



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B01J 37/20, C10G 49/02	A1	(11) International Publication Number: WO 93/02793 (43) International Publication Date: 18 February 1993 (18.02.93)
(21) International Application Number: PCT/US92/06263 (22) International Filing Date: 28 July 1992 (28.07.92) (30) Priority data: 737,630 30 July 1991 (30.07.91) US (71) Applicant: CRI INTERNATIONAL, INC. [US/US]; c/o Shell Oil Company, Intellectual Property, P.O. Box 2463, Houston, TX 77252-2463 (US). (72) Inventors: SEAMANS, James, Dallas ; 34 West Rockwing Place, Woodlands, TX 77381 (US). ADAMS, Charles, Terrell ; 739 Bison, Houston, TX 77079 (US). DOMINGUEZ, Wendy, Beth ; 2621 Avenue F, Rosenberg, TX 77471 (US). CHEN, Andrew, An-Ju ; 12231 Gladewick Drive, Houston, TX 77077 (US).	(74) Agents: CLENDENEN, Ronald, L. et al.; Shell Oil Company, Intellectual Property, P.O. Box 2463, Houston, TX 77252-2463 (US). (81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: A METHOD OF PRESULFURIZING A CATALYST		
(57) Abstract The invention relates to an improved method of presulfurizing a sulfidable metal or metal oxide-containing catalyst which minimizes sulfur stripping upon start-up of a reactor and improves catalyst activity. The method comprises contacting porous particles of the sulfidable catalyst with elemental sulfur at a temperature such that said elemental sulfur is incorporated in the pores of said catalyst by sublimation and/or melting and at the same time or subsequently heating the catalyst particles in the presence of a liquid olefinic hydrocarbon at a temperature greater than 150 °C.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MN	Mongolia
AU	Australia	FR	France	MR	Mauritania
BB	Barbados	GA	Gabon	MW	Malawi
BE	Belgium	GB	United Kingdom	NL	Netherlands
BF	Burkina Faso	GN	Guinea	NO	Norway
BG	Bulgaria	GR	Greece	NZ	New Zealand
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	PT	Portugal
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovak Republic
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CS	Czechoslovakia	LU	Luxembourg	SU	Soviet Union
CZ	Czech Republic	MC	Monaco	TD	Chad
DE	Germany	MG	Madagascar	TG	Togo
DK	Denmark	ML	Mali	UA	Ukraine
ES	Spain			US	United States of America

A METHOD OF PRESULFURIZING A CATALYST

This invention relates to a method of presulfurizing a metal oxide catalyst for use in hydrotreating and/or hydrocracking hydrocarbon feed stocks or in treating sulfur-containing effluent gas streams.

A hydrotreating catalyst is used to catalyze the hydrogenation of hydrocarbon feedstocks, and most particularly to hydrogenate particular components of the feed stock, such as sulfur-, nitrogen- and metals-containing organo-compounds and unsaturates. A hydrocracking catalyst is used to crack massive and complex petroleum derived molecules to provide smaller molecules with the concomitant addition of hydrogen to the molecules. A tail gas catalyst is used to catalyze the conversion of hazardous effluent gas streams to less harmful products, and most particularly to convert oxides of sulfur to hydrogen sulfide which can be recovered and readily converted to elemental sulfur.

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, transition element catalysts may be employed for these purposes. Catalysts comprising at least one element selected from V, Cr, Mn,

- 2 -

Re, Co, Ni, Cu, Zn, Mo, W, Rh, Pd, Pt, Ag, Au, Cd, Sn, Sb, Bi and Te have been disclosed as suitable for these purposes.

For maximum effectiveness the metal oxide catalysts are converted at least in part to metal sulfides. The metal oxide catalysts can be sulfided in a reactor by contact at elevated temperatures with hydrogen sulfide or a sulfur-containing oil or feed stock. However, it is advantageous to the user to be supplied with presulfurized catalysts, that is metal oxide catalysts having sulfur incorporated therein. These presulfurized catalysts can be loaded into a reactor and brought up to reaction conditions in the presence of hydrogen causing the sulfur to react with hydrogen and the metal oxides thereby converting them into sulfides without any additional process steps being needed. These presulfurized catalysts provide an economic advantage to the plant operator and avoid many of the hazards such as flammability and toxicity, which are encountered when using hydrogen sulfide, liquid sulfides, polysulfides and/or mercaptans to sulfide the catalysts.

The use of high boiling oils, such as vacuum gas oils, and hydrocarbon solvents to aid the incorporation of sulfur into a catalyst is described in US-A-4,943,547.

Hydrotreating catalysts have been presulfurized by incorporating sulfur compounds into the porous catalyst prior to hydrotreating a hydrocarbon feedstock. For example, US-A-4,530,917 discloses a method of

- 3 -

presulfurizing a hydrotreating catalyst with organic polysulfides.

US-A-4,117,136 discloses a method of catalyst presulfurizing wherein a catalyst is treated with elemental sulfur. Hydrogen is then used as a reducing agent to convert the elemental sulfur to hydrogen sulfide in situ.

US-A-4,089,930 discloses the pretreatment of a catalyst with elemental sulfur in the presence of hydrogen.

