

Description

This invention relates to a method of presulfiding a supported metal oxide catalyst for use in hydrotreating hydrocarbon feed stocks and, a hydrotreating process utilizing a presulfided metal oxide catalyst.

5 A hydrotreating catalyst may be defined as any catalyst composition which may be employed to catalyze the hydrogenation of hydrocarbon feedstocks. Such catalyst compositions are well known to those of ordinary skill in the art and several are commercially available. Metal oxide catalysts which come within this definition include cobalt-molybdenum, nickel-tungsten, and nickel-molybdenum. Typical supports for hydrotreating metal oxide catalysts include alumina, silica and silica-alumina supports.

10 In the past, ex-situ methods of presulfiding supported metal oxide catalyst have suffered from excessive stripping of sulphur upon start-up of a hydrotreating reactor. As a result of sulphur stripping, an increase in the product weight percent of sulphur is observed along with a decrease in catalyst activity.

The use of high boiling oils and hydrocarbon solvents to aid the incorporation of sulphur into a catalyst is not believed to have been previously taught by prior presulfiding methods. Hereforth, a high boiling oil is defined as an oil whose initial boiling point is greater than 204°C (400°F).

15 Hydrotreating catalyst are typically presulfided by incorporation sulphur compounds into the porous catalyst prior to hydrotreating a hydrocarbon feedstock. For example, U.S. Patent No. 4,530,917 to Berrebi discloses a method of presulfiding a hydrotreating catalyst with organic polysulfides.

U.S. Patent No. 4,177,136 to Herrington et al discloses a method of catalyst presulfiding wherein a catalyst is treated with elemental sulphur. Hydrogen is then used as a reducing agent to convert the elemental sulphur to H₂S in situ. Problems arise, however, upon start-up of a reactor due to excessive sulphur stripping.

U.S. Patent No. 4,089,930 to Kittrell et al discloses the pretreatment of a catalyst with elemental sulphur in the presence of hydrogen.

25 It is an object of the present invention to presulfide a hydrotreating catalyst in a manner which minimizes sulphur stripping upon start-up of a hydrotreating reactor.

It is yet a further object of the present invention to activate spent catalyst in such a manner as to minimize the amount of sulphur required for activation.

It is yet a further object of the present invention to prepare a safe, stable, presulfided hydrotreating catalyst.

30 It is yet a further object of the present invention to provide a technique for activating a presulfided hydrotreating catalyst in-situ.

The present invention relates to an improved method of presulfiding a hydrotreating catalyst which minimizes sulphur stripping upon start-up of a hydrotreating reactor and improves catalyst activity. The catalyst is preferably presulfided by one of two methods. The first method comprises the steps of

- 35 (a) contacting the supported metal oxide catalyst with powdered elemental sulphur, to form a mixture, at a temperature below the melting point of sulphur,
- (b) contacting the resultant mixture with a high boiling oil or a hydrocarbon solvent in a hydrogen-free environment, and, preferably,
- (c) heating said mixture to a temperature above the melting point of sulphur

The second method comprises the steps of

- 40 (a) preparing a mixture of elemental sulphur and a high boiling oil or hydrocarbon solvent at a temperature below the melting point of sulphur,
- (b) contacting the supported metal oxide catalyst with the mixture to form a resultant catalyst mixture, and, preferably,
- (c) heating the resultant catalyst mixture to a temperature above the melting point of sulphur.

45 Alternatively, the catalyst is mixed with elemental sulphur at a temperature below the melting point of sulphur and then heated, in the absence of oil and hydrocarbon solvents to a temperature above the melting point of sulphur but below temperatures where activity loss is observed.

Thus, in accordance with the present invention there is provided a method of presulfiding a hydrotreating catalyst, the various aspects of which are defined in independent claims 1, 2, 11 and 14. Preferred embodiments of this aspect of the invention are set out in sub-claims 3-10, 12, 13, 15-19 and 21.

50 In a second aspect, the present invention relates to a mixture as defined in claim 20.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

55 Several techniques may be employed to contact sulphur with catalyst particles. The use of solid sulphur eliminates many hazards such as flammability and toxicity, which are encountered when using H₂S, liquid sulphide, polysulfides and/or mercaptans. Powdered sulphur may be physically mixed with the catalyst particles prior to loading the catalyst particles in a reactor. The elemental sulphur and the catalyst particles may be mixed

together at a temperature below the melting point of sulphur, preferably in the range of from 82°C (180°F) to 99°C (210°F).

