

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 March 2002 (14.03.2002)

PCT

(10) International Publication Number
WO 02/20702 A1

(51) International Patent Classification⁷: **C10G 45/08**,
65/04

(21) International Application Number: PCT/EP01/09641

(22) International Filing Date: 20 August 2001 (20.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00203078.1 4 September 2000 (04.09.2000) EP
60/237,892 4 October 2000 (04.10.2000) US

(71) Applicant: **AKZO NOBEL N.V.** [NL/NL]; Velperweg 76,
NL-6824 BM Arnhem (NL).

(72) Inventors: **SONNEMANS, Johannes, Wilhelmus, Maria**; De Colignylaan 9, NL-3761 DD Soest (NL).
EIJSBOUTS, Sonja; Goudenregenstraat 1, NL-5253 BE
Nieuwkuijk (NL).

(74) Agent: **SCHALKWIJK, Pieter, Cornelis**; Akzo Nobel
N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box
9300, NL-6800 SB Arnhem (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR EFFECTING ULTRA-DEEP HDS OF HYDROCARBON FEEDSTOCKS

(57) Abstract: The present invention pertains to a process for reducing the sulfur content of a hydrocarbon feedstock to a value of less than about 200 ppm, comprising optionally subjecting a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive to a sulfidation step and/or activation step, and contacting a feedstock with a 95 % boiling point of about 450 °C or less with the optionally sulfided and/or activated catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 200 ppm, preferably less than about 50 ppm.



WO 02/20702 A1

PROCESS FOR EFFECTING ULTRA-DEEP HDS OF HYDROCARBON FEEDSTOCKS

The present invention relates to a process for effecting ultra-deep HDS of hydrocarbon feedstocks.

In an effort to regulate SO₂ emissions from the burning of fuels and to optimise the performance of tail-end catalysts, in particular exhaust treatment catalysts, the regulations as to the sulfur content of fuels, in particular diesel fuels, are becoming more and more strict. In Europe as of 2000 diesel feedstocks are required to have a sulfur content less than 350 ppm, while as of 2005, the sulfur content should be less than 50 ppm, with even further decreases not being excluded.

In consequence, there is an increasing need for catalyst systems which can decrease the sulfur content of a hydrocarbon feedstock with a 95% boiling point of about 450°C or less to less than about 200 ppm, preferably less than about 100 ppm, even more preferably less than about 50 ppm, calculated by weight as elemental sulfur on the total liquid product.

In the context of the present specification the term ultra-deep HDS means the reduction of the sulfur content of a hydrocarbon feedstock to a value of less than about 200 ppm, preferably less than about 100 ppm, and even more preferably to a value of less than about 50 ppm, calculated by weight as elemental sulfur on the total liquid product, as determined in accordance with ASTM D-4294. The indications Group VIB and Group VIII correspond to the Periodic Table of Elements applied by Chemical Abstract Services (CAS system).

The problem associated with effecting this ultra-deep HDS is that the last sulfur compounds present in the feed are the hardest to remove.

Depending on their source, petroleum fractions can comprise various types of sulfur compounds. In hydrotreated middle distillate fractions, the major sulfur components are benzothiophenes and dibenzothiophenes. In straight-run materials significant quantities of other components are present, such as thiophenes, mercaptanes, sulfides, and disulfides. Of these, the sulfides and disulfides are the most reactive, followed by the thiophenes, benzothiophenes, and dibenzothiophenes. Within the group of dibenzothiophenes some components are more reactive than others. In consequence, in conventional hydrodesulfurisation (HDS), in which the sulfur level is reduced to a value of, say, about 0.3 wt.%, the sulfides and thiophenes are removed. In deep HDS, to a sulfur level of, say, 200 to about 500 ppm, the benzothiophenes are removed. To effect ultra-deep HDS to a sulfur level of below about 200 ppm, the last compounds present, in particular a limited number of alkylated benzothiophenes, need to be removed in whole or in part, with the alkyldibenzothiophenes which have the alkyl on the 4- or 6- position being particularly difficult to remove.

