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EX-SITU PRESULPHIDED HYDROCARBON CONVERSION CATALYSTS

This invention relates to a process for preparing ex-situ sulphided hydrocarbon conversion catalysts, catalyst compositions resulting therefrom and their use in hydrocarbon conversion processes.

5 Many hydrocarbon conversion catalysts, such as hydrotreating, hydrocracking and tail-gas treating catalysts, are pyrophoric in their sulphided state. In the past, this pyrophoricity has been an obstacle which prevented the storage of such catalysts in a sulphided
10 state prior to their use in the respective hydrocarbon conversion operations. Because of their pyrophoric nature, they can react exothermically with oxygen when exposed to the atmosphere, to the extent that a fire hazard can result. The exothermic reaction occurs
15 between the metal sulphides and the oxygen, and even if does not occur to the extent of creating a fire hazard, it occurs at least to the extent of causing the generation of noxious fumes, including sulphur dioxide. It is known to protect such catalysts against attacks
20 by keeping them under blankets of inert gas or coating them with oil and keeping them in closed drums. However, such methods are not only unwieldy, but they do not afford protection when the catalysts are being transferred from storage drums into hydroprocessing
25 reactors.

A hydrotreating catalyst may be defined as any catalyst composition which may be employed to catalyze the hydrogenation of hydrocarbon feedstocks, and most particularly to hydrogenate particular components of

the feedstock, such as sulphur-, nitrogen- and metals-containing organo-compounds and unsaturates. A hydro-cracking catalyst may be defined as any catalyst composition which may be employed to crack large and complex petroleum derived molecules to attain smaller molecules with the concomitant addition of hydrogen to the molecules. A tail gas catalyst may be defined as any catalyst composition which may be employed to catalyze the conversion of hazardous effluent gas streams to less harmful products, and most particularly to convert oxides of sulphur to hydrogen sulphide which can be recovered and readily converted to elemental sulphur. A reduced catalyst may be defined as any catalyst composition that contains a metal in the reduced state such as an olefin hydrogenation catalyst. Such metals are typically reduced with a reducing agent such as, for example, hydrogen or formic acid. The metals on these reduced catalysts may be fully reduced or partially reduced.

Catalyst compositions for hydrogenation catalysts are well known and several are commercially available. Typically, the active phase of the catalyst is based on at least one metal of group VIII, VIB, IVB, IIB or IB of the periodic table. In general, the hydrogenation catalysts contain at least one element selected from Pt, Pd, Ru, Ir, Rh, Os, Fe, Co, Ni, Cu, Mo, W, Ti, Hg, Ag or Au supported usually on a support such as alumina, silica, silica-alumina and carbon. Such reduced catalysts can be classified as spontaneously combustible substances.

Catalyst compositions for hydrotreating and/or hydrocracking or tail gas treating are well known and several are commercially available. Metal oxide

catalysts which come within this definition include cobalt-molybdenum, nickel-tungsten, and nickel-molybdenum supported usually on alumina, silica and silica-alumina, including zeolite, carriers. Also,
5 other transition metal element catalysts may be employed for these purposes. In general, catalysts containing at least one element selected from V, Cr, Mn, Re, Co, Ni, Cu, Zn, Mo, W, Rh, Ru, Os, Ir, Pd, Pt, Ag, Au, Cd, Sn, Sb, Bi and Te have been disclosed as
10 suitable for these purposes.

For maximum effectiveness the metal oxide catalysts are converted at least in part to metal sulphides. The metal oxide catalysts can be sulphided in the reactor by contact at elevated temperatures with hydrogen
15 sulphide or a sulphur-containing oil or feed stock ("in-situ").

However, it is advantageous to the user to be supplied with sulphided catalysts, i.e., metal oxide catalysts wherein the metal oxides have been converted
20 to metal sulphides, which can be loaded into a reactor and brought up to reaction conditions without additional process steps being needed. These catalysts provide an economic advantage to the plant operator and avoid many of the hazards such as flammability and
25 toxicity, which the plant operator encounters when using hydrogen sulphide, liquid sulphides, polysulphides and/or mercaptans to sulphide the catalysts.

