

Description

Description for the following Contracting States : BE, DE, GB, IT, NL

The present invention is directed to a presulfiding agent, a process of presulfiding an oxidic hydrotreating catalyst to form a sulfided hydrotreating catalyst and a sulfided hydrotreating catalyst prepared in accordance with said process.

Hydrotreating is an essential step in the refining of crude petroleum, the major purposes of which is for (i) the conversion of organosulfur and organonitrogen compounds to hydrogen sulfide and ammonia, respectively, (ii) the removal of metals and (iii) the hydrogenation of olefins and aromatics present in the petroleum fraction. Catalysts for the hydrotreating process are metal oxides which have been sulfided prior to use (presulfided). By presulfiding under carefully controlled conditions, coke formation, which leads to catalyst deactivation by plugging the catalyst pores, is minimized.

There has already been proposed a presulfiding agent which is a dialkyl polysulfide of the formula: $R(S)_xR'$ wherein R and R' are C_1 - C_{20} alkyl groups and x an average number is in the range of 2 to 8. The process of presulfiding the oxidic hydrotreating catalyst requires that no reducing agent be introduced into the presulfiding procedure

Pretreatment of an oxidic hydrotreating catalyst is well known in the art of petroleum refining. US-A-4,443,330 discloses the upgrading of a coal liquid by feeding said liquid along with hydrogen and a sulfur-containing liquid to a catalytic reactor. The catalyst in the reactor is a metal oxide which is converted to the sulfided state by sulfur of hydrogen sulfide in the reactor. The catalyst is kept in a highly sulfided state by the reaction with the sulfur-containing liquid passed through the reactor. The sulfur-containing liquid may be a high boiling hydrocarbon sulfur compound of the formula RSR_1 where R and R_1 are alkyl groups having from 2 to 20 carbon atoms (methyl disulfide, dodecyl disulfide and diphenyl disulfide are also mentioned).

US-A-4,530,917 discloses the presulfiding (*ex situ*) in the absence of hydrogen of a metal oxide hydrotreating catalyst by means of a sulfurization agent having the formula: $R-S_n-R_1$ wherein n is 3 to 20 and R and R_1 are each an organic radical which may be a C_1 - C_{150} alkyl. The sulfurization agent may be diluted with a solvent therefor.

This invention provides a presulfiding agent comprising a blend of from at least 10 to about 90 weight percent dialkyl sulfide of the formula $R_1S_xR_2$ wherein R_1 and R_2 are independently alkyl groups having from 1 to 12 carbon atoms and x is 1 or 2, and from no more than 90 to about 10 weight percent of a dialkyl polysulfide of the formula $R_3S_yR_4$ wherein R_3 and R_4 are independently alkyl groups having from 1 to 20 carbon atoms and y, the sulfur rank of the polysulfide (average number of sulfur atoms per molecule), is 2 to 6 provided that the total number of carbon atoms in R_3 and R_4 do not exceed 30 and y is greater than x, the dialkyl sulfide being present in the blend in an amount ranging from 25 to 75 weight percent and said dialkyl being present in the blend in an amount ranging from 75 to 25 weight percent.

This invention also provides a process of presulfiding an oxidic hydrotreating catalyst to form a sulfided hydrotreating catalyst which comprises passing at an elevated temperature and pressure a presulfiding solution and hydrogen gas in contact with an inert, solid, porous catalyst support bearing molybdenum oxide in an amount ranging from 5 to 50 percent, based on the combined weight of the support and oxide, and cobalt oxide in an amount ranging from 0 to 20 percent, based on the combined weight of the support and oxides, said presulfiding solution comprising a liquid hydrocarbon solvent containing the presulfiding agent as defined above in an amount sufficient to provide a total sulfur content of from 0.5 to 5 percent based on the weight of said solution, said contact with said support continuing for a time sufficient to materially presulfide said metal oxides.

This invention also provides the sulfided hydrotreating catalyst prepared in accordance with the above described process.

The invention provides an improved presulfiding agent for sulfiding oxidic hydrotreating catalysts, said presulfiding agent being a blend of a dialkyl sulfide or dialkyl disulfide with one or more polysulfides, said presulfiding agent affording a catalyst composition of surprisingly high activity when used to presulfide an oxidic hydrotreating catalyst by contacting a solution of said presulfiding agent in a hydrocarbon carrier with said oxidic hydrotreating catalyst in the presence of hydrogen at elevated temperatures and pressures.

The presulfiding agent of this invention is a blend of 25 to 75 weight percent of a dialkyl sulfide or a dialkyl disulfide wherein the alkyl group or groups have from 1 to 6 carbon atoms and from 75 to 25 weight percent of a dialkyl disulfide or polysulfide wherein the alkyl groups have from 1 to 9 carbon atoms. Typically, the alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, t-octyl, nonyl, t-nonyl, decyl, undecyl, dodecyl, t-dodecyl, hexadecyl, heptadecyl, octadecyl, eicosanyl and homologs of these.