Prior art ex-situ methods of presulfurizing supported metal oxide catalysts have suffered from excessive stripping of sulfur upon start-up of a hydrotreating reactor in the presence of a hydrocarbon feedstock. As a result of sulfur stripping, a decrease in catalyst activity or stability is observed.

The present invention provides a method of presulfurizing porous particles of a sulfidable catalyst containing at least one metal or metal oxide, which method comprises

(a) contacting said porous catalyst particles with elemental sulfur at a temperature such that said elemental sulfur is incorporated in the pores of said catalyst by sublimation and/or melting and at the same time or subsequently

(b) heating said catalyst particles in the presence of a liquid olefinic hydrocarbon at a temperature greater than 150°C.

The method of the invention minimizes sulfur

stripping upon start-up of a reactor and improves catalyst activity. The method provides a safe, stable, presulfurized hydrotreating and/or hydrocracking or tail gas treating catalyst, either fresh or regenerated, that
5 can be started up rapidly.

In the method of the invention porous catalyst particles are contacted with elemental sulfur under conditions which cause the sulfur to be incorporated into the pores of the catalyst by sublimation, by melting or by
10 a combination of both sublimation and melting. The sulfur-incorporated catalyst particles are contacted with a liquid olefin at elevated temperatures for times sufficient to cause the sulfur-incorporated catalyst particles to have enhanced resistance to sulfur stripping during startup in a
15 hydrotreating and/or hydrocracking reactor in the presence of a hydrocarbon feedstock. When such olefinically treated presulfurized catalysts are used to tail gas treating, they can be started up more rapidly than conventional catalysts.

The mechanism by which the sulfur-incorporated
20 catalyst becomes more resistant to sulfur stripping upon heating at elevated temperatures in the presence of the olefin is not known and will be referenced herein as "reaction" or "reacts" for lack of better terminology. In any event, the result of this mechanism can readily be
25 determined without undue experimentation by measuring the resistance to sulfur stripping of catalysts subjected to differing temperature/time treatments with the olefin and

- 5 -

without the olefin and measuring the resistance to sulfur stripping of the resulting catalysts. Catalysts produced in accordance with the invention have enhanced resistance to sulfur stripping. A suitable method for determining sulfur stripping resistance is described in Example 1, Part C below wherein acetone is used as a stripping agent.

The catalysts referred to herein as "sulfidable metal oxide(s) catalysts" are in fact catalyst precursors, that is they are used as actual catalysts while in the sulfided form and not in the oxide form. While reference is made to metal oxide(s) catalysts, it should be understood that while the normal catalyst preparative techniques will produce metal oxide(s), it is possible to utilize special preparative techniques to produce the catalytic metals in a reduced form, such as the zero valent state. Since metals in the zero valent state will be sulfided as well as the oxides when subjected to sulfiding conditions, catalysts containing such sulfidable metals even in reduced or zero valent states will be considered for the purposes of this invention as sulfidable metal oxide(s) catalysts. Further, since the preparative technique of the invention can be applied to regenerated catalysts which may have the metal sulfide not completely converted to the oxides, "sulfidable metal oxide(s) catalysts" also refers to these catalysts which have part of their metals in the sulfided state.

The catalyst is typically presulfurized by one of two methods. The first method comprises contacting the

sulfidable catalyst with elemental sulfur at a temperature such that said elemental sulfur is incorporated in the pores of said catalyst by sublimation and/or melting and subsequently heating the sulfur-incorporated catalyst in
5 the presence of a liquid olefinic hydrocarbon at a temperature greater than 150°C. The second method comprises contacting a sulfidable metal oxide(s)-containing catalyst with a mixture of powdered elemental sulfur and a liquid olefinic hydrocarbon and heating the resultant
10 mixture to a temperature above 150°C. In this second method the heating rate is sufficiently slow for the sulfur to be incorporated into the pores of said catalyst by sublimation and/or melting before reaching the temperature at which the olefin reacts to make the sulfur more
15 resistant to stripping.

In the preferred embodiment the porous catalyst particles are first contacted with elemental sulfur at a temperature such that the sulfur is incorporated into the catalyst by sublimation and/or melting. While the catalyst
20 particles can be contacted with sulfur in the molten state, it is preferred to first mix the catalyst particles with powdered elemental sulfur and then heat the mixture to above the temperature at which sublimation of the sulfur occurs.

25 Generally the catalyst particles are heated in the presence of the powdered elemental sulfur at a temperature greater than 80°C. Preferably this first sulfur

impregnation step will be carried out at a temperature of from 90°C to 130°C or higher, say up to the boiling point of sulfur of about 445°C. The lower temperature limit is fixed by the sublimation/melting characteristics of sulfur
5 under the specific conditions of impregnation, whereas the upper temperature limit is fixed primarily by economics, higher temperatures being more costly to produce as well as more difficult to work with.

In a preferred embodiment the catalyst and sulfur are
10 heated together at a temperature of from 105°C to 125°C. Typically the catalyst and powdered sulfur are placed in a vibratory or rotary mixer and heated to the desired temperature for sufficient time to allow the sulfur to be incorporated into the pores of the catalyst. Times
15 typically will range from 0.1 to 10 hours or longer.

