



US 20070080099A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2007/0080099 A1**
Reid et al. (43) **Pub. Date:** **Apr. 12, 2007**

(54) **PROCESS AND CATALYST FOR REMOVAL
ARSENIC AND ONE OR MORE OTHER
METAL COMPOUNDS FROM A
HYDROCARBON FEEDSTOCK**

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(21) Appl. No.: **10/556,894**

(22) PCT Filed: **May 6, 2004**

(86) PCT No.: **PCT/EP04/04943**

§ 371(c)(1),
(2), (4) Date: **Nov. 21, 2006**

Related U.S. Application Data

(60) Provisional application No. 60/470,864, filed on May 16, 2003.

Foreign Application Priority Data

Jun. 3, 2003 (EP) 03076720.6

Publication Classification

(51) **Int. Cl.**
C10G 45/04 (2006.01)

(52) **U.S. Cl.** **208/251 H**

ABSTRACT

The invention pertains to a process and catalyst for removing arsenic and one or more other metal compounds, e.g. silicon, vanadium and nickel, from a hydrocarbon feedstock. The catalyst comprises a molybdenum compound and a nickel compound on a carrier. The catalyst has a surface area of at least 200 m²/g. Next to contaminant removal, the catalyst is also suitable for hydrodesulphurisation, hydrodenitrogenation and/or hydrogenation.

**PROCESS AND CATALYST FOR REMOVAL
ARSENIC AND ONE OR MORE OTHER METAL
COMPOUNDS FROM A HYDROCARBON
FEEDSTOCK**

[0001] The present invention pertains to a process for removing arsenic and one or more other metal compounds from a hydrocarbon feedstock and to a catalyst suitable for use therein. It particularly pertains to a process for removing arsenic and one or more other metal compounds from a hydrocarbon feedstock in which the feedstock is contacted in the presence of hydrogen with a catalyst comprising nickel and molybdenum on an inorganic carrier. It also pertains to a specific catalyst suitable for use in this process.

[0002] Due to scarcity of other hydrocarbon fuels and energy resources in general, shale oil and other heavy hydrocarbon feeds, including those derived from coal, bituminous sands, etc., are playing an increasing role in the production of commercial hydrocarbon fuels. Frequently, these feeds contain contaminants that poison and deactivate the catalysts used in the refining of these feeds to convert them into usable products. Arsenic is one of the more troublesome of these contaminants, because it is highly poisonous. An arsenic take-up of 0.5 wt. % can reduce the catalytic activity of a hydroprocessing catalyst to less than 5% of its initial activity. Additionally, the presence of arsenic on hydroprocessing catalysts limits reuse of the catalyst and may limit disposal options for the used catalyst. Arsenic poisoning is observed in distillate and VGO hydrotreating, but due to the fact that some arsenic-containing compounds are relatively low-boiling, especially following thermal conversion processes, it is also observed in lighter feeds. In fact, the presence of arsenic in lighter feeds may cause even more problems than in heavier feeds, because of the typically higher space velocity used in light feed applications. Various references describe the use of a nickel-molybdenum catalyst in the removal of arsenic from arsenic-containing feedstocks.

[0003] U.S. Pat. No. 3,804,750 describes a process for removing arsenic from shale oil by contacting the oil with a catalyst which may be a supported catalyst comprising 1-7 wt. %, preferably 2-5 wt. % of nickel sulfide and 10-30 wt. %, preferably 15-25 wt. % of molybdenum sulfide on a carrier. In the Example a catalyst containing 3.2 wt. % of Ni and 15 wt. % of Mo, calculated as oxides, is used.

[0004] U.S. Pat. No. 4,046,674 describes a process for removing arsenic from a mineral oil feedstock containing at least 2 ppmwt of arsenic using a catalyst comprising 30-70 wt. % of one or more nickel components and 2-20 wt. % of one or more molybdenum components composited with a refractory oxide.

[0005] U.S. Pat. No. 4,501,652 describes a hydrocarbon upgrading process in which spent nickel-arsenide-containing catalysts are utilised to upgrade a hydrocarbon feedstock. Nickel-molybdenum or nickel-tungsten catalysts are cited as examples of arsenic removal catalysts.

[0006] U.S. Pat. No. 5,421,994 describes a process for removing mercury and arsenic from a hydrocarbon feed, in which use is made of an arsenic recovery mass containing at least one metal selected from the group formed by nickel, cobalt, iron, palladium, and platinum, and at least one metal selected from the group formed by chromium, molybdenum,

tungsten, and uranium, deposited on a support in the example a reduced nickel on alumina catalyst is used.