In this temperature range, the elemental sulphur sublimes and is incorporated into the pores of the catalyst particles where, upon cooling, it condenses. The sulphur-catalyst mixture is then heated to a temperature above the melting point of sulphur preferably in the range of from 121°C (250°F) to 199°C (390°F). In the presence of hydrogen, activation of the catalyst takes place. That is, the metal oxides react with substantially all of the sulphur incorporated into the catalyst pores, thus producing H₂S and metal sulfides.

Mixing times for the powdered elemental sulphur and the catalyst can be minimized by heating the mixture at higher temperatures, within specified limitations, due to the increased vapour pressure of the sulphur. Preferably the amount of sulphur employed is 2 to 15% by weight of the catalyst charged. Most preferably, the amount of sulphur employed is about 6% to 8% by weight of the catalyst charged. Mixing times of the powdered sulphur and the catalyst particles are also minimized due to the reduced quantity of sulphur. While the use of greater amounts of sulphur does result in more sulphur being incorporated into the pores of the catalyst, the amount of sulphur stripping during reactor start-up is much greater than that of a 6 to 8% charge. When 6 to 8% sulphur by weight is employed, a minimum stripping effect is observed upon reactor start-up.

A significant aspect of the present invention is that improved results are obtained when catalyst presulfiding is accomplished by mixing the catalyst particles with powdered elemental sulphur and sequentially or simultaneously contacting the sulphur-catalyst mixture with a high boiling oil or hydrocarbon solvent and heating to a temperature above the melting point of sulphur. Hereforth, this step will be referred to as prewetting. Subsequent activity tests on catalyst produced using such a technique have shown excellent results.

Various high boiling oils and hydrocarbon solvents may be used as prewetting agents according to the claimed invention. Good results have been achieved when using oils with boiling ranges from approximately 371°C (700°F) to 538°C (1000°F). In particular, vacuum gas oils with low sulphur contents have been shown to be successful.

If the prewetting step is independent of mixing the powdered sulphur with the catalyst, it may be performed in-situ or off-site of the reactor. If prewetted in-situ, the feedstock used in the reactor can be used as the prewetting oil, minimizing costs for the refinery.

According to one embodiment of the present invention, catalyst particles are sequentially contacted with first, elemental sulphur, then an oil or solvent. The catalyst particles are contacted with the powdered elemental sulphur at a temperature below the melting point of sulphur and preferably in the range of from 82°C (180°F) to 99°C (210°F). The catalyst and the sulphur are then mixed for a sufficient amount of time to allow incorporation of the sulphur into the catalyst pores. A catalyst-sulphur mixture is thus produced. To this mixture a high boiling oil or hydrocarbon solvent is added thus producing a prewet mixture. The prewet mixture is preferably further heated to a temperature above the melting point of sulphur. Most preferably, to a temperature in the range of 121°C (250°F) to 232°C (450°F). The presulfided prewet catalyst so prepared may be conveniently activated by heating in the presence of hydrogen.

In another embodiment according to the present invention, the catalyst particles are contacted with both the powdered elemental sulphur and the high boiling oil or hydrocarbon solvent simultaneously. According to this method, a mixture of elemental sulphur and a high boiling oil or hydrocarbon solvent is first produced. A ratio of approximately 4:1 oil to sulphur by weight is preferred. The mixture is then heated to approximately 38°C (100°F) to promote homogenous mixing of the components. Toluene or other light weight hydrocarbon solvents may be added to decrease the viscosity of the mixture. Also, increased heat will achieve the same effect. The mixture is then added to a preweighed catalyst sample and mixed.

In a preferred embodiment, catalyst particles prewet by the simultaneous method described above are further heat treated at a temperature in the range of from 121°C (250°F) to 232°C (450°F) under a nitrogen atmosphere or other inert atmosphere.

Results of activity tests have shown that mixing the sulphur-catalyst particles with a high boiling oil or hydrocarbon solvent in an inert environment and heating to a temperature above the melting point of sulphur most significantly minimizes sulphur stripping upon reactor start-up. The elemental sulphur by itself was found to indeed presulfide the catalyst metals with only oil and hydrogen present and no other form of sulphur required. Alternatively, the catalyst may be activated with hydrogen at a later step, independent of mixing with a prewetting fluid.