It has been found that the reaction mechanisms by which these very refractive sulfur compounds are decomposed is different from those by which the less refractive compounds are decomposed. This is evidenced, e.g., by the fact that the catalysts which are known as particularly suitable for HDS appear to function less well in ultra-deep HDS. For example, conventionally, cobalt-molybdenum catalysts are more active in HDS than nickel-molybdenum catalysts. However, for ultra-deep HDS it has been found that nickel-molybdenum catalysts show better results than cobalt-molybdenum catalysts. Reference is made to the paper entitled "Ultra low sulfur diesel: Catalyst and Process options" presented at the 1999 NPRA meeting by T. Tippet et al.

The consequence of this difference in reaction mechanisms implies that the refiner who is faced with having to produce material with a lower sulfur content

cannot just apply his usual hydrodesulfurisation catalyst under more stringent conditions. On the contrary, he will have to specifically select the hydrotreating catalyst which is most effective in effecting ultra-deep HDS. This is the more so since the reaction conditions necessary to effect ultra-deep HDS are rather
5 severe in themselves, and the use of a dedicated catalyst makes it possible to select less severe reaction conditions, resulting in energy saving and a longer catalyst lifespan.

We have now found that a catalyst which comprises a Group VIB metal
10 component, a Group VIII metal component, and an S-containing organic additive is particularly efficient in reducing the sulfur content of a hydrocarbon feedstock to a value of less than about 200 ppm. In addition, this catalyst may make it possible to effect this ultra-deep HDS in combination with at least one of improved reduction of the amount of nitrogen, improved reduction of the total
15 amount of aromatics present, and improved reduction of the amount of polynuclear aromatics. Preferably, the catalyst according to the invention shows ultra-deep HDS in combination with at least improved reduction of the amount of nitrogen, more preferably also in combination with improved reduction of the total amount of aromatics present, and improved reduction of the amount of
20 polynuclear aromatics.

Therefore, the present invention is directed to a process for reducing the sulfur content of a hydrocarbon feedstock to a value of less than about 200 ppm, comprising optionally subjecting a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic
25 additive on a carrier to a sulfidation step or activation step, and contacting a feedstock with a 95% boiling point of about 450°C or less with the optionally sulfided or activated catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 200 ppm.

Incidentally it is noted that non-prepublished European patent application No. 1041133 describes effecting ultra-deep HDS with a catalyst comprising an O- or N-containing additive.

5 The additive-containing catalyst

In principle, the additive-containing catalyst can be any catalyst which comprises a Group VIB hydrogenation metal and/or a Group VIII hydrogenation metal, and an S-containing organic additive on a carrier. Catalysts comprising
10 the combination of a Group VIB hydrogenation metal and a Group VIII hydrogenation metal are preferred.

Catalysts which comprise a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive are known in themselves in the art.

15 For example, European patent application No. 0 300 629 and European patent application No. 0 357 295 describe hydrotreating catalysts comprising a support impregnated with at least one member of molybdenum, tungsten, and/or metals of Group VIII of the Periodic Table, and a mercapto-compound selected from mercaptocarboxylic acids, amino-substituted mercaptanes, di-mercaptanes,
20 and thioacids. The S-containing additive is incorporated into the catalyst composition to obviate the necessity of presulfiding, or to at least make the presulfiding less difficult.

European patent application No. 0 506 206 also describes a hydrotreating catalyst comprising an S-containing additive selected from the group of bi-
25 mercaptanes, aminosubstituted mercaptanes, and thiocarboxylic acids. The S-containing catalyst is again intended to avoid the necessity of presulfiding. Some of the catalysts described in this reference are activated by a treatment with hydrogen at a temperature from room temperature up to 400°C, preferably 100-300°C.

Similar subject-matter is described in European patent application No. 0 338 788, and European patent application No. 0 289 211.

US 5,139,990 describes a hydrotreating catalyst comprising a carrier and hydrogenation metal components which is treated with an aqueous medium
5 comprising a water-soluble or water-miscible S-containing organic additive, followed by drying the resulting catalyst and activating it with hydrogen at a temperature of 100-600°C.

