10, lock hopper 11, and pipeline 13 into a regenerator 14 to be contacted with air to perform regeneration, obtaining regenerated desulfurization adsorbent; wherein the temperature for performing this regeneration was 500°C, and the pressure was atmospheric pressure. The proportion of this portion

of at least partially activity-restored desulfurization adsorbent sent to the fluidized bed regenerator was 50% of the total desulfurization adsorbent circulation amount;

(5) the regenerated desulfurization adsorbent was sent via pipeline 17, lock hopper 11, and pipeline 12 into the fluidized bed sulfur transfer reactor 7 of step (1), where it was contacted with hydrogen to perform reduction treatment. The regenerated reduced desulfurization adsorbent, together with a portion of the at least partially activity-restored desulfurization adsorbent obtained in step (3), was returned to step (1) to continue the desulfurization reaction under non-hydrogenation conditions. The product composition is shown in Table 2.

Table 2. Composition of Product

	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Composition of Product (vol%)					
propane	8.81	8.76	18.86	18.81	8.79
propylene	29.11	28.92	28.73	28.78	28.94
iso-butane	27.33	27.40	20.05	20.51	27.38
n-butane	6.85	6.88	12.75	12.82	6.91
trans-butene	7.98	7.96	5.82	6.02	8.14
n-butene	7.11	7.17	3.15	3.35	6.9
iso-butene	6.31	6.32	4.80	5.11	6.37
cis-butene	6.45	6.51	4.18	4.57	6.54
1,3-butadiene	0.06	0.05	0.04	0.04	0.05
propylene loss rate /%	-0.14	0.17	0.31	0.14	0.1

sulfur / (mg/m ³)	1.59	1.26	1.38	1.87	1.85
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Example 10

This example performed desulfurization treatment on liquefied petroleum gas feedstock A under non-hydrogenation conditions and performed sulfur transfer and oxidation regeneration of the spent desulfurization adsorbent under hydrogenation conditions, specifically comprising the following steps:

(1) 800 g of desulfurization adsorbent a and liquefied petroleum gas feedstock A were subjected to a desulfurization reaction in a medium-scale unit fluidized bed desulfurization reactor, to obtain desulfurized liquefied petroleum gas and spent desulfurization adsorbent, wherein the reaction pressure was 2.5 MPa, the reaction temperature was 400°C, and the liquefied petroleum gas feed rate was 4 kg/h. The

desulfurized liquefied petroleum gas was discharged from the desulfurized hydrocarbon oil-gas outlet 3, and the sulfur content and hydrocarbon component content in the desulfurized liquefied petroleum gas were measured by chromatography (results are shown in Table 2). The metal sulfide content in the spent desulfurization adsorbent was measured. Sampling analysis and calculation showed that more than 10% of nickel on the surface of the spent desulfurization adsorbent was converted to nickel sulfide and trace amount of zinc sulfide was contained;

(2) the spent desulfurization adsorbent was transferred from the spent desulfurization adsorbent outlet 4 at a rate of 10 g/min via the first receiver 5 and pipeline 6 to a medium-scale unit fluidized bed sulfur transfer reactor 7, where it was contacted with hydrogen to conduct a sulfur transfer reaction. The sulfur transfer reaction temperature was 430 °C, the pressure was 2.5 MPa, the volume ratio of hydrogen to spent desulfurization adsorbent in the reactor was 500, and the average sulfur transfer reaction time was about 0.5 h, to obtain at least partially activity-restored desulfurization adsorbent.

(3) A portion of the at least partially activity-restored desulfurization adsorbent was sent from the activity-restored desulfurization adsorbent outlet 18 via the second receiver 19 and pipeline 20 to the fluidized bed desulfurization reactor to continue the desulfurization reaction, wherein the proportion of this portion of at least partially activity-restored desulfurization adsorbent sent to the fluidized bed desulfurization reactor 2 was 70% of the total desulfurization adsorbent circulation amount.