A versatile hydrotreating catalyst which shows good activity under various reactor conditions is a nickel-molybdenum catalyst. Cobalt-molybdenum and nickel-tungsten catalysts are also preferred although many other metal oxide catalysts may be presulfided according to the claimed invention.

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

the following examples.

EXAMPLES

- 5 The following examples further illustrate the practice and advantages of specific embodiments of the claimed invention. These examples are illustrative only; in no event are they to be considered as limiting the scope of the claimed invention.

Example 1 - Standard Method

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A sample of a nickel-molybdenum catalyst was dried at 371°C (700°F) for one hour and then cooled to ambient under vacuum. The sample was then placed in a flask and enough elemental sulphur was added to produce a sulphur level of 6%. The flask was then sealed and placed in a 111°C (231°F) oven for one hour. During this time period, the flask was rotated continually to provide uniform distribution of sulphur. The final sulphur level was 6% sulphur.

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Example IIA: Standard Method and Simultaneous Prewet

20 A sample of a nickel-molybdenum catalyst was dried at 371°C (700°F) for one hour and then cooled to ambient under vacuum.

Into a beaker the following were added:

- 1.) 60.89 grams of a Vacuum Gas Oil Feedstock;
- 2.) 14.10 grams of Elemental Sulphur.

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The mixture was heated to 39°C (102°F) and mixed. The mixture was removed from the heat and 15.51 grams of toluene were added and mixed.

To a preweighed catalyst sample (159.6 grams), 72.02 grams of the above mixture were added. The container was then sealed and mixed by shaking. The container was reopened and placed under vacuum for 16 hours to gently remove the majority of the toluene. The final sulphur level was 4.5% sulphur.

30 Example IIB - Standard Method and Sequential Prewet

A sample of a nickel-molybdenum catalyst was dried at 371°C (700°F) for one hour and then cooled to ambient under vacuum. The sample was then placed in a flask and enough elemental sulphur was added to produce a sulphur level of 6.6%. The flask was then sealed and placed in a 111°C (231°F) oven for one hour. During this time period, the flask was rotated continually to provide uniform distribution of sulphur.

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Into a beaker the following were added:

- 1) 35.01 grams of a vacuum gas oil feedstock;
- 2) 8.92 grams of toluene

The contents of the mixture were then mixed.

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To a preweighed sample of the above sulphur impregnated catalyst (42.72 grams), 15.28 grams of the prepared oil-toluene mixture were added. The container was then sealed and mixed by shaking. The container was reopened and placed under vacuum for 16 hours to gently remove the majority of the toluene. The final sulphur level was 5.5% sulphur.

45 Example III - Standard Method, Simultaneous Prewet and Heat

The catalyst prepared in Example IIA was heat treated at 200°C (392°F) for one hour under a nitrogen blanket.

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The sample was also cooled under a nitrogen blanket. The final sulphur level was 4.9%. It is expected that the Standard Method, Sequential Prewet and Heat would produce comparable results.

Activity tests were conducted on catalysts prepared according to Examples I-III. Oxide catalyst which were not presulfided were also tested as controls for each start-up procedure.

Three start-up procedures were used in testing the activity of each presulfided catalyst.

55 Fast Oil Start-Up

Catalyst Charge: 48cc + diluent
Reactor Pressure: 48bar (700 psig)

H₂ Flow Rate: 12 l/h at 1.01 bar and 15.6°C (1000 SCF/Bb1)
 Liquid Feed: Diesel Fuel
 Sulphur = 0.17 wt. %
 Specific Gravity = 0.872 g/cm³ at 16°C (31.1° API)
 5 LHSV = 1.5 hr⁻¹
 (approx. 63 gms/hr.)

The hydrogen feed rate and reactor pressure are established at ambient temperature. The liquid feed is introduced and the reactor temperature is increased to 121°C (250°F) during the first hour on stream.

10 The reactor temperature is then increased at a rate of about 25°C (45°F)/hour to 343°C (650°F). The reactor is then allowed to cool to 246°C (475°F) during the next two hours. Once the reactor is at 246°C (475°F), the diesel is discontinued and the standard 1.8 wt.% sulphur gas oil feedstock is started. Standard run conditions, heating rate, etc. followed. The standard gas oil feedstock consists of 2/3 vacuum gas oil and 1/3 light cycle oil. The specific gravity is 0.924 g/cm³ at 16°C (API gravity is 21.6°), the weight percent sulphur is 1.8% and the Total Nitrogen content is 880 ppm.