A more preferred presulfiding agent is a blend of dimethyl sulfide with a dialkyl polysulfide which is one or more of the compounds selected from the group of dimethyl disulfide, dimethyl polysulfide and ditertiary nonyl polysulfide. A most preferred presulfiding agent is a blend of dimethyl disulfide and either dimethyl polysulfide or ditertiary nonyl polysulfide.

The inert solid, porous catalyst support is preferably alumina (α - Al_2O_3) or silica (SiO_2) or a mixture of these materials. However, other solid catalyst supports including clays and carbon may be used.

The oxidic hydrotreating catalyst borne by the support is molybdenum oxide (MoO_3) or a combination of MoO_3 and cobalt oxide (CoO) where the MoO_3 is present in the greater amount. The MoO_3 is present on the catalyst support in an amount ranging from 5 to 50 percent, preferably from about 10 to 25 percent, based on the combined weight of the support and MoO_3 . When CoO is present it will be in amounts ranging up to 20 percent, preferably from 2 to 10 percent, based on the combined weight of the catalyst support and metal oxides.

The liquid hydrocarbon solvent for the presulfiding agent of this invention is preferably a low cut, liquid paraffinic hydrocarbon stock, more preferably a naphtha, kerosine or diesel cut having an end boiling point below 399°C (750°F). The solvent should contain minimum amounts of sulfur, nitrogen, aromatics and unsaturates.

In the process for preparing the sulfided hydrotreating catalyst, the presulfiding agent and the liquid hydrocarbon solvent are mixed together to form a solution containing at least 0.5 and up to 5 percent of sulfur, based on the weight of the solution. This solution is brought into contact with the oxidic hydrotreating catalyst bearing support in the presence of hydrogen. The preferred hydrogen flow rate is at least 507 by volume and more preferably, at least 90% of the maximum once-through hydrogen flow rate of the system. Maximum once-through hydrogen flow rate is determined by the maximum gas capacity of a given process reactor at given temperature and pressure conditions. The catalyst bearing support bed in the process reactor is heated to a temperature in the range of from at least 175°C (350°F) up to 230°C (450°F) and the presulfiding solution is preferably passed through or over the catalyst bed at a liquid hourly space velocity (LHSV) between 0.5 and 5 hr^{-1} at a pressure preferably ranging between 13 and 102 bars (200 - 1500 psig). The presulfiding solution/hydrogen gas feed is continued until the metal oxide catalyst is materially presulfided, i.e., when the catalyst has taken up at least 50 percent of the theoretical amount of sulfur required to effect stoichiometric conversion of the metal oxides (MoO_3 and CoO) to their respective reduced sulfides (MoS_2 and Co_9S_8) or until a sharp rise in the effluent concentration of H_2S is noted.

Optionally, rather than carrying out the presulfiding at one temperature, the initial presulfiding is carried out as above and, upon completion of the initial presulfiding, the temperature of the bed is raised by at least about 25°C (70°F) and the presulfiding solution is passed over the catalyst in the presence of hydrogen until the catalyst is materially presulfided or until a sharp rise in the effluent concentration of H_2S is noted.

Thus, the sulfided hydrotreating catalyst of this invention comprises a composition prepared in accordance with the above described process.

After the presulfiding operation is complete, the formed hydrotreating catalyst is used to refine petroleum or other hydrocarbon feedstock by contacting said catalyst with said feedstock in the presence of hydrogen at elevated temperature and pressure. The feedstock is preferably passed through the catalyst at a liquid hourly space velocity (LHSV) of from about 1 to 4 hr^{-1} . The temperature of the reaction preferably ranges from 287 to 482°C (550 to 900°F) while the pressure is preferably from 13 to 165 bars (200 - 2400 psig). The following example is set forth to illustrate this invention.

Example

Dimethyl Disulfide Presulfiding Agent

91 ml (73g) of a solid, particulate catalyst bearing molybdenum oxide (MoO_3) and cobalt oxide (CoO) was calcined at 455°C (850°F) for one hour. This oxidic hydrotreating catalyst, sold by Akzo Chemie as KF-165-1/16, comprised 16 weight % MoO_3 , 5 weight % CoO and a remainder of alumina (α - Al_2O_3) as the support. The catalyst was diluted by mixing with an equal volume of alumina and the mass charged into a 200 ml. trickle-bed reactor (elongated catalyst-packed tube). The reactor was purged with nitrogen and heated to 230°C (450°F) in a molten solder bath. To 7460g. of a diesel oil [API gravity = 37.7° ; total sulfur = 0.24%; total nitrogen = 84 ppm; distillation range = 203 - 355°C (398 - 672°F)] was added 110g of dimethyl disulfide (DMDS) to give a solution containing 1.0 wt% sulfur contributed by the presulfiding agent and a total sulfur content of 1.2 wt%. After a hydrogen flow rate of 2 SCFH at 34 bars (500 psig) total pressure was established, the presulfiding solution was fed at a rate of 206g/hour (LHSV= 2.7 hr^{-1}) for twelve hours, exposing the catalyst to a total of 30g of sulfur. The bath temperature was held at 230°C

(450°F) for four hours, raised to 315°C (600°F) at 14°C (25°F) /hour over a six hour period and held at 315°C (600°F) for two hours to thereby produce a hydrotreating catalyst.