US 4,636,487 describes a hydrotreating catalyst comprising a support and a hydroxymercaptide of one or more metals, which may be the reaction product
10 of a mercaptoalcohol and one or more metal compounds. The catalyst may be activated with hydrogen at a temperature of 66-316°C.

European patent application No. 0 496 592 describes a hydrotreating catalyst comprising a carboxylic acid and an organic sulfur compound which may be a mercaptocarboxylic acid.

15

As Group VIB metals suitable for use in the additive-containing catalyst for use in the process according to the invention may be mentioned molybdenum, tungsten, and chromium. Group VIII metals include nickel, cobalt, and iron. Catalysts comprising molybdenum as Group VIB metal component and nickel
20 and/or cobalt as Group VIII metal component are preferred. For use in the process according to the invention catalysts comprising nickel may be preferred, especially when the feed comprises less than about 0.1 wt.% of sulfur. The catalyst usually has a metal content in the range of about 0.1 to about 50 wt.% calculated as oxides on the dry weight of the catalyst not
25 containing the additive. The Group VIB metal will frequently be present in an amount of about 5 to about 40 wt.%, preferably about 15 to about 30 wt.%, calculated as trioxide. The Group VIII metal will frequently be present in an amount of about 1 to about 10 wt.%, preferably about 2 to about 7 wt.%, calculated as monoxide. The catalyst may also contain other components, such
30 as phosphorus, halogens, and boron. Particularly, the presence of phosphorus

in an amount of about 1 to about 10 wt.%, calculated as P_2O_5 , may be preferred.

The catalyst 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
5 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 alumina containing up to about 25 wt.% of other components, preferably silica.
10 A carrier comprising a transition alumina, for example an eta, theta, or gamma alumina is preferred within this group, with a carrier comprising gamma-alumina being especially preferred. Additionally, although it is considered less preferred at present, the catalyst may contain 0 to about 60 wt.% of zeolite.

The catalyst's pore volume (measured via N_2 adsorption)) generally is in the
15 range of about 0.25 to about 1 ml/g. The specific surface area will generally be in the range of about 50 to about 400 m^2/g (measured using the BET method). Generally, the catalyst will have a median pore diameter in the range of about 7 to about 20 nm, as determined by N_2 adsorption. The figures for the pore size distribution and the surface area given above are determined after calcination
20 of the catalyst at 500°C for one hour.

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 (see, *int. al.*, US 4,028,227). Highly suitable are cylindrical particles (which may be hollow or not) as well as symmetrical and asymmetrical polylobed particles
25 (3 or 4 lobes).

The additive present in the catalyst may be any S-containing organic additive. In the context of the present specification the term organic additive refers to an additive comprising at least one carbon atom and at least one hydrogen atom.

- Preferred compounds include the mercaptocarboxylic acids represented by the general formula HS-R1-COOR, wherein R1 stands for a divalent hydrocarbon group with 1 to about 10 carbon atoms and R stands for a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, or a linear or branched alkyl group having 1 to about 10 carbon atoms. Examples include mercaptoacetic acid (HS-CH₂-COOH), beta-mercaptopropionic acid (HS-CH₂CH₂-COOH), methylmercaptoacetate (HS-CH₂-COOCH₃), ethyl 2-mercaptoacetate (HS-CH₂-COOC₂H₅), ethylhexyl mercaptoacetate (HS-CH₂-COOC₈H₁₇), and methyl 3-mercaptopropionate (HS-CH₂CH₂-COOCH₃).
- Preferred compounds also include amino-substituted mercaptanes represented by the general formula H₂N-R₂-SH, wherein R₂ stands for a divalent hydrocarbon group having 1 to about 15 carbon atoms. Examples of these compounds include 2-amino ethanethiol (H₂N-CH₂CH₂-SH), and 4-amino thiophenol (H₂N-C₆H₄-SH).
- Preferred compounds also include di-mercaptanes represented by the general formula HS-R₃-SH, wherein R₃ stands for a divalent hydrocarbon group having 1 to about 15 carbon atoms. Examples of these compounds include ethanedithiol (HS-CH₂CH₂-SH) and 1,4-butanedithiol (HS-(CH₂)₄-SH).
- Preferred compounds also include thioacids of the formula R₄-COSH, wherein R₄ stands for a monovalent hydrocarbon group having 1 to about 15 carbon atoms. Examples of these compounds include thioacetic acid (CH₃-COSH) and thiobenzoic acid (C₆H₅COSH). Dithioacids of the formula HSOC-R₅-COSH wherein R₅ is a divalent hydrocarbon group with 1 to about 15 carbon atoms may also be suitable. An example is dithioadipic acid (HSOC-C₄H₁₀-COSH).
- Preferred compounds also include mercaptoalcohols of the general formula R₆S-R₅-(OH)_n, wherein R₅ represents an alkyl group having from 1 to about 15 carbon atoms or a phenyl group, R₆ represents a hydrogen atom or an alkyl group having 1 or about 2 carbon atoms, and n is 1 or about 2. Examples of these compounds include 2-mercaptoethanol, 2-(methylthio)ethanol, 2-(ethylthio)ethanol, 3-mercapto-2-butanol, 4-mercapto-phenol, 2-