The amounts of sulfur used will depend upon the amounts of catalytic metal present in the catalyst that needs to be converted to the sulfide. Typically the amount of sulfur used is determined on the basis of the
20 stoichiometric amount of sulfur required to convert all of the metal in the catalyst to the sulfide form. For example a catalyst containing molybdenum would require two moles of sulfur to convert each mole of molybdenum to molybdenum disulfide, with similar determinations being made for other
25 metals. On regenerated catalysts, existing sulfur levels may be factored into the calculations for the amounts of elemental sulfur required.

It has been found that the addition of presulfurizing sulfur in amounts down to 50 percent of the stoichiometric requirement results in catalysts having enhanced hydrodenitrication activity, which is an important property of hydrotreating and first stage hydrocracking catalysts. Thus, the amount of presulfurizing sulfur used for incorporation into the catalyst will typically range from 0.5 to 1.5 times the stoichiometric amount, and preferably from 0.7 to 1.2 times the stoichiometric amount.

For hydrotreating/hydrocracking and tail gas treating catalysts containing Group VIB and/or Group VIII metals the amount of sulfur employed is typically 2 to 15%, preferably 6% to 12%, by weight of the catalyst charged. It is preferred not to add so much sulfur to the catalyst that the pores are completely filled up. By leaving residual pore volume, the olefin can penetrate the pores and react therein.

The key step to the invention is to contact the sulfur impregnated metal catalyst with a liquid olefin at an elevated temperature and for sufficient time at a temperature such that the olefin reacts and provides a sulfurized catalyst that is more resistant to sulfur leaching than one not contacted with an olefin. Typically the contact temperature is greater than 150°C and typically is from 150°C to 350°C, preferably from 200°C to 325°C. Contact times will depend on temperature and the vapor pressure of the olefin, higher temperatures and higher

- 9 -

vapor pressures requiring shorter times. In general times will range from 0.1 to 10 hours.

The key property of the olefin is that it must be a liquid at the elevated temperature of contact. It is preferred that the olefin be a higher olefin, i.e. one having a carbon number greater than six, preferably greater than eight. The upper carbon number of useful olefins is determined by the melting point of the olefin in question. While waxy olefinic materials having carbon numbers around 60 can be used, they are inconvenient since they must be heated to a higher temperature in order to be converted into a liquid, although they can be used with a solvent to put them in liquid form. Olefins with carbon numbers ranging from 6 to 30, preferably from 8 to 25, are found most useful.

The term "olefin" as used herein refers to hydrocarbon molecules containing at least one carbon-carbon double bond and will include hydrocarbons containing at least one carbon-carbon double bond in addition to other functional moieties, such as, for example, carboxylate or halo, provided such additional moieties do not adversely react with the catalytic metals on the catalyst. The olefins may be monoolefins or polyolefins, cyclic or acyclic, linear or branched. Non-limiting examples of monoolefins include decene, undecene, dodecene, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, noadecene and eicosene, whether branched,

- 10 -

linear or cyclic, alpha or internal olefin. Similar materials in the form of di-, tri- and polyolefins may be used. Polycyclic olefins and polyolefins may also be used. The readily available
5 compound dicyclopentadiene can be used.

The olefins may also be mixed with non-olefinic hydrocarbons, such as alkanes or aromatic solvents. In general, the olefin content of any olefin-containing hydrocarbon used in the process of the invention should be
10 above 5%wt., preferably above 10%wt., and most preferably above 30%wt. Generally, higher olefin contents are used, say, about 50%wt, and most conveniently the olefin is used in the undiluted form. The term "olefinic hydrocarbon" as used herein refers to a hydrocarbon that contains olefinic
15 molecules with or without the presence of non-olefinic molecules. It is understood that the olefins may be provided as olefin precursors which are converted to olefins before or upon reaching the reaction temperature.

The minimum amount of olefin used should be such that
20 upon reaction at elevated temperature, a catalyst is obtained that has reduced sulfur leaching properties. The maximum amount of olefin used is determined primarily by economics. In a preferred embodiment the amount of olefinic hydrocarbon is used that will just fill the pore
25 volume of the sulfur impregnated catalyst or just slightly less, down to 60 percent, preferably down to 80 percent of the pore volume. A preferred target range is from 80 to 95

- 11 -

percent of the pore volume. In this manner, the treated catalyst will be "dry" and is more convenient to handle.

In another embodiment according to the present invention, the catalyst particles are contacted with both
5 the elemental sulfur, preferably powdered, and the olefinic hydrocarbon simultaneously. According to this method, a mixture of powdered elemental sulfur and olefinic hydrocarbon solvent is first produced. A weight ratio of olefin to sulfur of from 1:1 to 4:1 is suitable, with about
10 2:1 being a preferred ratio. The mixture may be heated to promote homogeneous mixing of the components, particularly if the olefinic hydrocarbon is not liquid at ambient conditions. Toluene or other light weight hydrocarbon solvents may be added to decrease the viscosity of the
15 mixture. Also, increased heat will achieve the same effect. The mixture is then added to a preweighed catalyst sample and mixed. The mixture is then heated to the olefin reaction temperature of above 150°C. Preferably the temperature is 150°C to 350°C and more preferably from
20 200°C to 325°C. The times are the same as in the preferred two-step embodiment described above, that is from 0.1 to 10 hours. During the heating process the sulfur first impregnates the pores of the catalyst and then the olefin reacts to form the sulfur leaching resistant catalyst.