(4) The remaining portion of the at least partially activity-restored desulfurization adsorbent was sent via pipeline 10, the lock hopper 11, and pipeline 13 into a regenerator 14 to be contacted with air to conduct regeneration, to obtain regenerated desulfurization adsorbent, wherein the temperature for performing this regeneration was 500°C, and the pressure was atmospheric pressure. The proportion of this portion of at least partially activity-restored desulfurization adsorbent sent to the fluidized bed regenerator was 30% of the total desulfurization adsorbent circulation amount.

(5) The regenerated desulfurization adsorbent was sent via pipeline 17, the lock hopper 11, and pipeline 12 into the fluidized bed sulfur transfer reactor 7 of step (1), where it was contacted with hydrogen to perform reduction treatment. The regenerated reduced desulfurization adsorbent, together with a portion of the at least partially activity-restored desulfurization adsorbent obtained in step (3), returned to step (1) to continue the desulfurization reaction under non-hydrogenation conditions. The relationship between sulfur content of product and reaction time is shown in Table 3.

Comparative Example 1

This comparative example performed desulfurization treatment on liquefied petroleum gas feedstock A under non-hydrogenation conditions, specifically comprising the following steps:

16 g of desulfurization adsorbent a and liquefied petroleum gas feedstock A were subjected to a desulfurization reaction in a small fixed-bed reactor. The reaction pressure was 2.5 MPa, the reaction temperature was 400°C, and the liquefied petroleum gas feed rate was 80 g/h. The relationship between the sulfur content of product and reaction duration is shown in Table 3.

Table 3. Sulfur content of desulfurized liquefied petroleum gas vs. reaction time in fluidized bed and fixed bed reactors

	Ex. 10	Comp. Ex. 1
Reaction time/h	sulfur content of product (mg/m ³)	
4	0.67	0.63
8	1.01	1.05
12	1.13	1.28
16	1.28	1.67
20	1.34	2.76
24	1.26	3.84
28	1.46	4.69
32	1.19	6.57
36	1.68	7.51
40	1.53	8.37

Comparative Example 2

This comparative example performed desulfurization treatment on liquefied petroleum gas feedstock A under hydrogen-containing conditions, specifically including the following steps:

This comparative example was carried out according to step (1) described in Example

5, except that the desulfurization adsorbent **a** and liquefied gas feedstock A were desulfurized in a medium-sized fluidized bed reactor under hydrogen conditions, and the molar ratio of hydrogen to liquefied gas in the reducing gas was 0.10 : 1.

Comparative Example 3

This comparative example demonstrates the desulfurization treatment of liquefied petroleum gas feedstock A under hydrogen-containing conditions, specifically including the following steps:

This comparative example is carried out according to step (1) described in Example 5, except that the desulfurization adsorbent **b** and liquefied gas feedstock A are desulfurized in a medium-sized fluidized bed reactor under hydrogen conditions, and the molar ratio of hydrogen to liquefied gas is 0.05 :1.

Table 4. Reaction conditions and properties of product of Comparative Examples

	Comp. Ex. 2	Comp. Ex. 3
Liquefied petroleum gas feedstock	Feedstock A	Feedstock A
Desulfurization adsorbent	Desulfurization adsorbent a	Desulfurization adsorbent b
Propylene loss rate/%	9.43	6.02
S/(mg/kg)	1.09	1.06

By comparing the data in Table 2 and Table 4, it can be seen that the present invention, by contacting liquefied petroleum gas containing sulfides and olefins with a desulfurization adsorbent under non-hydrogenation conditions to perform desulfurization reaction, not only achieves deep desulfurization of the liquefied petroleum gas but also avoids the loss of olefins caused by hydrogenation saturation of unsaturated olefins under hydrogenation desulfurization reaction conditions.

When the above method was applied to the desulfurization of gasoline light fractions, it can also avoid the octane number loss caused by traditional hydrodesulfurization process.