Several methods of presulphurizing metal oxide catalysts, i.e., converting at least part of the metal
30 oxides to metal sulphides, are known. Hydrotreating catalysts have been presulphurized by incorporating sulphur compounds into a porous catalyst prior to

hydrotreating a hydrocarbon feedstock. For example, U.S. Patent Specification No. 4,530,917 discloses a method of presulphurizing a hydrotreating catalyst with organic polysulphides. U.S. Patent Specification
5 No. 4,177,136 discloses a method of presulphurizing a catalyst by treating the catalyst with elemental sulphur. Hydrogen is then used as a reducing agent to convert the elemental sulphur to hydrogen sulphide in situ. U.S. Patent Specification No. 4,089,930 discloses
10 the pretreatment of a catalyst with elemental sulphur in the presence of hydrogen. U.S. Patent Specification No. 4,943,547 discloses a method of presulphurizing a hydrotreating catalyst by subliming elemental sulphur into the pores of the catalyst then heating the
15 sulphur-catalyst mixture to a temperature above the melting point of sulphur in the presence of hydrogen. The catalyst is activated with hydrogen. International (PCT) patent specification No. WO93/02793 discloses a method of presulphurizing a catalyst where elemental
20 sulphur is incorporated in a porous catalyst and at the same time or subsequently treating the catalyst with a liquid olefinic hydrocarbon.

However, these ex-situ presulphurized catalysts must be transported to the user or plant operator. In
25 transportation or shipping, these presulphurized catalysts are classified as spontaneously combustible substances which are further classified into two subgroups of material, pyrophoric substances or self-heating substances. Both groups have the same basic
30 properties of self-heating which may lead to spontaneous combustion, but differ in the degree of spontaneous combustion. Pyrophoric substances ignite, even in small quantities, within five minutes of coming

into contact with air whereas self-heating substances ignite in air only when in large quantities and after long periods of time. US Patent Specifications Nos. 3,563,912 and 4,177,136 amongst others propose
5 measures to avoid pyrophoricity of sulphided catalysts on exposure to air.

Further, some of the prior art ex-situ methods of presulphurizing supported metal oxide catalysts have suffered from excessive stripping of sulphur upon
10 start-up of a hydrotreating reactor in the presence of a hydrocarbon feedstock. As a result of sulphur stripping, a decrease in catalyst activity or stability is observed. Further, the stripping of sulphur can cause fouling of downstream equipment.

15 It is an object of the present invention to prepare an air and/or oxygen stable ex-situ presulphided catalyst, either fresh or regenerated, which contains only trace amounts of excess sulphur compounds and which has an activity that is equivalent to a
20 conventional in-situ sulphided catalyst.

The present invention provides a catalyst composition containing sulphided metal particles having an oxide-containing layer on the surface of said sulphided metal particles wherein said layer is formed
25 by contacting the sulphided metal particles with an oxygen-containing composition, preferably a mixture of oxygen and at least one inert gas, at a temperature in the range of from -20 °C to 150 °C and wherein said catalyst composition has reduced self-heating
30 characteristics. The resulting ex-situ presulphided catalyst composition has reduced self-heating characteristics when compared to sulphided catalysts which have not been coated, and is ready for use in the

reactor without additional processing and/or activation steps.

It has now been found that when the sulphided metal particles of a hydrocarbon conversion catalyst have an oxygen-containing protective surface layer, the catalyst has suppressed self-heating characteristics when compared to a catalyst without the protective oxygen-containing layer. Thus, the inventive process allows the ex-situ presulphided catalysts to be stored, or transported or shipped in any suitable packaging such as flow-bins, super-sacks, or sling-bins for example.

For the purpose of definition, the term "sulphided metal particles" refers to metal oxide particles which have been converted to the sulphide form. Further, the term "metal(s)" includes metal oxide(s) in partially reduced form. The term "presulphurized catalyst(s)" refers to catalysts wherein part of the metals are in the oxide form, and part of the metals may have been converted to the sulphide form. Presulphurized catalysts typically contain additional sulphur compounds which facilitate the sulphiding of the remaining metal oxides during the startup process. The term "presulphided catalyst(s)" refers to catalysts wherein the majority of the metal oxides have been converted to metal sulphides.