25 The presulfurized catalyst of the instant invention may be converted to a sulfided catalyst by contact with hydrogen at temperatures greater than 200°C, preferably

- 12 -

from 200°C to 425°C. Times can run from 0.5 hours to up to 3 days.

In preferred operation the presulfurized 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 presence of hydrogen, activation of the catalyst takes place. That is, the metal oxides and hydrogen react with substantially all of the sulfur incorporated into the catalyst pores, thus producing hydrogen sulfide, water and metal sulfides. In the hydrotreating and/or hydrocracking process, a hydrocarbon feedstock flow may be started simultaneously with the hydrogen or later.

The process of the present invention is further applicable to the sulfurizing of spent catalysts which have been oxy-regenerated. After a conventional oxy-regeneration process, an oxy-regenerated catalyst may be presulfurized as would fresh catalyst in the manner set forth above and specifically in a manner set forth by way of the following examples.

The invention is also intended to encompass a method for stabilizing (enhancing the resistance to sulfur leaching) a supported metal catalyst containing elemental sulfur, particularly a Group VIB and/or Group VIII metal catalyst, by contacting said catalyst with an olefinic

- 13 -

hydrocarbon at a temperature greater than 150°C.

The presulfurizing process is particularly suitable for application to hydrotreating and/or hydrocracking or tail gas treating catalysts. These catalysts typically
5 comprise Group VIB and/or Group VIII metals supported on porous supports such as alumina, silica or silica-alumina, including zeolite. The materials are well defined in the art and can be prepared by techniques described therein, such as in US-A-4,530,911 and US-A-4,520,128. Preferred
10 hydrotreating and/or hydrocracking or tail gas treating catalysts will contain a group VIB metal selected from molybdenum and/or tungsten and a Group VIII metal selected from nickel and/or cobalt supported on alumina. Versatile hydrotreating and/or hydrocracking catalysts which show
15 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-
20 supported cobalt-molybdenum catalyst.

Hydrotreating catalysts which are specifically designed for hydrodenitrification operations, such as alumina-supported nickel-molybdenum catalysts, presulfurized by the methods described herein have higher
25 initial activities, particularly hydrodenitrification activities, than catalysts sulfided by prior art methods. This higher initial activity, coupled with ability to avoid

- 14 -

sulfiding in the presence of hydrogen sulfide, provides the instant presulfurized catalysts with a significant commercial advantage. It allows the hydrotreating and/or hydrocracking reactor to get into full operation quicker, and, once at operating conditions, have a higher activity, allowing the reactor to be operated at either lower temperature or higher conversion. Tail gas treating reactors can also be started up more quickly.

Thus, the invention also relates to an improved process for starting up a hydrotreating and/or hydrocracking reactor, which comprises loading the catalyst presulfurized according to the methods described herein into the reactor and heating the reactor to operating conditions in the presence of hydrogen and optionally a hydrocarbon feedstock. The invention also relates to an improved hydrotreating and/or hydrocracking process which comprises contacting at hydrotreating and/or hydrocracking conditions a hydrocarbon feedstock and hydrogen with a catalyst which has been presulfurized according to the methods described herein and which has been heated to hydrotreating and/or hydrocracking temperature in the presence of hydrogen and optionally a hydrocarbon feedstock.

Hydrotreating conditions comprise temperatures of from 100°C to 425°C, pressures above 40 atmospheres. The total pressure will typically range from 2.8 to 17.2 MPa gauge (400 to 2500 psig). The hydrogen partial pressure

- 15 -

will typically range from 1.4 to 15.2 MPa gauge) (200 to 2200 psig). The hydrogen feed rate will typically range from 1.6 to 80 Nl/hr (33.77 to 1688.5 Nl (H₂)/l (oil)). The feedstock rate will typically have a liquid hourly space velocity ("LHSV") of from 0.1 to 15.

Hydrotreating conditions comprise temperatures of
5 from 300°C to 500°C, pressures above about 40 atmospheres. The total pressure will typically range from 2.8 to 20.7 MPa gauge (400 to about 3000 psig). The hydrogen partial pressure will typically range from 2.1 to 17.9 MPa gauge (300 to 2600 psig). The hydrogen feed
10 rate will typically range from 8 to 80 Nl/hr (168.85 to 1688.5 Nl (H₂)/l (Oil)). The feedstock rate will typically have a liquid hourly space velocity ("LHSV") of from 0.1 to 15. First stage hydrocrackers, which carry out considerable hydrotreating of the feedstock, may
15 operate at high temperatures than hydrotreaters and at lower temperatures than second stage hydrocrackers.