15 Standard run conditions are:

Reactor Temperature: 329°C (625°F)
 Reactor Pressure: 48bar (700 psig)
 LHSV: 1.5 hr⁻¹
 H₂ Flow Rate: 12 l/h at 1.01 bar and 15.6°C (1000 SCR/Bb1)

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Slow Oil Start-Up

Catalyst Charge: 48cc + diluent
 Reactor Pressure: 48bar (700 psig)
 25 H₂ Flow Rate: 12 l/h at 1.01 bar and 15.6°C (1000 SCF/Bb1)
 Liquid Feed: 62 gms./hr of Diesel Oil
 LHSV = 1.5 hr⁻¹
 (approx. 62 gms/hr.)

30 The reactor pressure, hydrogen flow rate and liquid feed rate are established at ambient temperature. The reactor temperature was increased at a rate of 13°C (24°F)/hour to 343°C (650°F).

When the reactor temperature reached 343°C (650°F), the heat was cut off and the temperature was reduced to 246°C (475°F). Immediately following the cut off of heat, the diesel oil was drained from the feed tank and the standard 1.8 wt.% sulphur feedstock was charged. Standard run conditions, heating rate, etc. followed.

35 Hydrogen Start-Up

(Feed in at 288°C (550°F))

Catalyst Charge: 48cc + diluent
 40 Reactor Pressure: 48bar (700 psig)
 H₂ Flow Rate: 12.5 l/h at 1.01 bar and 15.6°C (0.467 SCFH)
 Liquid Feed: 0.0 gms/hr.

45 The reactor was heated at a rate of 28°C (50°F)/hr until a temperature of 329°C (625°F) was reached. During this heat up period, liquid feed was introduced when the reactor temperature reached 288°C (550°F) at a feed rate of 65 gms/hr.

50 In certain start-up situations, the standard method presulfided catalysts have difficulties. With the slow diesel start-up, excessive sulphur is displaced from the catalyst resulting in less activity. With the hydrogen to 288°C (550°F) start-up, the standard method presulfided catalysts yield poor results because of the exposure to hydrogen at high temperature without a hydrocarbon present. The modified procedures of the simultaneous and sequential prewet methods with and without heat overcome these difficulties by producing a catalyst that can tolerate a wide range of conceivable start-up procedures.

The results presented below are for the three different types of start-up procedures. The test results verify that the use of vacuum gas oil and heat most greatly reduce the weight percent of sulphur in the product.

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	Product <u>sulphur</u> Wt	Product <u>Total Nitrogen</u> ppm
5		
10	<u>Fast Oil Start-Up</u>	
	Oxide catalyst	0.68-0.69 640-660
15	Example 1	0.54-0.58 560-600
	<u>Slow Oil Start-Up</u>	
20	Oxide catalyst	0.68-0.69 640-660
	Example I	0.67 633
	Example IIA	0.61 616
25	Example IIB	0.61 610
	Example III	0.57 585
30	<u>Hydrogen Start-Up</u> (Feed in at 288°C (550°F))	
35	Oxide catalyst	0.65 625
40	Example I	0.71-0.84 620-700
	Example IIA	0.58 595
	Example IIB	0.60-0.63 580-600
45	Example III	0.57 550

50 The present invention has been described in some detail, including alternative embodiments thereof. It will be appreciated, however, that those skilled in the art, upon consideration of the present disclosure, may make modifications and improvements on this invention and still be within the scope and spirit of this invention as set forth in the following claims. In particular the amount of sulphur employed may be between 4.5% and 8% of the catalyst.