In the present invention, a hydrocarbon conversion catalyst containing sulphided metal particles is contacted with an oxygen-containing compound at a temperature in the range of from -20 °C to 150 °C, preferably from -20 °C to 50 °C, and more preferably from 0 °C to 35 °C. Upon contact, the surface of the sulphided metal particles is coated with the oxygen-

containing compound. For the purpose of definition, the surface of the sulphided metal particles include the external surface of the catalyst as well as the internal pore surfaces of the catalyst. The word
5 "coating" or "coated" does not rule out some reaction leading to passivation of the catalyst surfaces.

When applied to sulphided catalysts, the treatment with an oxygen-containing compound provides a catalyst with suppressed self-heating characteristics without
10 substantially compromising sulphur retention or activity. The sulphided catalysts can be catalysts sulphided by an in-situ presulphiding method or an ex-situ presulphiding or presulphurizing method. The sulphided catalysts can be fresh or oxy-regenerated.

15 For example, the oxygen-containing compound can be coated on any of the sulphur-containing catalysts such as disclosed in U.S. Patent Specification Nos. 4,530,917; 4,177,136; 4,089,930; 5,153,163; 5,139,983; 5,169,819; 4,943,547 and in PCT patent
20 specification No. WO93/02793. The oxygen-containing compound can also be coated on a reduced hydrogenation catalyst such as disclosed in U.S. Patent Specification No. 5,032,565.

25 In the present invention, the sulphided catalyst is contacted with an oxygen-containing compound at a temperature and for a time effective to cause the catalysts to exhibit suppressed self-heating properties compared to catalysts without treatment with the oxygen-containing compound. In general, the reaction
30 conditions should be such that an effective protective layer is formed, but such that the metal sulphide particles are not substantially oxidized.

The mechanism by which the oxygen-containing compound suppresses self-heating characteristics of the sulphur-incorporated catalyst when contacted is not known and will be referenced herein as "reaction" or "reacts" for lack of better terminology. The suppressed self-heating result can be readily determined without undue experimentation by measuring the exothermic onset temperatures.

Generally, the ex-situ presulphided catalysts of the present invention have enhanced resistance to sulphur stripping during activation in a hydrotreating and/or hydrocracking reactor in the presence of a hydrocarbon feedstock. The potential for sulphur stripping is less than that for a presulphurized catalyst since in the presulphurized catalyst, the bulk of the sulphur has already reacted with the metal oxide particles and is bound in the form of metal sulphide particles. The enhanced resistance to sulphur stripping can readily be determined using one of several methods. For example, the sulphur retention of presulphurized catalysts and presulphided catalysts can be compared by Soxhlet Extraction of the catalysts followed by sulphur analysis of the liquid extract.

The underlying teaching of the prior art is that unless special measures are taken, exposure of sulphided catalysts to air is to be avoided because of their pyrophoric nature and the loss of activity resulting from oxidation. It has now been found that under controlled conditions a normally pyrophoric sulphided catalyst can be passivated by exposure to an oxygen-containing composition such as air, such that a substantially non-pyrophoric catalyst results without a significant loss of activity.

For the present invention suitably a presulphided catalyst is contacted with an oxygen-containing composition for a sufficient time such that the oxygen-containing composition impregnates (or reacts) with the catalyst and provides an ex-situ presulphided catalyst that is less spontaneously combustible but not substantially lower in activity than one not contacted with an oxygen-containing composition. This time can be assessed readily by the skilled person in the art by routine measures.

Typically the contact temperature is in the range of from -20 °C to 150 °C, preferably from -20 °C to 50 °C, and preferably from 0 °C to 35 °C. Typically the oxygen-containing compound will be in gaseous form when contacting the catalyst. The oxygen partial pressure will typically be in the range of from 0.01 psia (0.07 kPa) to 100 psia (689 kPa), preferably from 0.1 psia (0.7 kPa) to 50 psia (345 kPa), and more preferably from 1 psia (7 kPa) to 10 psia (69 kPa). The contact temperature will vary depending on the temperature, the oxygen partial pressure and the nature of the oxygen-containing composition. For example, when the oxygen-containing composition is air, the process temperature should preferably be less than 45 °C.

