PROCESS FOR THE SULPHURIZATION OF HYDROTREATING CATALYSTS

The present invention relates to hydrotreating hydrocarbon feedstocks and more particularly to a process for the sulphurization of catalysts for use for this purpose.

Catalysts for hydrotreating hydrocarbon feedstocks may be used under conditions appropriate for converting organosulphur compounds to hydrogen sulphide in the presence of hydrogen, which operation is known as hydrodesulphurization (HDS), and for converting organonitrogen compounds to ammonia in an operation which is known as hydrodenitrogenation (HDN).

These catalysts are generally based on metals from groups VIB and VIII of the Periodic Classification of the Elements, such as molybdenum, tungsten, nickel and cobalt. The most commonly used hydrotreating catalysts are formulated from cobalt-molybdenum (Co-Mo), nickel-molybdenum (Ni-Mo) and nickel-tungsten (Ni-W) systems on porous inorganic supports, such as aluminas, silicas or silicas/aluminas. These catalysts, manufactured industrially in very large tonnages, are supplied to the user in their oxide forms (for example, cobalt oxides-molybdenum oxide catalysts on alumina, symbolized by the abbreviation: Co-Mo/alumina).

However, these catalysts are active in hydrotreating operations only in the form of metal sulphides. Therefore, before being used, they have to be sulphurized.

As regards the activation of hydrotreating catalysts, the sulphurization of these catalysts is an important stage in obtaining their maximum performance with regard to HDS and HDN. As indicated by the authors of Hydrotreating Catalysis (Catalysis, Vol. 11, 1996, p. 25, edited by J.R. Anderson and M. Boudart), practical experience has shown that the sulphurization procedure can have a significant influence on the activity and stability of the catalyst, and much effort has been devoted to improving the sulphurization procedures.

The most direct method for the sulphurization of a catalyst consists of treating the latter with hydrogen sulphide mixed with hydrogen. This method, which has formed the subject-matter of many patents (for example, US patent specifications US 3,016,347, US 3,140,994, US 3,732,155, US 4,098,682, US 4,132,632, US 4,172,027, US 4,176,087 and US 4,334,982, United Kingdom patent specification GB 1,309,457

and French patent specification FR 2,476,118), is generally only used in the laboratory, as the use of hydrogen sulphide has major disadvantages which do not allow it to be employed on every industrial site.

Industrial procedures for the sulphurization of hydrotreating catalysts are generally carried out under hydrogen pressure with liquid feedstocks already comprising sulphur compounds as the sulphurizing agents. The method chiefly used in the past by refiners consisted of sulphurizing the catalysts with the sulphur-comprising oil feedstocks. However, this technique had significant disadvantages because of the difficulty of converting the sulphur compounds to hydrogen sulphide. To avoid reduction of the catalysts by the hydrogen, the sulphurization, initiated at low temperature, had to be taken slowly to high temperature in order to obtain complete sulphurization of the catalysts.

The use of sulphur-comprising additives has been proposed for improving the sulphurization of hydrotreating catalysts. Such methods consist of incorporating a sulphur compound (spiking agent) in a feedstock, such as a naphtha, or in a specific fraction, such as a VGO (vacuum gas oil) or an LGO (light gas oil). US patent specification US 3,140,994 was the first to describe the use of compounds of different natures which are liquid at ambient temperature, namely carbon disulphide, thiophene, mercaptans, dialkyl disulphides and diaryl disulphides. Organic sulphides, in particular dimethyl sulphide, have also been used. Dimethyl disulphide (DMDS) has been more particularly recommended for the sulphurization of the catalysts and an effective method for sulphurization with dimethyl disulphide is disclosed in European patent EP 064,429.

