PROCESS FOR SULPHIDING AN ADDITIVE-CONTAINING CATALYST

The present invention relates to a process for sulphiding organic additive-containing catalysts, in particular organic additive-containing hydrotreating catalysts.

Hydrotreating catalysts comprise hydrogenation metal components, generally a Group VI metal component such as molybdenum and/or tungsten and a Group VIII metal component, such as nickel and/or cobalt generally on an oxidic carrier.

Organic additive-containing hydrotreating catalysts are known in the art. For example, European patent application 0 601 722 describes hydrotreating catalysts comprising a gamma-alumina support impregnated with a Group VIB metal component, a Group VIII metal component, and an organic additive which is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds.

Japanese patent application 04-166231 describes a hydrotreating catalyst prepared by a process in which a support is impregnated with an impregnation solution comprising a Group VIB metal component, a Group VIII metal component, and, optionally, a phosphorus component. The support is dried at a temperature below 200°C, contacted with a polyol, and then dried again at a temperature below 200°C. Japanese patent application 04-166233 describes an alkoxycarboxylic acid-containing catalyst prepared by substantially the same process.

Japanese patent application 06-339635 describes a hydrotreating catalyst prepared by a process in which a support is impregnated with an impregnation solution comprising an organic acid, Group VIB and Group VIII hydrogenation metal components, and preferably a phosphorus component. The impregnated support is dried at a temperature below 200°C. The dried impregnated support

is contacted with an organic acid or polyol, after which the thus treated support is dried at a temperature below 200°C.

Japanese patent application 06-210182 describes an additive-containing catalyst based on a boria-alumina support comprising 3-15 wt.% of boria.

Non-prepublished European patent application No. 99201051.2 in the name of Akzo Nobel filed on April 8, 1999, describes a catalyst containing an organic compound comprising N and carbonyl.

The additive-containing catalysts of the above references all show an increased activity in the hydrotreating of hydrocarbon feeds as compared to comparable catalysts which do not contain an organic additive.

Before use, the hydrogenation metal components present in hydrotreating catalysts, including the additive-containing catalysts of the above references, will generally be converted into their sulphides. This process is conventionally indicated as sulphidation or presulphidation. It is generally done before the catalyst is used in hydrotreating to ensure a stable reactor performance.

The above-mentioned references indicate that the catalysts described therein can suitably be sulphided in the hydrotreating reactor by being contacted in the liquid phase with a sulphur-containing hydrocarbon feed in the presence of hydrogen. This can either be a feed to which a sulphur component, e.g., dimethyldisulphide, has been added (spiked feed) or, if the sulphur content of the feed to be hydrotreated is sufficiently high, the feed itself.

However, not all hydrotreating units are suitable for such *in situ* liquid sulphidation procedures. Some hydrotreating units use a gas phase sulphiding process, conventionally with H_2S and H_2 or with H_2 and a compound which decomposes into H_2S, such as DMDS.

Moreover, some hydrotreating units are required by the authorities to carry out a pressure test as part of their start-up procedure. This pressure test is generally

carried out in the presence of hydrogen at a pressure above operating pressure and a temperature above 100°C in the absence of liquid.

It has been found that when an additive-containing catalyst is subjected to a gas phase start-up procedure or a start-up procedure including a pressure test, the activity of the catalyst is not good.

There is therefore need for a process for sulphiding additive-containing catalysts which would make it possible to obtain catalysts suitable for units which cannot perform sulphidation in the liquid phase or which are required to carry out a pressure test as described above.

It has now been found that sulphided catalysts with a high activity can be obtained by way of a gas phase sulphidation process in which a catalyst composition comprising at least one hydrogenation metal component of Group VI and/or Group VIII of the Periodic Table and an organic additive is first contacted with an organic liquid, followed by the catalyst being contacted with hydrogen and a sulphur-containing compound in the gaseous phase, wherein less than 40% of the sulphur present in the sulphided catalyst is added with the organic liquid.

The sulphidation process

In the process according to the invention, the organic additive-containing catalyst is first contacted with an organic liquid. The organic liquid generally has a boiling range of 100-550°C, preferably 150-500°C. It generally is a petroleum fraction. By their nature, petroleum fractions comprise less than 12 wt.% of oxygen. Petroleum fractions comprising less than 8 wt.% of oxygen, preferably less than 5 wt.%, more preferably less than 2 wt.%, specifically less than 0.5 wt.% of oxygen, may be preferred. Although the olefin content of the organic liquid is not critical to the process according to the invention, petroleum fractions with and iodine number of 50 or less, specifically 30 or less, may be preferred.