[0007] T. Hisamitsu et al. (Hydrorefining of Shale Oil (Part 4) Pretreatment for Arsenic Removal, Sekiyu Gakkai-shi, Vol. 36, No. 6, pp. 479-484, 1993) compares a conventional hydrotreating catalyst comprising 12 wt. % Mo (18 wt. % MoO₃) and 3 wt. % Ni (3.8 wt. % NiO) on an alumina carrier with a catalyst comprising 5 wt. % Mo (7.5 wt. % MoO₃) and 33 wt. % Ni (42 wt. % NiO) on an alumina carrier in arsenic removal from a vacuum gas oil fraction separated from a shale oil.

[0008] JP laid-open patent application 60202190 describes the removal of arsenic from hydrocarbon feeds using a catalyst containing 0.5-20 wt. % of NiO and 0.5-20 wt. % of MoO₃. In the Examples, catalysts are used which contain 5 wt. % of NiO and 15 wt. % of MoO₃.

[0009] From the above it is clear that many documents recognize the problem of catalyst poisoning with arsenic. It is noted that not only arsenic, but also other metals present in a hydrocarbon feed, such as silicon, nickel or vanadium, may adversely affect a metal-containing catalyst which is exposed to such a hydrocarbon feed. For example, noble metal catalysts which are used for catalytic reforming, are deactivated by silicon. In other words, mere removal of arsenic is not always sufficient to prevent downstream metal-containing catalysts from deactivation.

[0010] As a result, there is need for a catalyst which is capable of removing arsenic and simultaneously remove one or more other metal components from the hydrocarbon feed.

[0011] It has been found that these problems can be solved by using a catalyst comprising nickel and molybdenum in a specified amount, whereby said catalyst further has a surface area of at least 200 m²/g.

[0012] Accordingly, the present invention is directed to a process for removing arsenic and one or more other metal compounds from a hydrocarbon feed, in which a hydrocarbon feed containing at least 20 ppb of arsenic and at least 0.3 ppm of the other metal compounds is contacted in the presence of hydrogen with a catalyst composition comprising a molybdenum compound and a nickel compound on a carrier, wherein the molybdenum compound is present in an amount of 6-18 wt. %, calculated as trioxide and the nickel compound is present in an amount of 6-20 wt. %, calculated as oxide, and wherein the catalyst composition has a surface area of at least 200 m²/g. The catalyst used in the process of the invention is capable of simultaneously removing arsenic and one or more other metal compounds from a hydrocarbon feed. It is noted that depending on the kind of hydrocarbon feed the type and amount of the other metal compound may vary. Preferably, one of the other metal compounds is silicon. The catalyst of the invention is capable of sufficiently removing silicon together with arsenic from relatively light hydrocarbon feeds, such as naphtha and distillate. The catalyst of the invention is also capable of removing arsenic together with nickel and vanadium, which are present in heavier hydrocarbon feeds, to a desirable level.

[0013] Next to the catalyst's ability to remove contaminants from a hydrocarbon feed, it is generally also active in hydrodesulphurisation and/or hydrodenitrogenation and/or hydrogenation.

[0014] In the context of the present specification, the term “wt. %” is used to refer to the weight percentage of a certain compound in a catalyst, calculated on the total weight of the catalyst.

[0015] As indicated above, the molybdenum content of the catalyst is 6-18 wt. %, calculated as trioxide, preferably 10-15 wt. %, calculated as trioxide. If the molybdenum content of the catalyst is too low, the gas make (of low molecular weight hydrocarbons, e.g. methane, ethane, propane and butane) of the catalyst becomes too high. The addition of molybdenum above the upper limit decreases the arsenic removal activity and furthermore decreases the effectiveness of the catalyst.

[0016] The nickel content of the catalyst is 6-20 wt. %, preferably 8-15 wt. %. A too low nickel content decreases the arsenic removal activity to an undesirable level. The effectiveness and capacity of such a catalyst becomes so low that process variables, e.g. amount of catalyst and space velocity of the feed, have to be adjusted in an economically unacceptable manner. It is noted that an increase in nickel content will increase the arsenic removal capacity. If, however, the nickel content is chosen above the upper limit, this will negatively impact the catalyst's activity in hydrodesulphurisation (HDS) and/or hydrodenitrogenation (HDN).