H. Hallie (Oil and Gas Journal, Dec. 20, 1982, pp 69-74) has reviewed these procedures for sulphurization under hydrogen which are carried out directly in hydrotreating reactors. These various techniques for the sulphurization of catalysts, known as "in situ" techniques, have been compared and studies have shown that sulphurization with a liquid feedstock to which has been added a sulphurizing agent which has the property of decomposing at low temperature (spiked feedstock) is the best sulphurization technique. The technique without an additional sulphurizing agent

(nonspiked feedstock) gives a less active sulphurized catalyst. Preferably, the sulphurizing agent added to the feedstock is dimethyl disulphide.

Organic polysulphides have also been described as sulphurizing agents for the sulphurization of hydrotreating catalysts. US patent US 4,725,569 discloses a method for the use of organic polysulphides of RS_xR' type (wherein R and R' are the same or different and x is greater than or equal to 3) which consists of impregnating the catalyst at ambient temperature with a solution comprising the polysulphide, subsequently removing the inert solvent and, finally, carrying out the sulphurization, under hydrogen, of the charged catalyst in the hydrotreating reactor. In European patent EP 298,111, the polysulphide of RS_xR' type, diluted in a liquid feedstock, is injected during the sulphurization of the catalyst in the presence of hydrogen.

Functionalized mercaptans, such as mercaptocarboxylic acids or esters, dithiols, aminomercaptans and hydroxymercaptans, as well as thiocarboxylic acids or esters, are described in European patent EP 289,211 for the sulphurization of hydrotreating catalysts.

More recently, new techniques for the sulphurization of hydrotreating catalysts comprising two stages have been developed. In a first stage, known as an "ex situ" stage, the catalyst is preactivated in the absence of hydrogen outside the refinery after having been impregnated with a sulphurizing agent. The complete sulphurization of the catalyst is carried out in the hydrotreating reactor in the presence of hydrogen. The "ex situ" presulphurization avoids the need for injecting a sulphurizing agent during the sulphurization of the catalyst under hydrogen. The "ex situ" techniques developed at present use organic polysulphides or sulphur as sulphur-comprising products.

An industrial technique for the presulphurization of catalysts under "ex situ" conditions, based on the use of organic polysulphides of the RS_xR' type (wherein R and R' are the same or different and $x \geq 3$), is described in European patent EP 130,850. This process consists of impregnating the catalyst, in oxide form, with a solution of organic polysulphides, such as tert-nonyl polysulphides (TPS 37 or TNPS, sold by Elf Atochem), in a hydrocarbon of the white spirit type. This preliminary stage of

incorporation of a sulphur compound of a specific nature in the catalyst is supplemented by a heat treatment of the catalyst in the absence of hydrogen at temperatures not exceeding 150°C. This operation has the effect of removing the organic solvent and of ensuring the attachment of the sulphur to the catalyst by means of the organic polysulphides. At this presulphurization stage, the catalyst is stable in air and can be handled without specific precautions. It is supplied in this state to the user who, after charging to the hydrotreating reactor, can bring the sulphurization of the catalyst to completion under hydrogen for the complete conversion of the metals to metal sulphides.

Other organic polysulphide compounds, with different structures, have also been described for the presulphurization of hydrotreating catalysts under "ex situ" conditions. The products recommended in French patent FR 2,627,104 and European patent EP 329,499 have the general formula R'-(S_y-R-S_x-R-S_y)-R' and are obtained from olefins and sulphur chloride by a series of successive stages which involve reaction with an organic monohalide, followed by reaction with an alkaline polysulphide. In European patent EP 338,897, the products described are synthesized from olefins and sulphur chloride with an additional reaction with an alkaline mercaptide or an alkaline polysulphide mercaptate.

The development of a technique for the "ex situ" presulphurization of the catalysts using sulphur in suspension in an oil (US patent US 4,943,547) has presented such problems of industrial application that it has been necessary to develop a new process for sulphurization with sulphur which consists of bringing the catalyst into contact with sulphur and an olefin of high boiling point. The catalyst, thus impregnated, is subsequently heat-treated at a temperature of greater than 150°C and then the sulphurization of the catalyst is brought to completion under hydrogen at temperatures of greater than 200°C.