Tail gas treatment reactors typically operate at temperatures ranging from 200°C to 400°C and at atmospheric pressure. About 0.5-5% vol. of the tail gas
20 fed to the reactor will comprise hydrogen. Standard gaseous hourly space velocities of the tail gas through the reactor will range from 500 to 10,000 hr⁻¹. There are several ways the catalysts can be started up in a tail gas treatment reactor. Claus unit feed or tail gas can
25 be used to start

- 16 -

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 reference to the following Examples.

Example I: Presulfurization Method

Part A: Sulfur impregnation

A commercial hydrotreating catalyst having the properties listed below was used to prepare the sulfurized catalysts.

Table 1: Catalyst Properties

	Nickel	2.6%wt
	Molybdenum	14.3%wt
	Phosphorous	2.9%wt
15	Support	gamma alumina
	Surface Area, m ² /g	164
	Water Pore Vol., cm ³ /g	0.44
	Size	0.13cm (1/20 inch) trilobes

A 430 gram sample of the above sample was dried at 370°C for one hour and then cooled to ambient under vacuum. The sample was then placed in a flask and enough sulfur, in powdered form, was added to produce a sulfur level of about 10% by weight. The flask was provided with a slow nitrogen purge and placed in a heating mantle at 107°C for 1 hour. During this time period the flask was vibrated continually to provide mixing of sulfur and catalyst. The final sulfur level was about 10.5% by weight of the total catalyst. The water pore volume of the sulfur-impregnated catalyst was determined to be about 0.3 cm³/g.

- 17 -

Part B: Olefin Reaction

The sulfur-impregnated catalyst from Part A was impregnated with the various hydrocarbons listed in Table 2. The catalyst was impregnated with hydrocarbon 5 sufficient to fill 90% of the pore volume. The eicosane, vacuum gas oil ("VGO") and the C₂₀ olefin, being solids or semi-solids at room temperature, were heated to 40°C before being applied to the catalyst. All other hydrocarbons were simply added to the catalyst. The catalyst was shaken with 10 the hydrocarbon until the catalyst appeared dry. This took approximately 10 minutes per sample.

100 Grams of the hydrocarbon-containing catalyst were loaded into a quartz reactor tube and placed in a furnace. The reactor outlet was tubed to a liquid trap, then to a 15 silicone oil-filled container to prevent air back-diffusion. Nitrogen flow was established to the reactor inlet at 230 cm³ /min, and the catalyst bed was purged of air for 30 minutes. The nitrogen flow was reduced to 30 cm³/min for the during of the heat treatment.

20 The reactor was heated to 205°C over the course of one hour and held there for 3 hours. After heat treatment was complete, the reactor contents were cooled to room temperature under nitrogen purge. The samples were analyzed for sulfur content.

25 Part C: Sulfur Leaching Tests

Acetone was used as an extractive solvent for measuring the ability of the catalysts to resist sulfur

leaching. Acetone is a more aggressive solvent for sulfur than the typical hydrotreating and/or hydrocracking feedstocks. Catalysts that are found to be resistant to sulfur leaching by acetone are also found to be resistant to leaching by hydrocarbon feedstocks and have thus acquired the benefits of the instant invention. Thus, the acetone extraction test as described herein can be used by one skilled in the art to determine if sulfur-leaching resistant catalysts as defined and claimed herein have been obtained.

A Soxhlet extractor was used in this test. The thimble of the extractor was filled with 20 cm³ of catalyst and the flask of the extractor was filled about 3/4 full (about 600 cm³) with acetone. The extractor was heated to the boiling point of acetone (57°C) and allowed to reflux for 18 hours. After extraction, the flask was cooled, the catalyst removed and dried at 40°C for 16 hours. The extracted catalysts were analyzed for sulfur content. The percent of sulfur retained after extraction is shown in Table 2 below. This percent of retained sulfur is calculated as the amount of sulfur on the catalyst after the extraction of Part C divided by the sulfur in the catalyst after the heat treatment of Part B times 100%.

Table 2: Sulfur Leaching Results

<u>"Reactant" Hydrocarbon</u>	<u>Amount of Sulfur After Extraction</u>
NEODENE® 10 olefins ^{a)}	92.2

- 19 -

	n-DECANE	15.6
	NEODENE® 14/16 OLEFINS ^{b)}	88.5
	n-C ₁₄ /C ₁₆ BLEND ^{c)}	30.6
	CHEVRON TETRAMER M ^{d)}	94.3
5	CHEVRON POLYMER 560 ^{e)}	88.5
	DIESEL FUEL	77.1
	VACUUM GAS OIL	85.2
	NEODENE® 20 OLEFINS ^{f)}	96.4
	EICOSANE	65.3

10

- a) An olefin product manufactured by Shell Chemical Co. whose composition is 96%wt. minimum C₁₀ alpha-monoolefin.
- b) An olefin product manufactured by Shell Chemical Co. whose composition is 94%wt. minimum alpha-monoolefin comprising 65%wt. C₁₄ alpha-monoolefin and 35%wt. C₁₆ alpha-monoolefin.
- 15 c) A blend of normal C₁₄ and C₁₆ alkanes blended to have the same C₁₄/C₁₆ ratio as b) above.
- d) An olefin product manufactured by Chevron Chemical Co. which is a tetramer of propylene.
- 20 e) An olefin product manufactured by Chevron Chemical Co. whose composition is C₁₂ - C₁₈ branched monoolefins.
- f) An olefin product manufactured by Shell Chemical Co. whose composition is 94%wt. minimum C₂₀ alpha-monoolefin.
- 25