55 Claims

1. A method of presulfiding a hydrotreating catalyst comprising the steps of:
(a) contacting said catalyst with powdered elemental sulphur at a temperature of at least 82°C but below

	<u>Product</u> <u>sulphur</u> Wt	<u>Product</u> <u>Total Nitrogen</u> ppm
5		
10	<u>Fast Oil Start-Up</u>	
	Oxide catalyst	0.68-0.69 640-660
	Example 1	0.54-0.58 560-600
15		
	<u>Slow Oil Start-Up</u>	
20	Oxide catalyst	0.68-0.69 640-660
	Example I	0.67 633
	Example IIA	0.61 616
25	Example IIB	0.61 610
	Example III	0.57 585
30		
	<u>Hydrogen Start-Up</u>	
	(Feed in at 288°C	
35	<u>(550°F))</u>	
	Oxide catalyst	0.65 625
40	Example I	0.71-0.84 620-700
	Example IIA	0.58 595
	Example IIB	0.60-0.63 580-600
45	Example III	0.57 550

The present invention has been described in some detail, including alternative embodiments thereof. It will be appreciated, however, that those skilled in the art, upon consideration of the present disclosure, may make modifications and improvements on this invention and still be within the scope and spirit of this invention as set forth in the following claims. In particular the amount of sulphur employed may be between 4.5% and 8% of the catalyst.

55 Claims

1. A method of presulfiding a hydrotreating catalyst comprising the steps of:
 - (a) contacting said catalyst with powdered elemental sulphur at a temperature of at least 82°C but below



the melting point of sulphur such that said elemental sulphur sublimates and is substantially incorporated in the pores of said catalyst, thereby forming a mixture, and

(b) heating said mixture in the presence of hydrogen to a temperature above the melting point of sulphur and below 199°C (390°F).

5 2. A method of presulfiding a hydrotreating catalyst comprising the steps of:

(a) contacting said catalyst with powdered elemental sulphur at a temperature below the melting point of sulphur such that said elemental sulphur sublimates and is substantially incorporated in the pores of said catalyst;

10 (b) mixing said sulphur-incorporated catalyst with at least one member selected from the group consisting of hydrocarbon solvents and high boiling oils, thereby producing a prewet mixture.

3. The method of claim 2, wherein said method further comprises heating said prewet mixture to a temperature above the melting point of sulphur.

4. The method of claim 2, wherein said method further comprises heating the prewet mixture.

15 5. The method of claim 2, wherein said method further comprises contacting said catalyst with powdered elemental sulphur in the absence of oxygen.

6. The method of claim 5, wherein said method further comprises contacting said catalyst with said powdered elemental sulphur in the presence of an inert gas.

7. The method of claim 1 or 2, wherein said catalyst contains at least one element selected from the group consisting of Co, Mo, Ni and W.

20 8. The method of claim 1 or 2, wherein the amount of elemental sulphur mixed with said catalyst is from 2 to 15% the weight of said catalyst.

9. The method of claim 8, wherein said elemental sulphur is about 6%-8% the weight of said catalyst.

10. The method of claim 2, wherein said member is a hydrocarbon feedstock.

11. A method of presulfiding a hydrotreating catalyst comprising the steps of

25 (a) preparing a presulfiding suspension containing particulate elemental sulphur by mixing together powdered elemental sulphur and one member from the group consisting of high boiling oils and hydrocarbon solvents,

(b) heating said suspension to a temperature below the melting point of sulphur, and

30 (c) contacting a hydrotreating catalyst with said suspension in a manner such that said elemental sulphur is substantially incorporated into the pores of said catalyst.

12. The method of claim 11, wherein said method further comprises heating said catalyst, after contacting with said mixture, to a temperature above the melting point of sulphur.

13. A presulfided hydrotreating catalyst produced by the process of claim 1, 2 or 11.

35 14. A method of hydrotreating a hydrocarbon feedstock comprising the steps of contacting the hydrocarbon feedstock with hydrogen and with a presulfided hydrotreating catalyst, wherein said catalyst is presulfided by the steps of:

(a) contacting said catalyst with elemental sulphur at a temperature below the melting point of sulphur,

(b) mixing said catalyst with one member selected from the group consisting of high boiling oils and hydrocarbon solvents, to form a prewet mixture, and

40 (c) heating said prewet mixture at a temperature above the melting point of sulphur.

15. The method of claim 14, wherein said catalyst is contacted with elemental sulphur at a temperature of 82°-99°C (180° to 210°F).

16. The method of claim 14, wherein said prewet mixture is heated to a temperature in the range of 121°-232°C (250° to 450°F).

45 17. The method of claim 14, wherein said catalyst contains at least one element selected from the group consisting of Co, Mo, Ni and W.

18. A method as in claim 2, wherein said method further comprises the step of exposing said prewet mixture to hydrogen.

50 19. A method as in claim 11, wherein said method further comprises the step of exposing said catalyst contacted with said suspension to hydrogen.