Examples of suitable petroleum fractions include fractions comprising heavy oils, lubricating oil fractions like mineral lube oil (360°C < BP < 500°C), atmospheric gas oils, vacuum gas oils, straight run gas oils (250°C < BP < 350°C), white spirit (180°C < BP < 220°C), middle distillates like diesel, jet fuel and heating oil, naphthas, and gasoline. Preferably white oil, gasoline, diesel, gas oil, or mineral lube oil is used.

The organic liquid ensures that the catalyst is able to withstand the conditions prevailing during the actual sulphidation step, that is, during the contacting of the catalyst with hydrogen and a sulphur-containing compound, or during the pressure test. The organic liquid is not particularly intended to bring sulphur into the catalyst. Nevertheless, petroleum cuts such as a gas oil or diesel may sometimes contain sulphur. Generally, the organic liquid will contain less than 10 wt.% of sulphur, preferably less than 5 wt.%. The amount of sulphur added with the organic liquid will be less than 40%, preferably less than 35% of the total amount of sulphur added to the catalyst with the organic liquid and by way of the sulphur-containing compound applied in the gaseous phase, more preferably less than 25%, even more preferably less than 15%.

The amount of organic liquid generally is 20-500% of the catalyst pore volume which can be filled with the liquid at issue under the conditions of application of the liquid. The pore volume can easily be determined by slowly adding liquid under said conditions to a certain amount of catalyst in a closed flask while shaking and determining by visual inspection when the liquid is no longer adsorbed. Another method is to add excess liquid and to remove the excess from the catalyst, e.g., by centrifugation. The person skilled in the art of pore volume impregnation is familiar with these procedures. To get the desired effect and avoid waste of material an amount of 50-200%, more in particular 50-125%, is preferred. Evidently, if excess liquid is present it can easily be removed, e.g., by drying the catalyst.

The way in which the catalyst is contacted with the organic liquid is not critical to the invention as long as it is ensured that each catalyst particle is contacted with the organic liquid. Conventional mixing methods may be applied. The organic liquid is generally contacted with the catalyst particles at a temperature between room temperature and 200°C. Increased temperatures may sometimes be desired because they decrease the viscosity of the liquid. The suitable contacting time may depend on whether the operation is carried out *ex situ* or *in situ*. For *ex situ* operation the temperature may preferably be between room temperature and 75°C. For *in situ* operation the temperature may preferably be between 100 and 175°C. The contacting of the catalyst with organic liquid is carried out in the substantial absence of hydrogen.

After the incorporation of an organic liquid, the catalyst is contacted in the gaseous phase with hydrogen and a sulphur-containing compound.
The sulphur-containing compound is H_2S and/or a compound which is decomposable into hydrogen sulphide under the conditions prevailing during the contacting of the catalyst with hydrogen and a sulphur-containing compound. Examples of suitable components decomposable into H_2S are mercaptans, CS_2, thiophenes, dimethyl sulphide (DMS), dimethyl disulphide (DMDS), and suitable S-containing refinery gasses and various polysulphides. The use of H_2S alone is preferred. The skilled person knows how to select a sulphur compound which will decompose under the conditions applied.

The total amount of sulphur-containing compound which is incorporated into the catalyst in the process according to the invention is generally selected to correspond to 50-500%, preferably 70-200%, more preferably 80-150%, of the stoichiometric sulphur quantity necessary to convert the hydrogenation metals into Co_9S_8, MoS_2, WS_2, and Ni_3S_2, respectively. Gas recycle may be attractive.

The concentration of sulphur-containing compound in the mixture of H_2 and sulphur-containing compound is generally selected to be between 1 and 99 wt.%, preferably between 10 and 80%, calculated as H_2S on the total of H_2S

and hydrogen. Of course, lower sulphur concentrations in this mixture will either lengthen the duration of this process step or increase the required space velocity.

The contacting in the gaseous phase with hydrogen and a sulphur-containing compound can be done in one step. In that case, it is preferably carried out at a temperature of 150-500°C, preferably 225-400°C. More precisely, when indicating a sulphiding temperature of, e.g., 350°C, it means that the final temperature plateau is at 350°C. The temperature of the first contact between sulphiding agent and catalyst may preferably take place at a lower temperature, for instance between room temperature and 200°C.