Example II: Use of Presulfurized Catalyst in Hydrotreating Process

Six types of catalysts, two comparative and four of

- 20 -

this invention, were used to demonstrate the advantages of the invention as applied to a hydrotreating process. These were:

- 1) COMP Catalyst - This is a comparative commercial hydrotreating catalyst listed in Table 1 which has been sulfided by an industry accepted sulfiding method using hydrogen and hydrogen sulfide as described below.
- 2) A₁₀₀ Catalyst - This is a catalyst prepared as described in Example I with 100% stoichiometric sulfur and using the normal C₁₄/C₁₆ olefin blend described in Table 2 as one treating hydrocarbon.
- 3) A₇₅ Catalyst - This is a catalyst prepared as described in Example I with 75% stoichiometric sulfur and using the normal C₁₄/C₁₆ olefin blend described in Table 2 as the treating hydrocarbon.
- 4) A₅₀ Catalyst - This is a catalyst prepared as described in Example I with 50% stoichiometric sulfur and using the normal C₁₄/C₁₆ olefin blend described in Table 2 as the treating hydrocarbon.
- 5) COMP_{C₁₄/16} Catalyst - This is a comparative catalyst prepared as described in Example I with 100% stoichiometric sulfur and using the normal-C₁₄/C₁₆ alkane blend described in Table 2 as the treating hydrocarbon.
- 6) A_{C₁₄/16} Catalyst - This is a catalyst prepared as described in Example I with 100% stoichiometric

- 21 -

sulfur and using the normal-C₁₄/C₁₆ olefin blend described in Table 2 as the treating hydrocarbon. This catalyst is substantially similar to the A₁₀₀ catalyst except the A₁₀₀ catalyst was a large scale preparation and this was a laboratory scale preparation.

Microreactors were utilized to test the hydrotreating activity of the catalysts. The catalysts were loaded into the reactor as follows: 30 cm³ of catalyst (basis compacted bulk density) was divided into 3 aliquots. The first aliquot contained 2.5 cm³ of catalyst and was diluted 10:1 (SiC to catalyst) with 60/80 mesh SiC. The remaining two aliquots contained 13.75 cm³ of catalyst each and were diluted 1:1 with 60/80 mesh SiC. These aliquots were loaded into the reactor tube with the dilute one on top (the inlet end).

Part A: Short Term Activity Tests

A blend of vacuum gas oil and light cycle oil (VGO/LCO) was used as feedstock and had the following properties:

%wt Sulfur	1.7
ppm Nitrogen	1120
Refractive Index	1.5183 (25°C)
Density	0.9242 (60°F or 15°C)

1) COMP Catalyst Activation

The COMP Catalyst was dried at 400°C for one hour in air, cooled in a desiccator and loaded into the reactor.

- 22 -

It was sulfided in a flow of 45 Nl/hr of 95%vol hydrogen/5%vol hydrogen sulfide according to the following schedule:

- a. ambient to 121°C at 5.6°C/min
- 5 b. 121°C to 204°C at 0.56°C/min
- c. hold at 204°C for 90 min
- d. heat from 204°C to 371°C at 1.1°C/min
- e. hold at 371°C for 60 min
- f. cool reactor and hold at 149°C
- 10 2) Diesel Activation

This method was used to activate catalysts of this invention using a diesel refined for cars and trucks and was as follows:

- a. Unit was pressurized to 4.8 MPa gauge (700
15 psig) and hydrogen circulation was established at 168.85
Nl (H₂)/l (oil) [8 Nl of hydrogen/hr].
- b. Diesel feed was started to the catalyst bed at
1.5 LHSV and ambient temperature.
- c. The reactor temperature was raised to 121°C in
20 one hour, then increased to 343°C at 27.8°C/hour.
Temperatures were held at 343°C for 30 minutes.
- d. Since the temperature ramp occurred overnight,
the reactor was also cooled overnight at 149°C for feed
switch in the morning.

25 3) Gas Activation

This method was used to activate catalysts of this invention using first hydrogen, followed by diesel, and

- 23 -

simulates the startup of certain commercial hydrotreaters. This method is as follows:

- a. Unit was pressurized to 5.1 MPa gauge (300 psig) and hydrogen circulation was established at 168.85 Nl (H₂)/l (oil) [Nl of hydrogen/hr].
- b. Temperature was ramped from ambient to 121°C at 27.8°C/hr.
- c. Temperature was ramped from 121°C to 204°C in one hour. Off gas was sampled for H₂S during period.
- d. When 204°C was reached, unit was pressured to 4.8 MPa gauge (700 psig) and held for one hour.
- e. Diesel feed (same as in 2) above) was introduced at 204°C.
- f. The temperature was ramped to 260°C at 27.8°C/hr and the unit cooled to 149°C with diesel feed continuing overnight.