Suitable contact times will depend on temperature and the oxygen partial pressures, with higher temperatures requiring shorter times and lower oxygen partial pressures requiring longer times. The time required can also depend on the nature of the catalyst. In general a suitable contact time will be in the range of from 10 seconds to 24 hours, preferably from 10 seconds to 5 hours, more preferably to 1 hour,

although longer times, for example up to 200 hours, can also be used.

When the oxygen-containing composition is in gaseous form when contacted with the sulphided catalyst, the gas flowrate over the catalyst is
5 suitably in the range of from 0.1 to 100 l/hr, preferably from 0.5 to 70 l/hr, more preferably from 1 to 60 l/hr.

Preferably the oxygen-containing compound is
10 sufficiently flowable or sublimable to give a sufficient contact with the metal oxide catalyst. An oxygen-containing composition which is gaseous at the contact temperature is more preferred for ease of handling. Preferably the oxygen-containing composition
15 is a mixture of oxygen and at least one inert gas, for example nitrogen, argon, helium, neon or mixtures thereof. It is preferred that the oxygen-containing composition is selected from the group consisting of air, carbon dioxide, aldehydes, ketones, ethers,
20 alcohols, vitamin E, water and mixtures thereof, with air being particularly preferred. It should be understood that if the oxygen-containing composition utilized is "wet" such as, for example, if water is used in the liquid or vapour form, or if the resulting
25 ex-situ presulphided catalyst is exposed to moisture prior to being loaded in the reactor, the catalyst must be dried prior to use in the reactor, as it is known that moisture can be detrimental to catalyst performance. The catalyst can be dried using any
30 conventional means, such as for example, by drying in air or nitrogen.

The minimum amounts of oxygen-containing composition to be used should be such that upon contact

with the catalyst, a catalyst is obtained with a protective oxygen-containing layer. The maximum amounts of oxygen-containing composition used are determined primarily by the contact temperature, i.e., when low contact temperatures are used, more oxygen-containing composition is required to accomplish the objective of putting a protective layer on the catalyst than when high contact temperatures are used. By way of example, a catalyst which has not been subjected to sufficient amounts of oxygen-containing composition to coat the catalyst with a protective layer will not exhibit reduced self-heating characteristics, as can be determined using a standard self-heating test, such as that outlined in the International Maritime Dangerous Goods (IMDG) Regulations Class 4 Division 5.1. A catalyst which has been subjected to so much oxygen-containing composition that the catalyst is substantially oxidized as opposed to having a protective layer of oxygen will exhibit extremely poor activity, i.e., at least fifteen percent less than that of a conventional sulphided catalyst, when placed in a reactor.

In preferred operation the ex-situ presulphided catalyst of the instant invention is loaded into a hydrotreating and/or hydrocracking reactor or tail gas reactor and hydrogen flow is started to the reactor and the reactor is heated up to operating (hydrotreating and/or hydrocracking or tail gas treating) conditions. In the hydrotreating and/or hydrocracking process, a hydrocarbon feedstock flow can be started simultaneously with the hydrogen or later.

The process of the present invention is further applicable to sulphided spent catalysts which have been

oxy-regenerated. After a conventional oxy-regeneration process, an oxy-regenerated catalyst may be pre-sulphided as would fresh catalyst in any conventional manner.

5 The present invention is also intended to encompass a method for stabilizing (reducing the self-heating characteristics) of a sulphided supported metal catalyst, particularly a Group VIB and/or Group VIII metal catalyst by contacting the catalyst with an
10 oxygen-containing composition at a temperature and time sufficient to impregnate the catalyst with a protective oxygen-containing layer.

 In applying the oxygen-containing composition to the catalyst, the oxygen-containing composition can be
15 added in batches and mixed or added continuously, for example, by proportionally flowing the desired compound over a fixed bed of catalyst.