20. A mixture comprising a metal oxide catalyst and a suspension, wherein said suspension comprises: an amount of elemental sulphur sufficient to sulfide active and promoter metals in said catalyst upon exposure to hydrogen; and

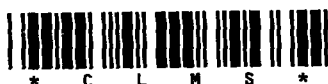
55 an amount of a hydrocarbon solvent or high boiling oil which can be substantially incorporated into said catalyst.

21. A method as claimed in any of claims 1-10, wherein the catalyst is contacted with powdered elemental sulphur at a temperature below 99°C (210°F).



Patentansprüche

1. Verfahren zum Vorsulfidieren eines Hydrobehandlungs-Katalysators, mit folgenden Schritten:
 - a) In-Berührung-Bringen des Katalysators mit pulverisiertem elementarem Schwefel bei einer Temperatur von mindestens 82°C, jedoch unterhalb des Schmelzpunkts von Schwefel, so daß der elementare Schwefel sublimiert und im wesentlichen in die Poren des Katalysators eingelagert wird, wodurch ein Gemisch entsteht, und
 - b) Erwärmen des Gemisches in Anwesenheit von Wasserstoff auf eine Temperatur oberhalb des Schmelzpunkts von Schwefel und unterhalb 199°C (390°F).
2. Verfahren zum Vorsulfidieren eines Hydrobehandlungs-Katalysators mit folgenden Schritten:
 - a) In-Berührung-Bringen des Katalysators mit pulverisiertem elementarem Schwefel bei einer Temperatur unterhalb des Schmelzpunkts von Schwefel, derart, daß der elementare Schwefel sublimiert und im wesentlichen in die Poren des Katalysators eingelagert wird,
 - b) Mischen des schwefelhaltigen Katalysators mit mindestens einem Vertreter der aus Kohlenwasserstoff-Lösungsmitteln und hochsiedenden Ölen bestehenden Gruppe, wodurch ein vorgeäßtes Gemisch hergestellt wird.
3. Verfahren nach Anspruch 2, wobei das Verfahren außerdem das Erwärmen des vorgeäßten Gemisches auf eine Temperatur oberhalb des Schmelzpunkts von Schwefel erwärmt wird.
4. Verfahren nach Anspruch 2, wobei das Verfahren außerdem das Erwärmen des vorgeäßten Gemisches umfaßt.
5. Verfahren nach Anspruch 2, wobei das Verfahren außerdem das In-Berührung-Bringen des Katalysators mit pulverisiertem elementarem Schwefel in Abwesenheit von Sauerstoff umfaßt.
6. Verfahren nach Anspruch 5, wobei das Verfahren außerdem das In-Berührung-Bringen des Katalysators mit dem pulverisierten elementarem Schwefel in Anwesenheit eines Inertgases umfaßt.
7. Verfahren nach Anspruch 1 oder 2, wobei der Katalysator mindestens ein aus der Co, Mo, Ni und W umfassenden Gruppe ausgewähltes Element enthält.
8. Verfahren nach Anspruch 1 oder 2, wobei die Menge von mit dem Katalysator vermishtem elementarem Schwefel von 2 bis 15 Gewichtsprozent des Katalysators beträgt.
9. Verfahren nach Anspruch 8, wobei der elementare Schwefel etwa 6% bis 8% des Gewichts des Katalysators ausmacht.
10. Verfahren nach Anspruch 2, wobei der genannte Vertreter ein Kohlenwasserstoff-Ausgangsmaterial ist.
11. Verfahren zum Vorsulfidieren eines Hydrobehandlungs-Katalysators, mit folgenden Schritten:
 - a) Zubereiten einer Vorsulfidierungs-Suspension, die teilchenförmigen elementaren Schwefel enthält, indem pulverisierter elementarer Schwefel und ein Vertreter der aus hochsiedenden Ölen und Kohlenwasserstoff-Lösungsmitteln bestehenden Gruppe zusammengemischt werden,
 - b) Erwärmen der Suspension auf eine Temperatur unterhalb des Schmelzpunkts von Schwefel, und
 - c) In-Berührung-Bringen des Hydrobehandlungs-Katalysators mit der Suspension in einer solchen Weise, daß der elementare Schwefel im wesentlichen in die Poren des Katalysators eingelagert wird.
12. Verfahren nach Anspruch 11, wobei das Verfahren außerdem das Erwärmen des Katalysators nach dem In-Berührung-Bringen mit dem Gemisch auf eine Temperatur oberhalb des Schmelzpunkts von Schwefel umfaßt.
13. Vorsulfidierter Hydrobehandlungs-Katalysator, der nach dem Verfahren nach Anspruch 1, 2 oder 11 hergestellt ist.
14. Verfahren zur Hydrobehandlung eines Kohlenwasserstoff-Ausgangsmaterials mit den Schritten des In-Berührung-Bringens des Kohlenwasserstoff-Ausgangsmaterials mit Wasserstoff und mit einem vorsulfidierten Hydrobehandlungs-Katalysator, wobei der Katalysator durch folgende Schritte vorsulfidiert wird:
 - a) In-Berührung-Bringen des Katalysators mit elementarem Schwefel bei einer Temperatur unterhalb des Schmelzpunkts von Schwefel,
 - b) Mischen des Katalysators mit einem aus der hochsiedende Öle und Kohlenwasserstoff-Lösungsmittel umfassenden Gruppe ausgewählten Vertreter zur Bildung eines vorgeäßten Gemisches, und
 - c) Erwärmen des vorgeäßten Gemisches auf eine Temperatur oberhalb des Schmelzpunkts von Schwefel.
15. Verfahren nach Anspruch 14, wobei der Katalysator bei einer Temperatur von 82°C bis 99°C (180°F bis 210°F) mit elementarem Schwefel in Berührung gebracht wird.
16. Verfahren nach Anspruch 14, wobei das vorgeäßte Gemisch auf eine Temperatur im Bereich von 121°C bis 232°C (250°F bis 450°F) erwärmt wird.
17. Verfahren nach Anspruch 14, wobei der Katalysator mindestens ein aus der Co, Mo, Ni und W umfas-