Catalysts with a higher activity may be obtained when the contacting in the gaseous phase with hydrogen and a sulphur-containing compound is carried out in two steps, with the first step being performed at a lower temperature than the second step. In this embodiment the first step is generally carried out at a final temperature of 50-250°C, preferably 100-225°C. The second step is generally carried out at a final temperature of 150-500°C, preferably 200-450°C, more preferably 225-400°C. In this two-step embodiment, the gaseous mixtures of H_2 and sulphur-containing compound applied in the two steps may be the same or different. If so desired, this part of the process may also be carried out in more than two steps, e.g., in three steps or in a continuous mode, as long as the first step, or the start of this part of the process, is carried out at a lower temperature than a further step, or later part of this part of the process.

The total pressure during the process according to the invention, more in particular, the pressure in the gaseous phase, is not critical. It will generally be between atmospheric pressure and 300 bar, depending on where the process is carried out. If the process is carried out *ex situ*, the pressure may, e.g., be between atmospheric pressure and 10 bar. If the process is carried out *in situ*, the pressure may be much higher, e.g., in the range of 25 to 300 bar.

The contacting in the gaseous phase with hydrogen and a sulphur-containing compound can be carried out in any suitable manner, including in fixed bed

processes and moving bed processes. Since the sulphiding step is exothermic by nature, it is important that the temperature of the catalyst is well-controlled. Generally, such control is easier in a moving bed process. In the context of the present specification, a moving bed process is intended to encompass all processes in which the catalyst moves relative to the reactor. Examples are ebullated bed processes, fluidized bed processes and processes carried out in a rotary furnace. In the latter, the contacting can be done either co-currently or counter-currently, with counter-current operation being preferred.

It is noted that the S-containing compound present in the gas phase does not refer to decomposition products from the S-containing compounds, if any, incorporated therein with the organic liquid, but refers to S-containing compound added extraneously to the hydrogen.

The various steps of the process according to the invention can be carried out *ex situ* or *in situ*. In the context of the present specification, the term *in situ* means in the reactor in which the catalyst will eventually be applied to effect hydrotreating. Conversely, *ex situ* means outside said reactor.

For example, it is possible to effect the contacting with the organic liquid *ex situ* while the contacting with hydrogen and a sulphur-containing compound is effected *in situ*, optionally with a pressure test being carried out before the contacting with hydrogen and a sulphur-containing compound. It is also possible to effect the complete process *ex situ*, or to effect the complete process *in situ*.

It is generally preferred to carry out the complete process *ex situ*, because this generates less downtime for the hydrotreating reactor and simplifies the reactor start-up.

If the process according to the invention is carried out *ex situ*, it may be desirable to passivate the sulphided catalyst prepared in this way, since sulphided catalysts are self-heating. Passivation can be done by contacting the sulphided catalyst with an oxygen-containing compound under controlled conditions. The use of an oxygen-containing gas, such as air, is a well-known embodiment. Alternatively, the sulphided catalyst may be passivated by being

contacted with an organic liquid, such as diesel, gas oil, white spirit, or lube oil. Passivation processes are known in the art. See, for example, EP-897 748 and NL 8900914, which describe the use of hydrocarbons, and V.M. Browne, S.P.A. Louwers, and R. Prins, *Catalysis Today* volume 10 number 3 pp 345-52 (1991) and S.P.A. Louwers, M.W.J. Craje, C. Geantet, A.M. van der Kraan, and R. Prins, *Journal of Catalysis* volume 144 number 2 pp. 579-96 (1993), both of which describe the use of oxygen.

The additive-containing catalyst

In principle, the additive-containing catalyst can be any catalyst which comprises a Group VIB hydrogenation metal component and/or a Group VIII hydrogenation metal component, and an organic additive, generally on a carrier. Catalysts comprising the combination of a Group VIB hydrogenation metal component and a Group VIII hydrogenation metal component are preferred. As the skilled person will recognise, the metals may be present in any form. When they are incorporated into the catalyst composition they are often in the form of their salts or oxides. After calcination they are converted partly or wholly into their respective oxides. After sulphidation and during use the metals are at least partly present in the sulphidic form.