 The inventive process is particularly suitable for application to hydrotreating and/or hydrocracking or
20 tail gas treating catalysts. These catalysts typically comprise Group VIB and/or Group VIII metals supported on porous supports such as alumina, silica, silica-alumina, and zeolite. The materials are well defined in the art and can be prepared by techniques described
25 therein, such as in U.S. patent specification No. 4,530,911, and U.S. patent specification No. 4,520,128. Preferred hydrotreating and/or hydrocracking or tail gas treating catalysts will contain a group VIB metal selected from molybdenum, tungsten and
30 mixtures thereof and a Group VIII metal selected from nickel, cobalt and mixtures thereof supported on alumina. Versatile hydrotreating and/or hydrocracking catalysts which show good activity under various

reactor conditions are alumina-supported nickel-molybdenum and cobalt-molybdenum catalysts. Phosphorous is sometimes added as a promoter. A versatile tail gas treating catalyst which shows good activity under various reactor conditions is an alumina-supported cobalt-molybdenum catalyst.

With respect to hydrotreating catalysts which are specifically designated for hydrodenitrification operations, such as alumina-supported nickel-molybdenum catalysts, the presulphided catalysts of the present invention which have a protective oxygen-containing layer have activities approximately equal to the activities of presulphurized or conventionally sulphided catalysts which do not have a protective oxygen-containing layer. The ability to avoid instantaneous combusting provides the present presulphided catalysts with a significant commercial advantage. The ex-situ method of this invention allows the hydrotreating, hydrocracking and/or tail gas treating reactors to be started up more quickly and consistently compared with conventionally sulphided catalysts by eliminating the in-situ presulphiding step.

Thus, the present invention relates to an improved process for starting up a hydrotreating and/or hydrocracking reactor, which comprises loading the ex-situ presulphided catalyst of the present invention into the reactor and heating the reactor to operating conditions in the presence of hydrogen and optionally a hydrocarbon feedstock. The invention is also an improved hydrotreating and/or hydrocracking process which comprises contacting at hydrotreating and/or hydrocracking conditions a hydrocarbon feedstock and

hydrogen with the ex-situ presulphided catalyst of the present invention which has been heated to hydro-treating and/or hydrocracking temperature in the presence of hydrogen and optionally a hydrocarbon feedstock.

Thus, the present invention further provides a process for converting a hydrocarbonaceous feedstock which comprises contacting the feedstock with hydrogen at elevated temperature in the presence of a catalyst composition according to the invention.

Hydrotreating conditions comprise temperatures in the range of from 100 °C to 425 °C, and pressures above 40 atmospheres (4052 kPa). The total pressure will typically be in the range of from 400 to 2500 psig (2758 to 17237 kPa). The hydrogen partial pressure will typically be in the range of from 200 to 2200 psig (1379 to 15169 kPa). The hydrogen feed rate will typically be in the range of from about 200 to about 10000 standard cubic feet per barrel ("SCF/BBL"). The feedstock rate will typically have a liquid hourly space velocity ("LHSV") in the range of from 0.1 to 15.

Hydrocracking conditions comprise temperatures in the range of from 300 °C to 500 °C, pressures above 40 atmospheres (4052 kPa). The total pressure will typically be in the range of from 400 to 3000 psig (2758 to 20684 kPa). The hydrogen partial pressure will typically be in the range of from 300 to 2600 psig (2068 to 17926 kPa). The hydrogen feed rate will typically be in the range of from 1000 to 10,000 standard cubic feet per barrel ("SCF/BBL"). The feedstock rate will typically have a liquid hourly space velocity ("LHSV") in the range of from 0.1 to 15. First stage hydrocrackers, which carry out considerable

hydrotreating of the feedstock may operate at higher temperatures than hydrotreaters and at lower temperatures than second stage hydrocrackers.

The hydrocarbonaceous feedstocks to be hydrotreated or hydrocracked in the present process can vary within a wide boiling range. They include lighter fractions such as kerosine fractions as well as heavier fractions such as gas oils, coker gas oil, vacuum gas oils, deasphalted oils, long and short residues, catalytically cracked cycle oils, thermally or catalytically cracked gas oils, and syncrudes, optionally originating from tar sands, shale oils, residue upgrading processes or biomass. Combinations of various hydrocarbon oils may also be employed.