4) Activity Testing

For activity testing the unit was pressured up to 4.8 MPa gauge (700 psig) and heated to 246°C with a hydrogen gas rate of 168.85 Nl (H₂)/l (oil) [8 Nl of hydrogen/hr]. The VGO/LCO feed was started to the unit at 1.5 LHSV (41.6 gm/hr). After the feed had wetted the entire bed (and product was noted in the separator), the temperature was raised to 329°C at 22.2°C/hr.

After the reactor was at 329°C, a 12 hour break-in period was begun. The product from this period was not analyzed. The run was continued with additional weight

- 24 -

periods of 12 hours and the products of each weight period were analyzed for nitrogen and sulfur. From these values rate constants were calculated for the hydrodenitrification ("HDN") reaction and the hydrodesulfurization ("HDS") reaction. Rate constants provide an indication of how active the catalyst is, the higher the rate constant, the faster the reaction process, and the higher the conversion of sulfur and nitrogen at a given space velocity (feed rate). For HDN the reaction order is 1.0 and the k value is calculated by the equation:

$$k = (\text{space velocity}) * \ln \left\{ \frac{\text{conc. of N in feed}}{\text{conc. of N in product}} \right\}$$

For HDS the reaction is not first order and many values are used, but 1.7 is the value most used and is used herein to calculate as follows:

$$R = \left\{ \frac{\text{space velocity}}{1.7-1} \right\} \left\{ \frac{1}{(\text{conc. of S in product})^{0.7}} - \frac{1}{(\text{conc. of S in feed})^{0.7}} \right\}$$

The relative rate constants are provided in Table 3. They have been normalized against the values of the third weight period for the COMP Catalyst.

- 25 -

Table 3: Short Term Activity Tests

	<u>Catalyst</u>	<u>Activation</u>	<u>Weight Period (12 hrs each)</u>	<u>HDS Rel. K Value</u>	<u>HDN Rel. K Value</u>
5	COMP	1) Standard	3rd	1.00	1.00
	A ₁₀₀	3) Gas	3rd	1.01	1.19
			4th	1.01	1.15
			5th	0.98	1.09
10			6th	1.00	1.12
	A ₁₀₀	2) Diesel	3rd	0.98	1.17
			4th	0.98	1.17
			5th	0.97	1.11
15			6th	1.00	1.13
			7th	0.99	1.11
	A ₇₅	2) Diesel	3rd	1.04	1.23
			4th	1.04	1.22
20			5th	1.05	1.22
			6th	1.05	1.22
	A ₅₀	2) Diesel	3rd	0.92	1.13
			4th	0.90	1.10
25			5th	0.90	1.08
	COMP _{C14/16}	2) Diesel	3rd	0.76	1.07
			4th	0.76	1.05
			5th	0.74	1.03
30			6th	0.72	0.87
	A _{C14/16}	2) Diesel	3rd	0.93	1.18
			4th	0.91	1.16
			5th	0.91	1.14
35			6th	0.92	1.16

As can be seen from the above table the catalysts of this invention show a clear advantage over a traditional hydrotreating catalyst with regard to hydrodenitrication activity.

Part B: Long Term Activity Tests

COMP Catalyst and A₁₀₀ Catalyst were used in long term tests to measure HDN activity.

The feed used was an Alaskan north slope diesel with

- 26 -

the following properties:

0.556 %wt Sulfur

269 ppm Nitrogen

31.1 API Gravity

5 13.29 %wt Aromatics

One hundred cc of catalyst was used in the microreactor with 1:1 dilution with 60/80 mesh SiC.

The operating conditions were as follows:

4.1 MPa gauge (600 psig)

10 168.85 Nl (H₂)/l (oil) [35.6 Nl of hydrogen/hr]

2.0 space velocity

90% desulfurization

The A₁₀₀ Catalyst was activated by pressuring the reactor to 600 psig with hydrogen. Hydrogen flow was started at 168.85 nl (H₂)/l (oil) and diesel feed brought in at 1.5 LHSV and ambient temperature. The reactor temperature was raised to 121°C at 1.7°C/min, then increased to 343°C at 0.56°C/min. The reactor was then cooled to the estimated start-of-run temperature of 302°C.

20 The COMP Catalyst was activated using the following:

a. 120 Nl/hr of a 95% H₂/5% H₂S mixture

b. Ramp temperature from ambient to 204°C at 0.56°C/min

c. Hold at 204°C for two hours

25 d. Ramp to 316°C at 0.55°C/min and hold for one hour

e. Ramp to 371°C at 0.55°C/min and hold for two

- 27 -

hours

f. Cool to 302°C for feed introduction

The operating procedure was as follows: At 302°C the feed rate was increased to 2.0 LHSV and a reactor temperature profile was taken and weight periods were started when the profile was flat and at target. The reactor lined out after about 190 hours with the reactor temperature being adjusted for 100 ppm sulfur in the product. This temperature was held for the remainder of the run. Sulfur and nitrogen were analyzed by a combustion technique. Sulfur detector was UV fluorescence and nitrogen detector was chemiluminescence.