(methylthio)phenol, 4-(methylthio)phenol, 2-(ethylthio)phenol, 3-mercapto-1,2,-propanediol, 3-methylthio-1,2, propanediol, and 3-ethylthio-1,2, propanediol.

Other suitable compounds include sulfoxides of the formula R7-SO-R8, wherein R7 and R8 are hydrocarbon groups with 1 to about 5 carbon atoms. An
5 example is dimethyl sulfoxide (CH₃-SO-CH₃).

Ammonium thiocyanate and thiourea may also be useful compounds, as may be the various dithiocarbamic acids and the salts thereof, such as ethylene bisdithiocarbamic acid and its salts, and dimethyl dithiocarbamic acid and its salts. Other suitable compounds include mercaptodiathiazoles and their salts,
10 such as 2,5-dimercapto-1,3,4,-diathiazoles and its salts.

Other compounds which may be useful are (poly)sulfides of the formula R9-S_x-R10, wherein x is a value of 1 to about 15 and R9 and R10 are alkyl groups, preferably branched alkyl groups, with 1 to about 30 carbon atoms. Related compounds are those with the formula HO-R11-S_x-R12-OH, wherein x is a
15 value of 1 to about 15 and R11 and R12 are alkyl groups with 1 to about 8 carbon atoms.

At this point in time the mercaptocarboxylic acids are considered preferred for reasons of activity. Other compounds, in particularly those which are soluble in or miscible with water, may be preferred for environmental reasons (less odour
20 and/or no organic solvent necessary).

A single compound as well as a combination of compounds may be used as additive.

The amount of additive present in the additive-containing catalyst depends on
25 the specific situation. It was found that the appropriate amount of additive generally lies in the range of about 0.01 to about 2.5 moles of additive per mole of hydrogenation metals present in the catalyst. If the amount of additive added is too low, the advantageous effect associated with its presence will not be obtained. On the other hand, the presence of an exceptionally large amount of
30 additive will not improve its effect. Generally, the aim is to select the amount of

sulfur incorporated into the catalyst by way of the additive to correspond to about 5 to about 200%, preferably about 50 to about 200%, more preferably about 80 to about 150%, of the stoichiometric sulfur quantity necessary to convert the hydrogenation metals into Co_9S_8 , MoS_2 , WS_2 , and Ni_3S_2 , respectively.

The way in which the additive is incorporated into the catalyst composition is not critical to the process according to the invention. The additive may be incorporated into the catalyst composition prior to, subsequent to, or simultaneously with the incorporation of the hydrogenation metal components.

For example, the additive can be incorporated into the catalyst composition prior to the hydrogenation metal components by being added to the carrier before the hydrogenation metal components are. This can be done by mixing the additive with the carrier material before it is shaped, or by impregnating the shaped carrier material with the additive. This embodiment is not preferred at this point in time.

Alternatively, the additive can be incorporated into the catalyst composition simultaneously with the hydrogenation metal components. This can be done, e.g., by mixing the additive and the hydrogenation metal components with the carrier material before shaping or by impregnating the carrier with an impregnation solution comprising the hydrogenation metal components and the additive, followed by drying under such conditions that at least part of the additive is maintained in the catalyst.