Tail gas treatment reactors typically operate at temperatures in the range of from 200 °C to 400 °C and at atmospheric pressure (101 kPa). About 0.5-5% vol. of the tail gas fed to the reactor will comprise hydrogen. Standard gaseous hourly space velocities of the tail gas through the reactor will be in the range of from 500 to 10,000 hr⁻¹. There are several ways the subject catalysts can be started up in a tail gas treatment reactor. Claus unit feed or tail gas can be used to start up the subject catalysts. Supplemental hydrogen, as required, may be provided by a gas burner operating at a substoichiometric ratio in order to produce hydrogen.

The invention will be described by the following Examples.

Examples

The catalysts used in the following Examples and Comparative Example were subjected to the following sulphiding procedure.

A 24.5 gram sample of the catalyst was loaded into a testing unit having a set pressure of sulphiding gas (5% H₂S/95% H₂) of 1 psig (7 kPa). A sulphiding gas flow rate of 1 litre/minute was then started over the catalyst, which was heated to 204 °C and held for 2 hours, then heated to 316 °C for 1 hour and finally heated to 371 °C for 2 hours, after which it was cooled to 25 °C in the sulphiding gas flow.

In order to establish the activity of a conventionally sulphided catalyst, the above sulphided catalyst was immediately tested according to the test procedure outlined below. The test results were used for comparison with the catalysts prepared in the examples below.

Example 1 (Dry Air)

C-424 Ni/M/P, 1/16" (1.6 mm) trilobe, sulphided hydrotreating catalyst, available from Criterion Catalyst Company L.P., was coated with an oxygen-containing compound according to the procedure set forth below.

A 24.5 gram sample of the above sulphided catalyst was placed in a reactor tube 5/8" (15.9 mm) inside diameter. The catalyst was then exposed to dry air (dew point approximately -68 °C) for 1 hour at 25 °C and an air flow rate of 60 normal litres/hour. During this process, the temperature of the catalyst bed was monitored using a multi-point thermocouple. Upon exposure to air, an exotherm was observed, with the top portions of the bed reaching approximately 40 °C. After about 15 minutes of air flow, the catalyst returned to its starting temperature. The air flow was continued for another 45 minutes after which the catalyst testing procedure set forth below was carried out. The results

of the catalyst testing are presented in Table 1 below. As can be seen in Table I below, the catalyst had equivalent activity to a conventionally sulphided catalyst. The catalyst is thus distinguished from oxidized sulphided catalysts which are known to lose considerable activity on oxidation.

Example 2 (Nitrogen + Dry Air for 4 Hours)

C-424 Ni/M/P, 1/16" (1.6 mm) trilobe, sulphided hydrotreating catalyst, available from Criterion Catalyst Company L.P., was coated with an oxygen-containing compound according to the procedure set forth below.

A 24.5 gram sample of the C-424 catalyst was placed in a reactor tube and then sulphided as in the above procedure. Instead of cooling the catalyst in sulphiding gas, it was purged with nitrogen during the cooling, at a rate of approximately 60 normal litres/hour nitrogen flow. After the sample cooled to approximately 25 °C, the sample was exposed to a 1:1 mixture of dry air and nitrogen at a total flow rate of 1 litre per hour for four hours. Thereafter, the nitrogen flow was stopped and the air flow was increased to 1 litre per hour. The air flow was continued for seventeen hours. The catalyst was then evaluated using the catalyst testing procedure set forth below. The results of the catalyst testing are presented in Table 1 below. As can be seen in Table I below, the nitrogen purge and air exposure did not affect the activity of the catalyst compared with a conventionally sulphided catalyst.

Example 3 (Dry Air for 1 Week)

C-424 Ni/M/P, 1/16" (1.6 mm) trilobe, sulphided hydrotreating catalyst, available from Criterion

Catalyst Company L.P., was coated with an oxygen-containing compound according to the procedure set forth below.

5 A 24.5 gram sample sulphided as above and air exposed as in Example 1 was purged with dry air for an additional 170 hours. The sample was then tested according the catalyst testing procedure outlined below. The results of the catalyst testing are presented in Table 1 below. As can be seen in Table I
10 below, the catalyst again has an activity equivalent to that of a conventionally sulphided catalyst. This example demonstrates that the catalyst activity can be preserved even after extended air exposure.