[0017] The catalyst of the invention generally has a (BET) specific surface area which is at least 200 m²/g, preferably at least 225 m²/g, more preferably at least 250 m²/g. The surface area generally is at most 600 m²/g, preferably at most 500 m²/g, more preferably at most 400 m²/g. Such a relatively high surface area enables an improved uptake capacity of metal compounds which are believed to adsorb to the carrier used in the catalyst. A catalyst having a surface area lower than 200 m²/g yields a catalyst which has a metal removal capacity, and in particular the removal capacity for silicon, which is too low to make the process economically attractive.

[0018] Generally, the catalyst has a median pore diameter (MPD) of at most 15 nm, preferably at most 14 nm, more preferably at most 13 nm. The MPD is generally at least 9 nm, preferably at least 9.5 nm, more preferably at least 10 nm. The median pore diameter is defined as the pore diameter at which half of the total pore volume is present in pores with a diameter above the MPD and half of the pore volume is present in pores with a diameter below the MPD. The specified MPD improves the accessibility into the catalyst of the metals to be removed. A further advantage of choosing the MPD above 9 nm is that the arsenic removal capacity is also increased. It is noted that if the MPD is chosen below 9 nm, the removal capacity of metals like silicon, nickel or vanadium, for instance, is low, which is undesirable. If, on the other hands the MPD of the catalyst is above 15 nm, which generally leads to a catalyst having a specific surface area below 200 m²/g, the removal activity of the said metals decreases, and consequently the effectiveness of the catalyst diminishes. A further disadvantage of an MPD above 15 nm is a reduction in hydrodesulphurisation, hydrodenitrogenation or hydrogenation activity of the catalyst.

[0019] The catalyst's pore volume (Hg, 140° contact angle) generally is at least 0.25 ml/g, preferably at least 0.4 ml/g, more preferably at least 0.5 ml/g. The pore volume is generally at most 1.2 ml/g, preferably at most 1.0 ml/g, more

preferably at most 0.9 ml/g. The catalyst preferably has a macropore volume, defined as the percentage of pore volume present in pores with a diameter of at least 1000 Å of less than 5%, preferably less than 2%.

[0020] The carrier may comprise the conventional oxides, e.g., alumina, silica, silica-alumina, alumina with silica-alumina dispersed therein, silica-coated alumina, magnesia, zirconia, boria, and titania, as well as mixtures of these oxides. As a rule, preference is given to the carrier comprising, alumina, silica-alumina, alumina with silica-alumina dispersed therein, or silica-coated alumina. Special preference is given to the carrier consisting essentially of alumina or a carrier consisting essentially of alumina containing up to 25 wt. % of other components, more preferably up to 10 wt. %, still more preferably up to 5 wt. %, the other components preferably being silica. A carrier consisting essentially of alumina is particularly preferred. In the context of the present specification, the words “consisting essentially of” mean that other components than the component required may be present, but only in such limited amounts that they do not detrimentally affect the properties of the catalyst. The alumina present in the carrier is preferably a transition alumina, for example an eta, theta, or gamma alumina, with gamma-alumina being especially preferred. It is preferred for the catalyst to contain less than 2 wt. % of phosphorus, calculated as P₂O₅, more preferably less than 1 wt. %, still more preferably less than 0.5 wt. %.

[0021] The catalyst of the invention generally has a saturation capacity ratio of the other metal and arsenic of at least 3; preferably at least 4, most preferably at least 5, and generally at most 20, preferably at most 17, and most preferably at most 15. With saturation capacity is meant the maximum amount of a certain metal which can be taken up by the catalyst.

[0022] The saturation capacity ratio of silicon and arsenic is generally at least 3, preferably at least 4, most preferably at least 5, and generally at most 20, preferably at most 17, and most preferably at most 16. The catalyst of the invention generally has a saturation capacity ratio of nickel and/or vanadium, and arsenic of at least 3, preferably at least 4, most preferably at least 5, and generally at most 20, preferably at most 17, and most preferably at most 15.

[0023] Catalysts within the most preferred ranges mentioned above are considered most preferred for the removal of arsenic, preferably in combination with silicon, from naphtha-type feeds and distillate feeds, in particular naphtha-type feeds.

[0024] The catalyst is suitably in the form of spheres, pellets, beads, or extrudates. Examples of suitable types of extrudates have been disclosed in the literature.