senden Gruppe ausgewähltes Element enthält.

18. Verfahren nach Anspruch 2, wobei das Verfahren außerdem einen Schritt umfaßt, in welchem das vorgenähte Gemisch Wasserstoff ausgesetzt wird.

19. Verfahren nach Anspruch 11, wobei das Verfahren außerdem einen Schritt umfaßt, in welchem der mit der Suspension in Berührung gebrachte Katalysator Wasserstoff ausgesetzt wird.

20. Gemisch aus einem Metalloxid-Katalysator und einer Suspension, wobei die Suspension enthält:
eine zur Sulfidierung aktiver und Promotor-Metalle in dem Katalysator nach dem Zusammenbringen mit Wasserstoff ausreichende Menge elementaren Schwefels, und

eine Menge eines Kohlenwasserstoff-Lösungsmittels oder eines hochsiedenden Öls, die im wesentlichen in den Katalysator eingelagert werden kann.

21. Verfahren nach einem der Ansprüche 1 bis 10, wobei der Katalysator bei einer Temperatur unterhalb 99°C (210°F) mit pulverisiertem elementarem Schwefel in Berührung gebracht wird.

15 Revendications

1. Procédé de présulfuration d'un catalyseur d'hydrogénation consistant :

a) à mettre en contact ledit catalyseur avec du soufre élémentaire pulvérulent, à une température d'au moins 82°C mais inférieure au point de fusion du soufre, de manière à ce que ledit soufre élémentaire se sublime et soit incorporé, en substance, dans les pores dudit catalyseur, pour former un mélange, et
b) à chauffer ledit mélange en présence d'hydrogène à une température supérieure au point de fusion du soufre et inférieure à 199°C (390°F).

2. Procédé de présulfuration d'un catalyseur d'hydrogénation consistant :

a) à mettre en contact ledit catalyseur avec du soufre élémentaire pulvérulent à une température inférieure au point de fusion du soufre, de manière à ce que ledit soufre élémentaire se sublime et soit incorporé, en substance, dans les pores dudit catalyseur ;

b) à mélanger ledit catalyseur incorporant du soufre avec au moins une substance choisie dans le groupe des solvants hydrocarbonés et des huiles à haut point d'ébullition, pour conduire à un mélange pré-imbibé.

3. Procédé selon la revendication 2, caractérisé en ce qu'il consiste en outre à chauffer ledit mélange pré-imbibé à une température supérieure au point de fusion du soufre.