Comparative Example (Base Case - No Coating)

15 A sulphided hydrotreating catalyst as described in Example 1 above was subjected to the essentially the same presulphiding procedure set forth above, but the catalyst was not impregnated with an oxygen-containing compound. The catalyst was then subjected to the
20 catalyst testing procedure set forth below. The results of the activity testing are presented in Table 1 below.

Example 4 (Wet Air + Nitrogen Drying for 4 Hours)

25 C-424 Ni/M/P, 1/16" (1.6 mm) trilobe, sulphided hydrotreating catalyst, available from Criterion Catalyst Company L.P., was coated with an oxygen-containing compound according to the procedure set forth below.

30 A sample of the above sulphided catalyst was passivated for 1 hour in dry air as in Example 1. The sample was then exposed to water-saturated air at 25 °C for one hour. After the air exposure, a nitrogen flow of 60 normal litres per hour was started over the catalyst bed, which was heated to 200 °C and held at

that temperature for four hours. Following the drying procedure, the catalyst was cooled to 25 °C, and the activity was evaluated using the procedure set forth below. The results of the activity testing are presented in Table 1 below.

Catalyst Testing Procedure

The reactor containing the catalyst (approximately 30 cc) is first pressurized to 1100 psig (7584 kPa) with pure hydrogen after which a hydrogen flow of 45 litres/hour is established. The catalyst is then heated to 204 °C at which point the hydrocarbon feed flow of approximately 60 cc/hour is started. The test feed used for the examples has the characteristics listed in Table 2. After feed introduction, the temperature of the reactor is raised to 332 °C. The total duration of the test, defined as the period from the time the reactor reaches 332 °C until the end of the final measurement period, is held constant at approximately 65 hours. During the last 16 hours of the test, the reactor product is collected and analyzed for sulphur and nitrogen content, and the hydrogen content is determined. Rate constants are calculated assuming first order HDN and hydrogenation, and 1.5 order HDS.

Table 1			
	RELATIVE ACTIVITY		
	HDS	HDN	HYDRO
Example 1	1.01	1.01	0.99
Example 2	0.97	1.01	1.00
Example 3	1.00	0.88	1.02
Comparative Example	1.00	1.00	1.00
Example 4	0.97	0.96	1.02

Table 2	
Feed Analysis	
Sulphur	2.32 wt%
Nitrogen	826 ppm
Hydrogen	9.28 wt%
Carbon	87.77 wt%
Oxygen	.306 wt%
Simulated Distillation, ASTM D2887:	
IBP = 330 °F	
Wt% Overhead	Temp (°F)
10	525
20	567
30	587
40	600
50	612
60	628
70	650
80	671
90	701
FBP	952

C L A I M S

1. A catalyst composition containing sulphided metal particles having an oxide-containing layer on the surface of said sulphided metal particles wherein said layer is formed by contacting the sulphided metal particles with an oxygen-containing composition at a temperature in the range of from -20 °C to 150 °C, and wherein said catalyst composition has reduced self-heating characteristics.
2. A composition as claimed in claim 1, in which the oxygen-containing compound is a mixture of oxygen and at least one inert gas.
3. A composition as claimed in claim 2, wherein the inert gas is selected from the group consisting of nitrogen, argon, helium, neon and mixtures thereof.
4. A composition as claimed in claim 2 or claim 3, wherein the mixture of oxygen and inert gas is air.
5. A composition as claimed in any one of claims 1 to 4, wherein the catalyst comprises at least one metal sulphide of a metal selected from the group consisting of Group VIB and Group VIII of the Periodic Table.
6. A process for preparing a catalyst composition as claimed in claim 1, which comprises contacting the sulphided metal particles with an oxygen-containing composition at a temperature in the range of from -20 °C to 150 °C, and wherein said catalyst composition has reduced self-heating characteristics.
7. A process for starting up a hydrotreating and/or hydrocracking reactor which comprises loading a



catalyst composition as claimed in any one of claims 1 to 5 into the reactor and heating the reactor to the operating conditions in the presence of hydrogen and optionally a hydrocarbon feedstock.

- 5 8. A process for converting a hydrocarbonaceous feedstock which comprises contacting the feedstock with hydrogen at elevated temperature in the presence of a catalyst composition as claimed in any one of claims 1 to 5.