Very recently, in French patent FR 2,758,478, it has been shown that the joint use of, for example, a tertiary mercaptan and another sulphurization agent, such as dimethyl disulphide, makes it possible to obtain hydrotreating catalysts which are more

active with regard to the hydrodesulphurization of hydrocarbon feedstocks than catalysts sulphurized in the absence of tertiary mercaptan.

The aim of the present invention is to improve the sulphurization of catalysts and to increase the activity of the catalysts, in particular for the hydrotreating of hydrocarbon feedstocks.

It has now been found, surprisingly, that the joint use of a sulphurization agent and an ester of orthophthalic acid allows catalysts to be obtained which are more active with regard to hydrodesulphurization of hydrocarbon feedstocks than the catalysts sulphurized in the absence of an orthophthalic acid ester.

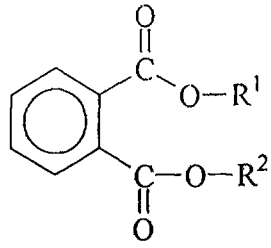
According to a first aspect of the present invention there is provided a process for the sulphurization of a metal hydrotreating catalyst which process comprises treating the catalyst with a sulphurization agent, wherein an orthophthalic acid ester is added to the sulphurization agent.

The present invention applies both to techniques for the sulphurization of the catalysts under "in situ" conditions and to those carried out under "ex situ" conditions.

In "in situ" sulphurizations, the sulphur compounds may be introduced during the treatment of the catalysts in the presence of hydrogen for the conversion of metal oxides to metal sulphides. According to the present invention, the orthophthalic acid ester may be introduced at the same time as the sulphur compounds which are generally used to generate, in the presence of hydrogen, hydrogen sulphide which ensures the conversion of the metal oxides to metal sulphides.

In "ex situ" presulphurizations, the sulphur compounds may be incorporated in the catalysts before converting the metal oxides to metal sulphides. According to the present invention, the orthophthalic acid ester can be incorporated as a mixture with the sulphur compound.

The orthophthalic acid esters used according to the present invention suitably have the general formula



in which each of R^1 and R^2, which may be the same or different, represents an alkyl (linear or branched), cycloalkyl, aryl, alkylaryl or arylalkyl radical which comprises up to 18 carbon atoms and which may be unsubstituted or substituted by one or more heteroatoms.

Preferably the orthophthalic acid esters according to the invention are those in which R^1 and R^2 are the same and each represents an alkyl radical comprising from 1 to 8 carbon atoms. More preferably, the orthophthalic acid esters are dimethyl orthophthalate, diethyl orthophthalate or bis(2-ethylhexyl) orthophthalate, due to their industrial accessibility and their moderate cost.

Sulphurization agents suitable for use according to the present invention include sulphurization agents known to a person skilled in the art, such as the feedstock to be hydrodesulphurized itself, carbon disulphide, organic sulphides, disulphides or polysulphides, such as di(tert-nonyl) polysulphides and di(tert-butyl) polysulphides, thiophene compounds or sulphur-comprising olefins obtained by heating olefins with sulphur. In one embodiment the sulphurization agent is dimethyl disulphide (DMDS).

The proportion of orthophthalic acid ester which can be used as a mixture with sulphur-comprising compounds of different natures is generally from 0.05% to 5% by weight. Preferably the proportion used is from 0.1 to 0.5% (1000 to 5000 ppm).

The catalysts sulphurized may be based on metal oxide(s). Metal catalysts suitable for sulphurization according to the present invention may be based on molybdenum, tungsten, nickel and/or cobalt oxides which are deposited on a porous inorganic support.

The metal catalysts may be, for example, mixtures of cobalt and molybdenum oxides, mixtures of nickel and molybdenum oxides or mixtures of nickel and tungsten oxides, the mixtures of oxides being supported by an alumina, a silica or a silica/alumina.