As Group VIB metals may be mentioned molybdenum, tungsten, and chromium. Group VIII metals include nickel, cobalt, and iron. Catalysts comprising molybdenum and/or tungsten as Group VIB metal component and nickel and/or cobalt as Group VIII metal component are the most common. The catalyst usually has a metal content in the range of 0.1 to 50 wt.% calculated as oxides on the dry weight of the catalyst not containing the additive. The Group VIB metal will frequently be present in an amount of 5-40 wt.%, preferably 15-30 wt.%, calculated as trioxide. The Group VIII metal will frequently be present in an amount of 1-10 wt.%, preferably 2-7 wt.%, calculated as monoxide. The catalyst may also contain other components, such as phosphorus, halogens,

and boron. Particularly, the presence of phosphorus in an amount of 1-10 wt.%, calculated as P_2O_5, may be preferred.

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

The catalyst's pore volume (measured via N_2 adsorption) generally is in the range of 0.25 to 1 ml/g. The specific surface area will generally be in the range of 50 to 400 m^2/g (measured using the BET method). Generally, the catalyst will have a median pore diameter in the range of 7-20 nm, as determined by N_2 adsorption. The figures for the pore size distribution and the surface area given above are determined after calcination 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 (2, 3 or 4 lobes).

The additive present in the catalyst may be any 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 those selected from the group of compounds comprising at least two oxygen atoms and 2-20 carbon atoms, preferably 2-10 carbon atoms and the compounds built up from these compounds. Preferably, the organic compounds are substantially saturated, as is evidenced by a iodine number of

less than 20. Organic compounds selected from the group of compounds comprising at least two oxygen-containing moieties, such as a carboxyl, carbonyl or hydroxyl moieties, and 2-10 carbon atoms and the compounds built up from these compounds are preferred. Examples of suitable compounds include citric acid, tartaric acid, oxalic acid, malonic acid, malic acid, butanediol, pyruvic aldehyde, glycolic aldehyde, and acetaldol. At this point in time, preference is given to an additive that is selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms per molecule, and the (poly)ethers of these compounds. Suitable compounds from this group include aliphatic alcohols such as ethylene glycol, propylene glycol, glycerin, trimethylol ethane, trimethylol propane, etc. Ethers of these compounds include diethylene glycol, dipropylene glycol, trimethylene glycol, triethylene glycol, tributylene glycol, tetraethylene glycol, tetrapentylene glycol. This range can be extrapolated to include polyethers like polyethylene glycol. Other ethers which are suitable for use in the present invention include ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, and diethylene glycol monobutyl ether. Of these, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, proplylene glycol, dipropylene glycol, and polyethylene glycol with a molecular weight between 200 and 600 are preferred.

Another group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms per molecule are the saccharides. Preferred saccharides include monosaccharides such as glucose and fructose. Ethers thereof include disaccharides such as lactose, maltose, and saccharose. Polyethers of these compounds include the polysaccharides.

A further group of additives are those compounds comprising at least one covalently bonded nitrogen atom and at least one carbonyl moiety. Examples include aminopolycarboxylic acids, such as nitrilo-triacetic acid and diethylene-triamine-pentaacetic acid. In this case the organic compound preferably comprises at least two nitrogen atoms and preferably at least two carbonyl moieties. It is further preferred that at least one carbonyl moiety is present in a carboxyl group. It is furthermore preferred that at least one nitrogen atom is

covalently bonded to at least two carbon atoms. A preferred organic compound is a compound satisfying formula (I)

$$(R1R2)N - R3 - N(R1'R2') \qquad (I)$$

wherein R1, R2, R1' and R2' are independently selected from alkyl, alkenyl, and allyl with up to 10 carbon atoms optionally substituted with one or more groups selected from carbonyl, carboxyl, ester, ether, amino, or amido. R3 is an alkylene group with up to 10 carbon atoms which may be interrupted by -O- or -NR4-. R4 is selected from the same group as indicated above for R1. The R3 alkylene group may be substituted with one or more groups selected from carbonyl, carboxyl, ester, ether, amino, or amido. As has been set out above, it is essential that the organic compound of formula (I) comprises at least one carbonyl moiety.