It is also possible to incorporate the additive into the catalyst composition subsequent to the hydrogenation metal components. This can be done, e.g., by first incorporating the hydrogenation metal components into the catalyst composition, e.g., by mixing them with the carrier material or by impregnating the carrier with them, optionally followed by drying and/or calcining, and subsequently incorporating the additive, e.g., by impregnation.

Depending on the nature of the additive and the way in which it is incorporated into the catalyst composition, the additive may be used in the solid form, in the liquid form, or dissolved in a suitable solvent. It may be preferred for the additive to be incorporated into the catalyst dissolved in water.

5

The catalyst may be activated by contacting it with hydrogen at a temperature of about 100 to about 600°C as described in, e.g., EP 0 506 206, EP 0 338 788, EP 0 289 211, US 4,636,487, and US 5,139,990. Optionally, the catalyst may be contacted with an organic liquid either prior to or simultaneously with
10 the contacting with hydrogen. Such a process is the subject of non-prepublished International patent application No. PCT/EP01/03877, which is incorporated herein by reference.

If so desired, the catalyst may be subjected to a sulfiding step before its use in
15 effecting ultra-deep HDS, said sulfiding step taking place *ex situ*, *in situ* or in a combination of *ex situ* and *in situ*. In the context of the present specification, the indication sulfiding step or sulfidation step is meant to include any process step in which a sulfur-containing compound is added to the catalyst composition and in which at least a portion of the hydrogenation metal components present in
20 the catalyst is converted into the sulfidic form, either directly or after an activation treatment with hydrogen.

Suitable sulfidation processes are known in the art. *Ex situ* sulfidation processes take place outside the reactor in which the catalyst is to be used in hydrotreating hydrocarbon feeds. In such a process the catalyst is contacted
25 with a sulfur compound, e.g. a polysulfide or elemental sulfur, outside the reactor and, if necessary, dried. In a second step, the material is treated with hydrogen gas at elevated temperature in the reactor, optionally in the presence of a feed, to activate the catalyst, i.e. bring it into the sulfided state.

In situ sulfidation processes take place in the reactor in which the catalyst is to
30 be used in hydrotreating hydrocarbon feeds. Here, the catalyst is contacted in

the reactor at elevated temperature with a hydrogen gas stream mixed with a sulfiding agent, such as hydrogen sulfide or a compound which under the prevailing conditions is decomposable into hydrogen sulfide. It is also possible to use a hydrogen gas stream combined with a hydrocarbon feed comprising a sulfur compound which under the prevailing conditions is decomposable into hydrogen sulfide. In the latter case it is possible to use a hydrocarbon feed comprising an added sulfiding agent (a so-called spiked feed), but it is also possible to use a sulfur-containing hydrocarbon feed without any added sulfiding agent, since the sulfur components present in the feed will be converted into hydrogen sulfide in the presence of the catalyst. The hydrocarbon feed may be the feed to be subjected to ultra-deep HDS in the process according to the invention, but it may also be a different feed, later to be replaced with the feed to be subjected to ultra-deep HDS. Combinations of the various sulfiding techniques may also be applied. In the context of the present invention it may be preferred to sulfide the catalyst by contacting it with an, optionally spiked, hydrocarbon feed.

A further process for presulfiding catalysts comprising an organic S-containing catalyst is the subject of non-prepublished International patent application No. PCT/EP01/03895, which is incorporated herein by reference. This patent application is directed to a presulfiding process in which a catalyst comprising a sulfur-containing additive is presulfided in two steps, the first step being carried out at a lower temperature than the second step. Non-prepublished International patent application No. PCT/EP01/03843, which is incorporated herein by reference, also describes a suitable presulfiding procedure for catalysts containing an S-containing additive. In the process described in this reference the presulfiding is carried out ex-situ.

Another process, which may be preferred over those of the two above-mentioned references is described in non-prepublished International patent application No. PCT/EP01/03886, which is also incorporated herein by reference. This patent application is directed to a presulfiding process in which

a catalyst comprising a sulfur-containing additive is first contacted with an organic liquid followed by being contacted with hydrogen and a sulfur-containing compound in the gaseous phase.