According to a second aspect the invention provides a sulphurized metal hydrotreating catalyst prepared by the process of the invention.

The invention also provides a process for hydrotreating a hydrocarbon feedstock which process comprises contacting the feedstock with a sulphurized metal hydrotreating catalyst prepared by the process of the invention. The invention further provides the use of such a catalyst in the hydrotreating of hydrocarbon feedstocks.

The following Examples illustrate the invention without limiting it.

Comparative EXAMPLE 1 (Sulphurization with dimethyl disulphide)

The test was carried out on a pilot unit of Catatest type with 75 ml of a commercial hydrodesulphurization catalyst composed of cobalt and molybdenum oxides supported on alumina.

Use was made, as sulphurization feedstock, of a gas oil resulting from the atmospheric distillation of crude oil (Gas Oil Straight Run; hereinafter GOSR) to which 2% by weight of dimethyl disulphide had been added.

The sulphurization was carried out under a pressure of 35 bar, an hourly space volume (HSV) of 2 h^{-1} and an H_2/hydrocarbon (HC) ratio of 250 Sl/l in the following way:

- rise in temperature from 150°C to 220°C at the rate of 30°C/h under the sulphurization feedstock;
- continuous monitoring of the content of H_2S in the gases exiting from the reactor;
- temperature stationary phase at 220°C maintained until 0.3% by volume of H_2S in the gases is obtained;
- rise in temperature to 350°C at the rate of 30°C/h;

- stationary phase of 14 hours at 350°C;

- stopping the sulphurization feedstock and switching over to the test feedstock.

The activity of the sulphurized catalyst was evaluated with a test feedstock also composed of a gas oil resulting from the atmospheric distillation of crude oil but without additive.

The characteristics of the test feedstock (GOSR) are collated in the following Table 1:

Table 1

Type of feedstock		**GOSR**
Relative density, 15°C	g/cm^3	0.8741
Nitrogen	ppm	239
Sulphur	% pds	1.1
ASTM D86		
SP	°C	227.3
5% vol.	°C	274.5
10% vol.	°C	292.0
30% vol.	°C	315.5
50% vol.	°C	332.0
70% vol.	°C	348.0
90% vol.	°C	367.0
95% vol.	°C	373.0
FP	°C	373.7

After the sulphurization stationary phase at 350°C, the test feedstock was injected as replacement for the sulphurization feedstock and the temperature was brought to 360°C, the other conditions (pressure, H_2/HC ratio and HSV) remaining identical.

After a stabilization phase, the activity of the catalyst was measured at 360°C and expressed in terms of relative volume activity with regard to hydrodesulphurization (RVA), this RVA being calculated in the following way:

After each activation with DMDS, with or without additive, the activity constant with regard to HDS (k) is calculated from the residual sulphur content in the test feedstock. The RVA is the ratio of this activity constant to that of the reference test (catalyst sulphurized with DMDS), expressed as a percentage, i.e. 100 x k/k_{ref}. Thus, the RVA of the catalyst sulphurized with DMDS is 100%.

EXAMPLE 2

The sulphurization feedstock used in Example 1 was replaced by the same gas oil GOSR to which has been added 2% of a mixture composed of DMDS comprising 2000 ppm of diethyl orthophthalate (DEP). The RVA, calculated at 360°C, is listed in Table 2. Only the temperature of 360°C is considered because it is this which makes it possible to obtain a residual sulphur content in the region of 500 ppm in accordance with the specification for a gas oil.

EXAMPLE 3

Example 1, using DMDS alone as sulphurization agent, was repeated for confirmation. The result is listed in Table 2.

EXAMPLE 4

Example 2, using a DMDS comprising 2000 ppm of DEP as sulphurization agent, was repeated for confirmation. The result is listed in Table 2.

EXAMPLE 5

The sulphurization feedstock according to Example 1 was replaced by the gas oil GOSR to which has been added 2% of DMDS comprising 1000 ppm of DEP.