The results of these runs are shown in Tables 4 and 5 and are reported as %HDN and %HDS which is the difference in N and S in the product and feed over the N and S in the feed, expressed as a percentage.

TABLE 4: A₁₀₀ Catalyst

	Run <u>Hrs.</u>	<u>Deg. C</u>	<u>%HDN</u>	<u>%HDS</u>
20	191	331	55.0	90.5
	216	329	53.2	90.3
	271	329		89.9
25	287	330	52.0	90.3
	311	330	52.4	90.1
	335	330	52.4	89.7
	359	330	52.4	89.7

30

- 28 -

TABLE 5: COMP CATALYST

	<u>Run</u> <u>Hrs.</u>	<u>Deg. C</u>	<u>%HDN</u>	<u>%HDS</u>
5	190	329	50.2	90.5
	214	329	49.8	90.5
	268	329	49.8	90.5
10	286	330	49.4	90.5
	310	330	49.1	90.3
	324	329	49.1	90.3
	348	330	48.3	90.6

15 As can be seen from the above, the catalyst produced in accordance with the invention retains an improved HDN activity even over a long test term.

- 29 -

CLAIMS

1. A method of presulfurizing porous particles of a sulfidable catalyst containing at least one metal or metal oxide, which method comprises
 - 5 (a) contacting said porous catalyst particles with elemental sulfur at a temperature such that said elemental sulfur is incorporated in the pores of said catalyst by sublimation and/or melting and at the same time or subsequently
 - 10 (b) heating said catalyst particles in the presence of a liquid olefinic hydrocarbon at a temperature greater than 150°C.
2. A method according to claim 1 wherein the catalyst contains at least one oxide of a metal from Group VIB and
15 Group VIII of the Periodic Table.
3. A method according to claim 1 wherein powdered sulfur is used in step (a).
4. A method according to claim 1, 2 or 3 wherein step
20 (a) is carried out before step (b) at a temperature of from 90°C to 130°C.
5. A method according to claim 1, 2 or 3 wherein the amount of sulfur used in step (a) is from 0.7 to 1.2 times the stoichiometric amount required to convert the metal or metal oxides to sulfides.
- 25 6. A method according to claim 1, 2 or 3 wherein step (b) is carried out subsequent to step (a) at a temperature of from 200°C to 325°C.

- 30 -

7. A method according to claim 1, 2 or 3 wherein the duration of step (a) and/or step (b) is from 0.1 to 10 hours.
8. A method according to claim 1, 2 or 3 wherein the olefinic hydrocarbon contains olefins having from 6 to 30 carbon atoms.
9. A method according to claim 8 wherein the olefinic hydrocarbon contains olefins having from 8 to 25 carbon atoms.
10. A method for stabilizing a supported Group VIB and/or Group VIII metal catalyst containing elemental sulfur which comprises contacting said catalyst with an olefinic hydrocarbon at a temperature greater than 150°C.
11. A method according to claim 1 which comprises the further step of heating the catalyst to a temperature of from 200°C to 425°C in the presence of hydrogen to cause the sulfur to react with the metal oxides to produce metal sulfides and thereby provide a catalyst suitable for hydrotreating and/or hydrocracking a hydrocarbon stream or tail gas treating a sulfur-containing gas stream.
12. A method according to claim 11 wherein heat in the presence of hydrogen is carried out at least in part in the presence of a hydrocarbon to provide a catalyst for hydrotreating and/or hydrocracking a hydrocarbon stream.
13. A method according to claim 11 which comprises the further step of hydrotreating and/or hydrocracking hydrocarbon streams or tail gas treating sulfur-containing

gas streams by contacting the streams in the presence of hydrogen with the hydrotreating and/or hydrocracking or tail gas treating catalyst.

14. A method according to claim 1 or 11 which comprises
5 the further step of loading the catalyst into a
hydrotreating and/or hydrocracking or tail gas treating reactor and heating the reactor up to a hydrotreating and/or hydrocracking or tail gas treating temperature of from 100° to 425°C in the presence of hydrogen.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/06263

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶	
According to International Patent Classification (IPC) or to both National Classification and IPC	
Int.Cl. 5 B01J37/20;	C10G49/02

II. FIELDS SEARCHED	
Minimum Documentation Searched ⁷	
Classification System	Classification Symbols
Int.Cl. 5	B01J ; C10G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 359 356 (CRI VENTURES INC) 21 March 1990 cited in the application ---	
A	US,A,4 177 136 (HERRINGTON ET AL) 4 December 1979 cited in the application ---	
A	EP,A,0 064 429 (IFP) 10 November 1982 -----	

^o Special categories of cited documents : ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "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. "&" document member of the same patent family
---	--

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03 NOVEMBER 1992	07.12.92
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	LO CONTE C.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9206263
SA 63290**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 03/11/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0359356	21-03-90	US-A- 4943547	24-07-90
		DE-U- 6890237	10-09-92
		JP-A- 2211256	22-08-90
		US-A- 5041404	20-08-91

US-A-4177136	04-12-79	None	

EP-A-0064429	10-11-82	FR-A- 2503733	15-10-82
		JP-A- 57182390	10-11-82