5 The feed

The feedstock suitable for use in the process according to the invention has a 95% boiling point, as determined in accordance with ASTM D-2887, of about 450°C or less, preferably about 420°C or less, more preferably about 400°C or less. That is, 95 vol.% of the feedstock boils at a temperature of about 450°C or less, preferably about 420°C or less, more preferably about 400°C or less. Generally, the initial boiling point of the feedstock is above about 100°C, preferably above about 180°C.

15 The feedstock to be used in the process according to the invention may or may not have been subjected to a previous hydrodesulfurisation step, depending on the envisaged process conditions.

If the reaction conditions can be selected suitable for more severe hydrotreating, the catalyst used in the process of the invention is sufficiently active to be able to convert fractions with a sulfur content of, e.g., about 0.1 wt.% ppm to about 2 wt.%, preferably 1 to about 2 wt.%, into product with a sulfur content less than about 200 ppm, preferably less than about 100 ppm, more preferably, less than about 50 ppm. Such feedstocks generally contain about 20 to about 1200 ppm nitrogen, preferably about 30 to about 800 ppm, more preferably about 70 to about 600 ppm. The metal content of such feedstocks preferably is less than about 5 ppm, more preferably less than about 1 ppm (Ni+V). Examples of suitable feedstocks of this type are feedstocks comprising one or more of straight run gas oil, light catalytically cracked gas oil, and light thermally cracked gas oil, and (mild) hydrocracked oils.

On the other hand, the invention is also suitable for the ultra-deep hydrodesulfurisation of hydrocarbon feeds of the above description which had already been subjected to a hydrotreating operation, and which have sulfur contents of generally less than about 0.1 wt.%, more specifically about 150 to
5 about 500 ppm. [Obviously, applying the process according to the invention to feeds with a sulfur content less than about 200 ppm will only be useful if a sulfur content below that value is desired, e.g., less than about 100 ppm, or less than about 50 ppm.]

10 If it is desired to subject the above-mentioned starting hydrocarbon feedstock to a first hydrotreating (hydrodesulfurisation) step to reduce its sulfur content to a value less than about 0.1 wt.%, this can be carried out in various ways. One can, e.g., use a conventional hydrodesulfurisation catalysts comprising a Group VIB metal component, a Group VIII metal component, and, optionally,
15 phosphorus on a carrier comprising alumina. Suitable hydrodesulfurisation catalysts are commercially available, and include for example KF 756 and KF 901 of Akzo Nobel. It is also possible to effect such first hydrodesulfurisation step by means of a two-step process, such as those described in EP 0 464 931, EP-A 0 523 679 or EP 870 807. If so desired, one may also use an
20 additive-based catalyst to effect such first hydrodesulfurisation step.

The present invention also pertains to a two-step process for converting a starting feedstock having a sulfur content of above about 0.1 wt.% into a product having a sulfur content of less than about 200 ppm, wherein the
25 process comprises optionally sulfiding and/or activating a first and a second catalyst comprising a Group VIB metal component and a Group VIII metal component, with at least the second catalyst additionally comprising an S-containing organic additive, contacting a feedstock with a 95% boiling point of about 450°C or less and a sulfur content of about 0.1 wt.% or more with the first
30 catalyst under conditions of elevated temperature and pressure to form a

product with a sulfur content of less than about 0.1 wt.%, preferably less than about 500 ppm, and contacting the effluent from the first catalyst, optionally after fractionation or intermediate phase separation, with the second catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 200 ppm, preferably less than about 100 ppm, more preferably less than about 50 ppm.

It is considered preferred at this point in time for the first catalyst to comprise molybdenum as Group VIB metal component and cobalt and/or nickel as Group VIII metal component, with the second catalyst comprising molybdenum as Group VIB metal component and nickel as Group VIII metal component. The two-step process can be carried out in one or two reactors, as may be desired. If both catalysts contain an organic additive, the two catalysts may be the same or different.