The result is listed in Table 2.

Table 2: Results

EXAMPLE	1	2	3	4	5
Sulphurization agent	DMDS alone	DMDS + 2000 ppm of DEP	DMDS alone	DMDS + 2000 ppm of DEP	DMDS + 1000 ppm of DEP
RVA at 360°C	100	113	100	112	115

Example 2 clearly shows that the joint use of DEP and DMDS during the sulphurization results in a catalyst which is significantly more active than that of Example 1 (sulphurization without orthophthalate).

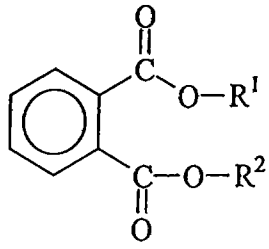
Example 3 shows the good reproducibility of the method.

Examples 4 and 5 confirm the enhancing effect of the phthalates on the hydrodesulphurizing activity and also show the low proportion which can be used to obtain this effect.

CLAIMS

1. Process for the sulphurization of a metal hydrotreating catalyst which process comprises treating the catalyst with a sulphurization agent, wherein an orthophthalic acid ester is added to the sulphurization agent.

2. Process according to claim 1, wherein the orthophthalic acid ester has the general formula



in which each of R^1 and R^2, which may be the same or different, represents an alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl radical which comprises up to 18 carbon atoms and which is unsubstituted or substituted by one or more heteroatoms.

3. Process according to claim 2, wherein R^1 and R^2 are the same and each represents an alkyl radical comprising from 1 to 8 carbon atoms.

4. Process according to claim 1, wherein the orthophthalic acid ester is dimethyl orthophthalate, diethyl orthophthalate or bis(2-ethylhexyl) orthophthalate.

5. Process according to any one of the preceding claims, wherein the amount of orthophthalic acid ester used is from 0.05 to 5% with respect to the weight of sulphurization agent.

6. Process according to claim 5, wherein the amount of orthophthalic acid ester used is between 0.1 and 0.5% with respect to the weight of sulphurization agent.

7. Process according to any one of the preceding claims, wherein the sulphurization agent is a feedstock to be hydrodesulphurized, carbon disulphide, an organic sulphide, disulphide or polysulphide, a thiophene compound or a sulphur-comprising olefin.

8. Process according to any one of claims 1 to 6, wherein the sulphurization

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agent is dimethyl disulphide.

9. Process according to any one of the preceding claims, wherein the processing is carried out in the presence of hydrogen according to the "in situ" sulphurization technique.

10. Process according to any one of claims 1 to 8, wherein the processing is firstly carried out in the absence of hydrogen according to the "ex situ" presulphurization technique.

11. Process according to any one of the preceding claims, wherein the metal catalyst to be sulphurized is a catalyst based on molybdenum, tungsten, nickel and/or cobalt oxides which are deposited on a porous inorganic support.

12. Process according to any one of claims 1 to 10, wherein the metal catalyst to be sulphurized is a mixture of cobalt and molybdenum oxides, a mixture of nickel and molybdenum oxides or a mixture of nickel and tungsten oxides, the mixture of oxides being supported by an alumina, a silica or a silica/alumina.

13. Process according to claim 1 substantially as hereinbefore described.

14. Process for the sulphurization of a metal hydrotreating catalyst substantially as described in Example 2, 4 or 5.

15. A sulphurized metal hydrotreating catalyst prepared by the process claimed in any one of the preceding claims.

16. Process for hydrotreating a hydrocarbon feedstock which process comprises contacting the feedstock with a sulphurized metal hydrotreating catalyst prepared by the process claimed in any one of claims 1 to 14.

17. Process according to claim 16 substantially as hereinbefore described.

18. Use of a metal catalyst, sulphurized by the process claimed in any one of claims 1 to 14, in the hydrotreating of hydrocarbon feedstocks.