Comparative Example 4

This comparative example was implemented according to the operating method of Example 5, except that selectively hydrodesulfurized catalytic gasoline feedstock A (total sulfur content being 93 mg/kg) was used as the feedstock, wherein the sulfides were basically thiophene-type sulfides. The operating conditions in step (1) were: a pressure of 2.0 MPa, a temperature of 300°C, a weight hourly space velocity of 5 h⁻¹.

The desulfurized gasoline obtained in step (1) was sampled and its sulfur content was

measured by chromatography to be about 80 mg/kg. Measurement of the spent desulfurization adsorbent obtained in step (2) showed that only trace amounts of nickel were converted to nickel sulfide.

Comparison between Example 5 and Comparative Example 4 shows that, in Comparative Example 4 no chemical reaction between sulfur and nickel is incurred to generate nickel sulfide, indicating that the thiophene-type sulfides in the selectively hydrodesulfurized catalytic gasoline feedstock A is not chemically reacted with nickel, but these sulfides is adsorbed onto the desulfurization adsorbent by physical adsorption. Since the physical adsorption force of thiophene-type sulfides on the adsorbent is weak, under the high-temperature and high gas flow rate operating conditions in the fluidized bed, most thiophene-type sulfides cannot be firmly adsorbed on the adsorbent and are desorbed. Therefore, in Comparative Example 4, the desulfurization efficiency of the fluidized bed was significantly reduced compared to that of the fixed bed. Thus, hydrocarbon oils containing only thiophene-type sulfides cannot be efficiently desulfurized in a fluidized bed desulfurization reactor under non-hydrogenation conditions.

The above describes in detail the preferred embodiments of the present invention. However, the present invention was not limited to the specific details in the above embodiments. Within the technical concept of the present invention, various simple modifications can be made to the technical solutions of the present invention, and these simple modifications all belong to the protection scope of the present invention.

In addition, it should be noted that the various specific technical features described in the above specific embodiments can be combined in any suitable manner as long as there is no contradiction. To avoid unnecessary repetition, the present invention will not further describe various possible combination methods.

Furthermore, the various different embodiments of the present invention can also be combined arbitrarily, as long as they do not violate the spirit of the present invention, and they should also be considered as the content disclosed by the present invention.

Claims

1. A method for treating a hydrocarbon oil containing sulfides and optionally olefins, characterized in that the method comprises the following step (1): contacting the hydrocarbon oil, preferably hydrocarbon oil in gaseous state, in the absence of hydrogen in a desulfurization reactor, with a desulfurization adsorbent comprising a metal active component M to perform a selective desulfurization reaction and generate a metal active component sulfide referred to as a metal sulfide, obtaining an at least partially desulfurized hydrocarbon oil and a spent desulfurization adsorbent containing the metal sulfide; wherein at least a portion, preferably all, of the sulfides in the hydrocarbon oil are non-thiophene type sulfides, and the metal active component M is one or more selected from cobalt, nickel, iron, manganese, copper, molybdenum, tungsten, silver, tin, and vanadium; preferably step (1) is conducted in a continuous manner.
2. The method according to claim 1, wherein the desulfurization adsorbent further comprises a carrier, wherein the carrier contains a sulfur-loading component in oxide form, and the metal active component M is supported on the carrier.
3. The method according to claim 2, wherein the method further comprises the following step (2): transferring the spent desulfurization adsorbent to a sulfur transfer reactor to contact with a hydrogen donor to perform a sulfur transfer reaction to reduce the metal sulfide into the metal active component M, and converting the sulfur-loading component in oxide form into a sulfide, obtaining an at least partially activity-restored desulfurization adsorbent, optionally returning at least a portion of the at least partially activity-restored desulfurization adsorbent to the desulfurization reactor of step (1), preferably the step (2) is conducted in a continuous manner.
4. The method according to claim 3, wherein the desulfurization reactor is a fluidized bed reactor and/or the sulfur transfer reactor is a fluidized bed reactor.
5. The method according to any one of claims 1-4, wherein, in step (1), conditions for the selective desulfurization reaction comprise: a temperature of 150-550°C, preferably 300-450°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa; and/or, weight hourly space velocity of the hydrocarbon oil containing sulfides and olefins is 0.1-30 h⁻¹, preferably 1-20 h⁻¹.
6. The method according to any one of claims 1-5, wherein the sulfur content, calculated as sulfur element, in the hydrocarbon oil containing sulfides is 10-5000 µg/g, preferably 30-3000 µg/g, and the mass percentage content of olefins is 2-100%, preferably 5-85%.
7. The method according to any one of claims 1-6, wherein the hydrocarbon oil containing sulfides is one or more selected from dry gas, liquefied petroleum gas, and catalytic gasoline; preferably, the hydrocarbon oil containing sulfides is one or more