15 The process conditions

The process according to the invention is carried out at elevated temperature and pressure. The temperature generally is about 200 to about 450°C, preferably about 280 to about 430°C. The reactor inlet hydrogen partial pressure generally is about 5 to about 200 bar, preferably about 10 to about 100 bar, more preferably about 15 to about 60 bar. The liquid hourly space velocity preferably is between about 0.1 and about 10 vol./vol.h, more preferably between about 0.5 and about 4 vol./vol.h. The H₂/oil ratio generally is in the range of about 50 to about 2000 NI/I, preferably in the range of about 80 to about 1000 NI/I. For the two-step process described above, the reaction conditions for both steps may be selected independently from each other, taking the above-mentioned general and preferred ranges into account.

The process conditions are selected in such a way that the sulfur content of the total liquid effluent is less than about 200 ppm, preferably less than about 100 ppm, more preferably less than about 50 ppm. The exact process conditions

will depend, int. al., on the nature of the feedstock, the desired degree of hydrodesulfurisation, and the nature of the catalyst. In general, a higher temperature, a higher hydrogen partial pressure, and a lower space velocity will decrease the sulfur content of the final product. The selection of the appropriate process conditions to obtain the desired sulfur content in the product is well within the scope of the person skilled in the art of hydroprocessing.

Example 1

10 Preparation of additive-containing catalyst

Extrudates of a gamma-alumina carrier were impregnated to pore volume saturation with an impregnation solution comprising a molybdenum compound, a nickel compound, and phosphoric acid, after which the impregnated carrier was dried at a temperature of 140°C for a period of 16 hours. The dried extrudates were impregnated with a solution of thioglycolic acid (TGA), and dried. The final catalyst contained 20 wt.% of molybdenum, calculated as trioxide, 5 wt.% of nickel, calculated as oxide, and 7 wt.% of phosphorus, calculated as P_2O_5 . All weight percentages are calculated on the dry catalyst base, not including the additive. The molar ratio between TGA and the total of Ni and Mo is 0.4.

The catalyst according to the invention was tested in an upflow tubular reactor side by side with commercial catalyst KF 756 of Akzo Nobel. Each reactor tube contained 75 ml of catalyst homogeneously intermixed with 70 ml of carborundum particles. The catalysts were sulfided using the feed specified below in which dimethyl disulfide had been dissolved to a total S content of 2.5 wt.%.

The feed applied was a Kuwait petroleum gas oil feedstock with the following properties.

Nitrogen (ASTM D-4629) (ppmwt)	86
Sulfur (ASTM D-4294) (ppmwt)	1.2 wt. %
Density 15°C (g/ml)	0.84
Dist. (°C)	ASTM D-86
IBP	184
5 vol. %	219
10 vol. %	231
30 vol. %	265
50 vol. %	287
70 vol. %	310
90 vol. %	345
95 vol. %	360
FBP	373

The catalysts were tested under the two test conditions given below.

	Condition 1	Condition 2
pressure (bar)	40	20
Temperature (°C)	330	340
LHSV (h ⁻¹)	2	1.5
H ₂ /oil ratio (NI/l)	300	300

- 5 The products from the different runs were analysed. The results thereof are given below.

Condition 1

	Catalyst according to the invention	Comparative catalyst
product S (ppm)	21	279
product N (ppm)	0.9	14

- 10 Condition 2

	Catalyst according to the invention	Comparative catalyst
product S (ppm)	51	132
product N (ppm)	5	35

This example shows that the catalyst according to the invention which contains an S-containing additive gives a much lower S and N level in the final product than the comparative commercial catalyst.

CLAIMS

1. A process for reducing the sulfur content of a hydrocarbon feedstock to a value of less than about 200 ppm, comprising optionally subjecting a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive to a sulfidation step and/or activation step, and contacting a feedstock with a 95% boiling point of about 450°C or less with the optionally sulfided and/or activated catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 200 ppm.
2. The process of claim 1 wherein the sulfur content of the product is less than about 50 ppm.
3. The process of claim 1 or 2 wherein the S-containing organic additive is a mercaptocarboxylic acid represented by the general formula HS-R1-COOR, wherein R1 stands for a divalent hydrocarbon group with 1 to about 10 carbon atoms and R stands for a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, or a linear or branched alkyl group having 1 to about 10 carbon atoms.
4. The process of any one of the preceding claims, wherein the sulfur content of the feedstock is between about 150 ppm and about 2 wt. %.
5. The process of claim 4, wherein the sulfur content of the feedstock is between about 0.1 wt. % and about 2 wt. %.
6. The process of claim 4, wherein the sulfur content of the feedstock is between about 150 ppm and about 500 ppm.