Preferably, at least two of R1, R2, R1' and R2' have the formula - R5 - COOX, wherein R5 is an alkylene group having 1-4 carbon atoms, and X is hydrogen or another cation, such as an ammonium, a sodium, a potassium, and/or a lithium cation. If X is a multivalent cation, one X can adhere to two or more - R5 - COO groups. Typical examples of such a compound are ethylenediamine(tetra)acetic acid (EDTA), hydroxyethylenediaminetriacetic acid, and diethylenetriaminepentaacetic acid.

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 the specific situation. It was found that the appropriate amount of additive generally lies in the range of 0.01-2.5 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 additive will not improve its effect.

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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.

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. This latter method is described in EP 601 722.

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. The method with intermediate calcination is described in WO 96/41848. At present, the additive-containing catalysts prepared by the processes described in EP 0601 722 and WO 96/41848 are considered preferred as source for the additive-based catalyst to be sulphided in the process according to the invention.

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 solid form, in liquid form, or dissolved in a suitable solvent. It may be preferred for the additive to be incorporated into the catalyst dissolved in water.

Use of the sulphided catalyst prepared according to the invention

The catalyst sulphided by the process according to the invention can be used in the hydrotreating of hydrocarbon feeds. The hydrotreating generally takes place under conventional hydrotreating conditions, such as temperatures in the range of 250-450°C, pressures in the range of 5-250 bar, space velocities in the range of 0,1- 10 h^{-1}, and H_2/oil ratios in the range of 50-2000 Nl/l. Examples of suitable feeds include middle distillates, kerosine, naphtha, vacuum gas oils, heavy gas oils and residues. Preferably, the hydrocarbon feed contains at least 0.2 wt% of sulphur, calculated as atomic sulphur S. Examples of suitable hydrotreating reactions are (deep) hydrodesulphurisation, hydrodenitrogenation, hydrodearomatisation, and hydrodemetallisation. (Deep) hydrodesulphurisation, hydrodenitrogenation, and hydrodearomatisation are preferred.

The catalyst which is sulphided by the process according to the invention can be applied either in a reactor which is started up in the gas phase or in a reactor which is started up in the liquid phase, optionally in the presence of optionally spiked feed.

Example 1

Starting material

A conventional hydrotreating catalyst containing 26 wt.% molybdenum, calculated as trioxide, 4.7 wt.% nickel, calculated as oxide, and 6.7 wt.% phosphorus, calculated as P_2O_5, on a gamma-alumina carrier was impregnated by pore volume impregnation with a solution of diethylene glycol in water, containing 0.44 mole diethylene glycol per mole of the total of molybdenum and nickel. Then, the catalyst is dried rotating with hot air to a product temperature of 130°C.

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Comparative presulphiding procedure

The additive-containing starting catalyst catalyst (10 ml) was sulphided in the gas phase at atmospheric pressure using a mixture of 10 vol.% H_2S in H_2 (flow = 5 l/hr) in one step. The temperature was increased by 0.5°C per minute to 300°C (=10 hr) and held at that temperature for 3 hours.

One-step presulphiding according to the invention

The additive-containing starting catalyst was pore volume impregnated with SRGO (straight run gas oil) in an amount corresponding to 0.18 g SRGO per gram catalyst. This additive-containing SRGO-impregnated Ni-Mo-P/γ-Al_2O_3 catalyst (10 ml) was sulphided in the gas phase in one step in the same way as described above.

Two-step presulphiding according to the invention

The additive-containing starting catalyst was pore volume impregnated with SRGO (straight run gas oil) in an amount corresponding to 0.18 g SRGO per gram catalyst. This additive-containing SRGO-impregnated Ni-Mo-P/γ-Al_2O_3 catalyst (10 ml) was sulphided in the gas phase at atmospheric pressure using a mixture of 10 vol.% H_2S in H_2 (flow = 5l/hr) in two steps. The temperature was first increased by 0.5°C per minute to 180°C and held at 180°C for 3 hours. Then, the temperature was increased by 0.5°C per minute to 300°C and held at 300°C for 3 hours.

Testing

The catalysts were tested in an upflow tubular reactor using a SRGO with the properties given in table 1. The reaction conditions are given in table 2.