[0025] Highly suitable are cylindrical particles (which may be hollow or not) as well as symmetrical and asymmetrical tri- or quadrulobes.

[0026] The catalyst may be prepared by processes known in the art.

[0027] The feedstock to be used in the process according to the invention contains at least 20 ppb (weight parts per billion) of arsenic, specifically between 0.02 and 2 ppm. It may additionally contain other contaminants. For example, silicon may be present. If so, it is generally present in an

amount of at least 0.5 ppm, specifically between 1 ppm and 100 ppm. Nickel and vanadium may be present. If so, they are generally present in a combined amount of at least 0.3 ppm, preferably between 100 and 2000 ppm. These feedstocks generally also comprise sulphur-containing compounds and nitrogen-containing compounds. The sulphur-containing compounds are generally present in an amount of at least 10 ppm, the nitrogen-containing compound generally, in an amount of at least 2 ppm. Unsaturated compounds such as olefins, di-olefins and aromatics, may also be present.

[0028] A particularly preferred embodiment of the process according to the invention is the removal of arsenic from arsenic-containing naphtha type feeds, preferably in combination with silicon removal. Suitable naphtha feeds generally have an arsenic content of at least 20 ppb (weight parts per billion) of arsenic, specifically between 0.02 and 2 ppm. They preferably have a silicon content of at least 0.5 ppm, specifically between 1 ppm and 100 ppm. Nickel and vanadium are generally present in an amount of less than 10 ppm, specifically no nickel or vanadium are present in the feed. The feedstock generally has an initial boiling point of about 0-120° C., preferably about 30-90° C. and a final boiling point of about 150-250° C., preferably about 160-220° C.

[0029] In the process of this embodiment the catalyst of the invention is generally also active in hydrodesulphurisation and hydrodenitrogenation, as well as saturation processes of e.g. olefins and di-olefins.

[0030] A further embodiment of the process according to the invention is the removal of arsenic from distillate feeds.

[0031] Suitable distillate feeds generally have an arsenic content of at least 20 ppb (weight parts per billion) of arsenic, specifically between 0.02 and 2 ppm. They may or may not contain silicon. If silicon is present, it is generally present in an amount of at least 0.5 ppm, specifically between 1 ppm and 100 ppm.

[0032] The feedstock generally has an initial boiling point of about 80-260° C., preferably about 200-240° C. and a final boiling point of about 230-390° C., preferably about 250-370° C.

[0033] In the process of this embodiment the catalyst of the invention is generally also active in hydrodesulphurisation and in hydrodenitrogenation, as well as in saturation processes of e.g. olefins, di-olefins and aromatics.

[0034] A third embodiment of the process according to the invention is the removal of arsenic in fuel oil processing, generally in combination with nickel and vanadium removal.

[0035] The feedstock to be used in the process according to the invention contains at least 20 ppb (weight parts per billion) of arsenic, specifically between 0.02 and 2 ppm. Nickel and vanadium are generally present, preferably in an amount of at least 9.3 ppm, preferably between 0.3 and 10 ppm. Silicon may or may not be present, if it is, it is generally present in an amount of at least 0.5 ppm, specifically between 1 ppm and 100 ppm. The feedstock generally has an initial boiling point of about 250-450° C., preferably about 280-375° C. and a final boiling point of above 370° C.

[0036] In the process of this embodiment the catalyst of the invention is generally also active in hydrodesulphurisation and in hydrodenitrogenation, as well as in saturation processes of e.g. aromatics.

[0037] The process is generally carried out under such conditions that at least 50% of the arsenic is removed from the feed, preferably at least 80%, more preferably at least 90%, still more preferably at least 99%. If silicon is present, generally at least 50% of the silicon is removed from the feed, preferably at least 80%, more preferably at least 90%, still more preferably at least 98%. If nickel and vanadium are present, generally at least 30% is removed from the feed, preferably at least 60%.

[0038] Alternatively, the process is generally carried out under such conditions that at most 50% of the arsenic is still present in the effluent of the catalyst bed, preferably at most 20%, more preferably at most 10%, still more preferably at most 1%. If silicon is present, generally at most 50% of the silicon is present in the effluent of the catalyst bed, preferably at most 20%, more preferably at most 10%, still more preferably at most 2%. If nickel and vanadium are present, generally at most 70% is present in the effluent of the catalyst bed, preferably at most 40%.