7. A two-step process for converting a starting feedstock having a sulfur content of above about 0.1 wt.% into a product having a sulfur content of about 200 ppm or less, wherein the process comprises optionally sulfiding and/or activating a first and a second catalyst comprising a Group VIB metal component and a Group VIII metal component, with at least the second catalyst additionally comprising an S-containing organic additive, contacting a feedstock with a 95% boiling point of about 450°C or less and a sulfur content of about 0.1 wt.% or more with the first catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 0.1 wt.%, and contacting the effluent from the first catalyst, optionally after fractionation or intermediate phase separation, with the second catalyst under conditions of elevated temperature and pressure to form a product with a sulfur content of less than about 200 ppm.
8. The process of claim 7 wherein the first catalyst comprises molybdenum as Group VIB metal component and cobalt and/or nickel as Group VIII metal component, while the second catalyst comprises molybdenum as Group VIB metal component and nickel as Group VIII metal component.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/09641

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G45/08 C10G65/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP 1 041 133 A (AKZO NOBEL NV) 4 October 2000 (2000-10-04) the whole document ----	1-8
Y	EP 0 870 817 A (AKZO NOBEL NV) 14 October 1998 (1998-10-14) the whole document ----	1-8
Y	EP 0 300 629 A (SUMITOMO METAL MINING CO) 25 January 1989 (1989-01-25) cited in the application the whole document ----	1-8
A	EP 0 357 295 A (SUMITOMO METAL MINING CO) 7 March 1990 (1990-03-07) cited in the application the whole document -----	1-8

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E earlier document but published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
O document referring to an oral disclosure, use, exhibition or other means	*&* document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 28 November 2001	Date of mailing of the international search report 06/12/2001
---	--

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Michiels, P
--	---------------------------------------

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/09641

Patent document cited in search report	Publication date	Patent family member(s)	Publication date			
EP 1041133	A	04-10-2000	EP 1041133 A1 04-10-2000			
			JP 2000313890 A 14-11-2000			
EP 0870817	A	14-10-1998	EP 0870817 A1 14-10-1998			
			JP 10310782 A 24-11-1998			
			SG 76541 A1 21-11-2000			
EP 0300629	A	25-01-1989	JP 1011644 A 17-01-1989			
			JP 1011645 A 17-01-1989			
			JP 1974647 C 27-09-1995			
			JP 7000178 B 11-01-1995			
			JP 1011646 A 17-01-1989			
			JP 1011647 A 17-01-1989			
			JP 1011649 A 17-01-1989			
			JP 1720081 C 14-12-1992			
			JP 4006418 B 05-02-1992			
			DE 3861642 D1 28-02-1991			
			EP 0300629 A1 25-01-1989			
			US 4981828 A 01-01-1991			
			EP 0357295	A	07-03-1990	JP 1836905 C 11-04-1994
						JP 2056249 A 26-02-1990
JP 5049339 B 26-07-1993						
JP 1836906 C 11-04-1994						
JP 2071844 A 12-03-1990						
JP 5049340 B 26-07-1993						
JP 1836908 C 11-04-1994						
JP 2078441 A 19-03-1990						
JP 5049341 B 26-07-1993						
JP 1836909 C 11-04-1994						
JP 2078442 A 19-03-1990						
JP 5049342 B 26-07-1993						
JP 1836910 C 11-04-1994						
JP 2083041 A 23-03-1990						
JP 5049343 B 26-07-1993						
CA 1332934 A1 08-11-1994						
DE 68926764 D1 08-08-1996						
DE 68926764 T2 31-10-1996						
EP 0357295 A2 07-03-1990						
US 4992403 A 12-02-1991						