Table 1: feedstock properties

Type feed	Straight run gas oil
Nitrogen (ASTM D-4629) (ppmwt)	115
Sulphur (ASTM D-4294) (wt.%)	1.2
Density 15°C (g/ml)	0.84
Dist. (°C) (ASTM D 1160)	
IBP	121
5 vol.%	177
10 vol.%	203
30 vol.%	254
50 vol.%	292
70 vol.%	330
90 vol.%	386
95 vol.%	412
FBP	476

Table 2: Reaction conditions

	1st condition	2nd condition
Temperature (°C)	340	340
Pressure (bar)	30	30
H_2/oil (Nl/l)	125	250
LHSV (h-1)	2.0	1.0

The oil product from the reactor was analysed, and the relative volume activities of the catalysts for hydrodesulphurisation, hydrodenitrogenation, and hydrodearomatisation were calculated, with the activity the starting material activated using the comparative presulfiding procedure being set at 100. The results are given in Table 3 below.

Table 3: test results

	Comparative presulfiding procedure		One-step presulfiding procedure according to the invention		Two-step presulfiding procedure according to the invention	
condition	1st	2nd	1st	2nd	1st	2nd
RVA HDS	100	100	188	193	204	203
RVA HDN	100	100	119	117	125	121
RVA HAD	100	100	143	138	136	145

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This shows that one-step presulfiding procedure according to the invention, which includes a catalyst prewetting step, shows a highly improved activity as compared to the comparative presulfiding procedure. The activity obtained after a two-step presulfiding procedure, which is in accordance with a preferred embodiment of the invention, was even higher.

Example 2

A conventional hydrotreating catalyst containing 24 wt.% molybdenum, calculated as trioxide, 4 wt.% nickel, calculated as oxide, and 7 wt.% phosphorus, calculated as P_2O_5, on a gamma-alumina carrier was impregnated by pore volume impregnation with a solution of ethylene diamine tetra-acetic acid (EDTA) in water, containing 0.11 mole EDTA per mole of the total of molybdenum and nickel. Then, the catalyst was dried rotating with hot air to a product temperature of 130°C.

The catalyst was presulphided according to the invention by prewetting it with SRGO followed by two-step gaseous presulphiding in the same way as described in example 1. The catalyst was subsequently tested in accordance with the process described in example 1. Table 4 shows the results obtained.

Table 4

	Feed	Product 1st condition	Product 2nd condition
Sulphur content	1.2 wt.%	0.16 wt.%	0.03 wt.%
Nitrogen content	115 ppm	54 ppm	25 ppm
Aromatics content	28.4 wt.%	26.9 wt.%	25.8 wt.%

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CLAIMS

1. A process for sulphiding a catalyst composition comprising at least one hydrogenation metal component of Group VI and/or Group VIII of the Periodic Table, and an organic additive wherein the catalyst composition is first contacted with an organic liquid in the substantial absence of hydrogen, followed by the catalyst being contacted with hydrogen and a sulphur-containing compound in the gaseous phase, wherein less than 40% of the sulphur present in the sulphided catalyst is added with the organic liquid.

2. The process of claim 1 wherein the sulphur-containing compound applied in the gaseous phase is H_2S.

3. The process of either of the preceding claims wherein the organic liquid is a hydrocarbon with a boiling range of 150-500°C, preferably gasoline, white spirit, diesel, gas oil, mineral lube oil, or white oil.

4. The process of any one of the preceding claims wherein the contacting of the catalyst with hydrogen and a sulphur-containing compound in the gaseous phase takes place in one step at a final temperature of 150-500°C.

5. The process of any one of claims 1-3 wherein the contacting of the catalyst with hydrogen and a sulphur-containing compound in the gaseous phase is carried out in two steps, with the first step being performed at a final temperature which is lower than that of the second step.

6. The process of claim 5 wherein the first step is carried out at a final temperature of 100-250°C and the second step is carried out at a final temperature of 150-500°C.

7. The process according to any one of the preceding claims wherein the organic additive is selected from the group of compounds comprising at least two hydroxyl-groups and 2-10 carbon atoms per molecule, and the (poly)ethers of these compounds.

8. The process according to any one of the preceding claims 1 to 6 wherein the organic additive is an organic compound which comprises at least two nitrogen atoms and at least two carbonyl moieties.

9. The process according to any one of the preceding claims wherein both the contacting with the organic liquid and the contacting with hydrogen and a sulphur-containing compound are carried out *ex situ*.

10. The process of claim 9 wherein the *ex situ* sulphided catalyst is passivated after the treatment with hydrogen and the sulphur-containing compound.