selected from catalytic cracking dry gas, catalytic cracking liquefied petroleum gas, dry gas from deep catalytic cracking, liquefied petroleum gas from deep catalytic cracking, ethylene and/or propylene products from steam cracking.

8. The method according to any one of claims 3-7, wherein, in step (2), conditions for the sulfur transfer reaction comprise: a temperature of 300-550°C, preferably 350-450°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa.

9. The method according to any one of claims 3-8, wherein the hydrogen donor is one or more selected from hydrogen, a mixed gas containing hydrogen, and a hydrogen donor; preferably, in the mixed gas containing hydrogen, the volume fraction of hydrogen is 10-99%, preferably 30-90%; preferably, the hydrogen donor is one or more selected from cyclohexane, methylcyclohexane, tetralin, and decalin; preferably, the volume ratio of hydrogen in the hydrogen donor to the spent desulfurization adsorbent is (10-3000):1.

10. The method according to any one of claims 3-9, wherein the sulfur content of the at least partially activity-restored desulfurization adsorbent, calculated as sulfur element, is 0.5-12%, preferably 1-10%, relative to the total weight of the desulfurization adsorbent.

11. The method according to any one of claims 3-10, wherein the method further comprises the following step (3): subjecting a remaining portion of the at least partially activity-restored desulfurization adsorbent to oxygen-containing coke burning regeneration, obtaining regenerated desulfurization adsorbent, subjecting the regenerated desulfurization adsorbent to reduction treatment in a reducing gas atmosphere, obtaining a reduced desulfurization adsorbent, then returning the reduced desulfurization adsorbent to the desulfurization reactor of step (1).

12. The method according to claim 11, wherein, in step (3), the oxygen-containing coke burning regeneration is conducted in the presence of an oxygen-containing gas, and the oxygen-containing gas has an oxygen volume fraction of 5-50 vol%; preferably, the oxygen-containing gas is one selected from air, a mixture of oxygen and nitrogen, a mixture of air and nitrogen; preferably, reaction conditions for the oxygen-containing coke burning comprise: a temperature of 300-800°C, preferably 350-600°C; a pressure of 0.1-3.0 MPa, preferably 0.1-1.0 MPa.

13. The method according to claim 11, wherein, in step (3), conditions for the reduction treatment of the regenerated desulfurization adsorbent comprise: a temperature of 300-550°C, preferably 350-450°C; a pressure of 0.1-5 MPa, preferably 1.5-4 MPa; a volume hourly space velocity of hydrogen in the reducing gas of 10-3000 h⁻¹; preferably, the reducing gas is one or more selected from hydrogen, a mixed gas containing hydrogen, and a precursor compound capable of producing hydrogen; preferably, in the mixed gas containing hydrogen, the volume fraction of hydrogen is 10-99%, preferably 30-90%.

14. The method according to any one of claims 1-13, wherein the metal active component is selected from cobalt, copper, and nickel, and/or the sulfur-loading component is selected from ZnO, TiO₂, ZrO₂, MnO₂, Fe₂O₃, CuO, MgO, CaO, SrO, GeO, SnO, PbO; preferably, the sulfur-loading component is selected from ZnO; based on the total weight of the desulfurization adsorbent, the content of the metal active component is 2-30 wt%, and the total content of the carrier containing a sulfur-loading component is 70-98 wt%.