4. Procédé selon la revendication 2, caractérisé en ce qu'il consiste en outre à chauffer le mélange pré-imbibé.

5. Procédé selon la revendication 2, caractérisé en ce qu'il consiste en outre à mettre en contact ledit catalyseur avec du soufre élémentaire pulvérulent en l'absence d'oxygène.

6. Procédé selon la revendication 5, caractérisé en ce qu'il consiste en outre à mettre en contact ledit catalyseur avec ledit soufre élémentaire pulvérulent en présence d'un gaz inerte.

7. Procédé selon la revendication 1 ou 2, caractérisé en ce que ledit catalyseur contient au moins un élément choisi dans le groupe du Co, Mo, Ni et W.

8. Procédé selon la revendication 1 ou 2, caractérisé en ce que la proportion de soufre élémentaire mélangé avec ledit catalyseur est comprise entre 2 et 15 % du poids dudit catalyseur.

9. Procédé selon la revendication 8, caractérisé en ce que la proportion du soufre élémentaire est comprise entre 6 et 8 % du poids dudit catalyseur.

10. Procédé selon la revendication 2, caractérisé en ce que ladite substance est un substrat hydrocarboné.

11. Procédé de présulfuration d'un catalyseur d'hydrogénation consistant :

a) à préparer une suspension de présulfuration contenant du soufre élémentaire particulaire en mélangeant le soufre élémentaire pulvérulent avec une substance choisie dans le groupe des huiles à haut point d'ébullition et des solvants hydrocarbonés.

b) à chauffer ladite suspension à une température inférieure au point de fusion du soufre, et

c) à mettre en contact le catalyseur d'hydrogénation avec ladite suspension de manière à ce que ledit soufre élémentaire soit incorporé, en substance, dans les pores dudit catalyseur.

12. Procédé selon la revendication 11, caractérisé en ce qu'il consiste en outre à chauffer ledit catalyseur, après l'avoir mis en contact avec ledit mélange, à une température supérieure au point de fusion du soufre.

13. Catalyseur d'hydrogénation présulfuré préparé par le procédé selon l'une des revendications 1, 2 et 11.

14. Procédé d'hydrogénation d'un substrat hydrocarboné consistant à mettre en contact le substrat hydrocarboné avec de l'hydrogène et un catalyseur d'hydrogénation présulfuré, caractérisé en ce que ledit catalyseur est présulfuré selon les étapes suivantes :

a) mise en contact dudit catalyseur avec le soufre élémentaire, à une température inférieure au point de



fusion du soufre,

b) mélange dudit catalyseur avec une substance choisie dans le groupe des huiles à haut point d'ébullition et solvants hydrocarbonés, pour former un mélange pré-imbibé, et

c) chauffage dudit mélange pré-imbibé, à une température supérieure au point de fusion du soufre.

5 15. Procédé selon la revendication 14, caractérisé en ce que ledit catalyseur est mis en contact avec le soufre élémentaire, à une température de 82-99°C (180° à 210°F).

16. Procédé selon la revendication 14, caractérisé en ce que ledit mélange pré-imbibé est chauffé à une température comprise entre 121 et 232°C (250° à 450°F).

10 17. Procédé selon la revendication 14, caractérisé en ce que ledit catalyseur contient au moins un élément choisi dans le groupe du Co, Mo, Ni et W.

18. Procédé selon la revendication 2, caractérisé en ce qu'il consiste en outre à exposer ledit mélange pré-imbibé à de l'hydrogène.

19. Procédé selon la revendication 11, caractérisé en ce qu'il consiste en outre à exposer à de l'hydrogène ledit catalyseur mis en contact avec ladite suspension.

15 20. Mélange comprenant un catalyseur d'oxyde métallique et une suspension, caractérisé en ce que ladite suspension comprend :

une quantité de soufre élémentaire suffisante pour sulfurer les métaux actifs et promoteurs dudit catalyseur par exposition à de l'hydrogène, et

20 une quantité de solvant hydrocarboné ou d'huile à haut point d'ébullition qui peut être incorporée, en substance, dans ledit catalyseur.

21. Procédé selon l'une quelconque des revendication 1 à 10, caractérisé en ce que le catalyseur est mis en contact avec le soufre élémentaire pulvérulent, à une température inférieure à 99°C (210°F).

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