[0039] The process of the present invention is generally carried out in a guard bed operation, that is, to guard downstream arsenic sensitive catalysts from arsenic. It can be carried out in a separate guard bed chamber in a guard bed upstream of the arsenic-sensitive catalyst.

[0040] The process is generally carried out at a hydrogen partial pressure of 10-200 bar, preferably 30-150 bar, and a temperature of 200-480° C., preferably 300-415° C. The hydrogen to feed ratio is generally from 200-2000 NI/I, preferably 500-1000 NI/I. The Liquid Hourly Space Velocity (LHSV), measured in units of volumetric flow rate of feed per unit volume of catalyst is generally between 0.1 and 10 h⁻¹ and preferably between 0.5 and 6 h⁻¹.

EXAMPLE

[0041] The following catalysts were tested in the removal of arsenic from an arsenic-containing feedstock.

[0042] Comparative Catalyst 1, which comprises 4 wt. % of nickel, calculated as oxide and 12 wt. % of molybdenum, calculated as trioxide, on an alumina carrier, the catalyst having a surface area of about 250 m²/g, a total pore volume (Hg, 140° contact angle) of about 0.65-0.7 ml/g, and a MPD of about 11 nm.

[0043] Catalyst A according to the invention, which is the same as Comparative Catalyst 1, except that it contains 8 wt. % of NiO.

[0044] Catalyst B according to the invention, which is the same as Comparative

[0045] Catalyst 1, except that it contains 12 wt. % of NiO.

[0046] The three catalysts were tested in the removal of arsenic from an arsenic-contaminated coker naphtha. After the test it was found that the catalysts showed the following arsenic and silicon content, normalised to fresh catalyst composition:

TABLE 1

	As content spent catalyst (wt. %)	Si content spent catalyst (wt. %)
Comparative Catalyst 1	1.03	0.95
Catalyst A	1.66	1.04
Catalyst B	2.00	1.08

[0047] From the above Table 1 it appears that the catalysts according to the invention have an improved arsenic and silicon, removal activity as compared to the comparative catalyst which has a lower nickel content.

1. A process for removing arsenic and one or more other metal compounds from a hydrocarbon feed, in which a hydrocarbon feed containing at least 20 ppb of arsenic and at least 0.3 ppm of the other metal compounds is contacted in the presence of hydrogen with a catalyst composition comprising a molybdenum compound and a nickel compound on a carrier, wherein the molybdenum compound is present in an amount of 6-18 wt. %, calculated as trioxide and the nickel compound is present in an amount of 6-20 wt. %, calculated as oxide, and wherein the catalyst composition has a surface area of at least 200 m²/g.

2. The process of claim 1 wherein the molybdenum compound is present in an amount of 10-15 wt. %, calculated as trioxide and the nickel compound is present in an amount of 8-15 wt. %, calculated as oxide.

3. The process of claim 1 or 2 wherein the catalyst composition has an MPD of at least 9 nm, preferably between 9 and 15 nm.

4. The process according to any one of the preceding claims wherein one of the other metal compounds is silicon.

5. The process of any one of the preceding claims wherein the feed is a naphtha type feed which has an arsenic content of at least 20 ppb (weight parts per billion) of arsenic, preferably between 0.02 and 2 ppm, an initial boiling point of about 0-120° C., preferably about 30-90° C. and a final boiling point of about 150-250° C., preferably about 160-220° C.

6. The process of claim 5, wherein the naphtha type feed has a silicon content of at least 0.5 ppm, specifically between 1 ppm and 100 ppm.

7. The process of any one of the preceding claims which is carried out at a hydrogen partial pressure of 10-200 bar, preferably 30-150 bar, a temperature of 200-480° C., preferably 300-415° C., a hydrogen to feed ratio of 200-2000 NI/I, preferably 500-1000 NI/I, and a LHSV of 0.1-10 h⁻¹, preferably 0.5-3 h⁻¹.

8. A hydroprocessing catalyst comprising a molybdenum compound and a nickel compound on a carrier, wherein the molybdenum compound is present in an amount of 6-18 wt. %, calculated as oxide and the nickel compound is present in an amount of 6-20 wt. %, calculated as oxide, wherein the catalyst has a surface area of at least 200 m²/g.

9. A hydroprocessing catalyst according to claim 8 wherein the catalyst has an MPD of at least 9 nm, preferably between 9 and 15 nm.

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