15. The method according to any one of claims 2-14, wherein the carrier containing a sulfur-loading component comprises 20-85 wt%, preferably 25-75 wt% of the sulfur-loading component, 10-75 wt%, preferably 15-60 wt% of alumina, and 5-70 wt%, preferably 15-60 wt% of silica, based on the total weight of the carrier containing a sulfur-loading component.

16. The method according to any one of claims 1-15, wherein the sulfides are one or more selected from mercaptans, thioethers, carbonyl sulfide, and hydrogen sulfide.

17. A system for treating hydrocarbon oil, characterized in that the system comprises a non-hydrogen desulfurization reactor (2) and a hydrogen-condition sulfur transfer reactor (7), wherein a bottom of the non-hydrogen desulfurization reactor (2) is provided with a hydrocarbon oil inlet for feeding the hydrocarbon oil, a lower part is provided with a desulfurization adsorbent inlet, a top is provided with a desulfurized oil-gas outlet, and an upper part is provided with a spent desulfurization adsorbent outlet; a bottom of the hydrogen-condition sulfur transfer reactor (7) is provided with a hydrogen donor inlet, a lower part is provided with a spent desulfurization adsorbent inlet and an optional regenerated desulfurization adsorbent inlet, an upper part is provided with an outlet for at least partially activity-restored desulfurization adsorbent, and a top is provided with a gas outlet; the spent desulfurization adsorbent outlet of the non-hydrogen desulfurization reactor (2) is connected via a pipeline to the spent desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7), and the activity-restored desulfurization adsorbent outlet of the hydrogen-condition sulfur transfer reactor (7) is connected via a pipeline to the desulfurization adsorbent inlet of the non-hydrogen desulfurization reactor (2); wherein the pipelines (6, 20) are provided with a device for respectively forcing the spent desulfurization adsorbent and the at least partially activity-restored desulfurization adsorbent into the hydrogen-condition sulfur transfer reactor (7) and the non-hydrogen desulfurization reactor (2) and a device for preventing gas from flowing between the non-hydrogen desulfurization reactor (2) and the hydrogen-condition sulfur transfer reactor (7).

18. The system according to claim 17, characterized in that the system further comprises a first receiver (5) and a second receiver (19), the first receiver (5) has a first material inlet and a first material outlet, and the second receiver (19) has a second material inlet and a second material outlet; wherein the spent desulfurization adsorbent outlet of the

non-hydrogen desulfurization reactor (2) is connected to the first material inlet of the first receiver (5), the first material outlet of the first receiver (5) is connected to the spent desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7); and the activity-restored desulfurization adsorbent outlet of the hydrogen-condition sulfur transfer reactor (7) is connected to the second material inlet of the second receiver (19), the second material outlet of the second receiver (19) is switchably connected to the desulfurization adsorbent inlet of the non-hydrogen desulfurization reactor (2).

19. The system according to claim 18, characterized in that the system further comprises a lock hopper (11) and a regenerator (14); wherein a bottom of the regenerator (14) is provided with an oxygen-containing gas inlet, a lower part is provided with a regenerated desulfurization adsorbent outlet, an upper part is provided with a desulfurization adsorbent inlet, and a top is provided with a flue gas outlet; the lock hopper (11) has a third material inlet, a third material outlet, and a regenerated desulfurization adsorbent inlet; the second material outlet of the second receiver (19) is further switchably connected to the third material inlet of the lock hopper (11), the third material outlet of the lock hopper (11) is switchably connected to the desulfurization adsorbent inlet of the regenerator (14), the regenerated desulfurization adsorbent outlet of the regenerator (14) is connected to the regenerated desulfurization adsorbent inlet of the lock hopper (11), and the third material outlet of the lock hopper (11) is further switchably connected to the regenerated desulfurization adsorbent inlet of the hydrogen-condition sulfur transfer reactor (7).

20. The system according to any one of claims 18-19, characterized in that the desulfurization reactor is a fluidized bed reactor and/or the sulfur transfer reactor is a fluidized bed reactor.

21. The system according to any one of claims 19-20, characterized in that the regenerator (14) is a fluidized bed reactor.