The bath temperature was then raised to 338°C (640°F) over a two hour period while the feed was switched from the presulfiding solution to a vacuum gas oil [API gravity = 22.5°; total sulfur = 1.37%; total nitrogen = 822 ppm; distillation range = 270-524°C (518 - 975°F)]. The feedstock LHSV was 2.5hr⁻¹ and the flow was maintained for 72 hours, with liquid product samples being taken every 24 hours.

The average sulfur analysis of the samples was 0.779 wt% and the hydrosulfurization rate constant, k, was calculated using the following relationship:

$$k = (\text{LHSV}) \times \frac{1}{n-1} \left[\frac{1}{S^{n-1}} - \frac{1}{S_0^{n-1}} \right]$$

where LHSV is the feedstock liquid hourly space velocity, n is the catalyst HDS (hydrodesulfurization) reaction order (n=1.65 for the above identified MoO₃, CoO, alumina hydrotreating catalyst), S is the average weight % sulfur in the product samples and S₀ is the weight % sulfur in the feedstock. The calculated k for the above run was 1.41 and this value was used as the basis for calculating the relative volume activities (RVA's) of catalysts sulfided with test sulfiding agents.

A sample of the spent catalyst was taken, extracted with toluene and analyzed for total carbon, hydrogen and sulfur, and the pore volume and surface area were determined by mercury perfusion at 4880 bars (60,000 psi). The results are shown in Table 1 below.

Dimethyl Polysulfide Presulfiding Agent

The above procedure was followed except that pure dimethyl polysulfide (DMPS) containing 76 weight % total sulfur was used in place of DMDS as the presulfiding agent. 110g of DMPS was blended with 7490g of diesel oil to give a solution containing 1.0 wt% sulfur contributed by the DMPS. The RVA (relative volume activity) of the catalyst was calculated using the formula:

$$\text{RVA}_T = (k_T/k_R) \times 100$$

where RVA_T is the RVA of a catalyst sulfided with test agent T, k_T is the HDS-rate constant for a catalyst sulfided with test agent T calculated as described above for k, and k_R is the HDS-rate constant for a catalyst sulfided with DMDS, calculated above to be 1.41.

The results, including spent catalyst analysis, for duplicate runs where DMPS was used as the sulfiding agent, are given in Table 1 below. The average RVA of 140 is significantly greater than that for DMDS.

DMDS/DMPS Blend Presulfiding Agent

The procedure shown for DMDS above was repeated except that a 1:1 weight blend of DMDS and DMPS was used as the presulfiding agent and 55g of the 1:1 blend was dissolved in 3905g of diesel oil to give a solution containing 1.0 wt% sulfur contributed by the blend. The results are given in Table 1 below.

TABLE 1
Spent Catalyst Analysis

Presulfiding Agent	RVA (HDS)	%C	%H	%S	Pore Volume (ml./g.)	Surface Area M ² /g
Catalyst Prior to Sulfurization	--	--	--	--	0.52 ¹	268 ¹
DMDS	100 ²	8.19 ³	1.32	5.32	0.27	215
DMPS	143) 140 ⁴	10.56 ³	1.79	5.51	0.2	196
DMPS	137)	--	--	--	--	--
DMDS/DMPS Blend	155	9.07 ³	1.55	5.39	0.33	287

1. Actual lot analysis - manufacturer's data
2. By definition
3. Single sample
4. Average of duplicate runs
5. Average of analyses of duplicate samples

As can be seen from the above table, the RVA of 155 for the blend of DMDS and DMPS is significantly greater than that observed of DMDS and DMPS and such RVA is also significantly greater than that expected on the basis of the individual RVA values for DMDS and DMPS.

Description for the following Contracting States : ES, FR, SE

The present invention is directed to a presulfiding agent, a process of presulfiding an oxidic hydrotreating catalyst to form a sulfided hydrotreating catalyst and a sulfided hydrotreating catalyst prepared in accordance with said process.

Hydrotreating is an essential step in the refining of crude petroleum, the major purposes of which is for (i) the conversion of organosulfur and organonitrogen compounds to hydrogen sulfide and ammonia, respectively, (ii) the removal of metals and (iii) the hydrogenation of olefins and aromatics present in the petroleum fraction. Catalysts for the hydrotreating process are metal oxides which have been sulfided prior to use (presulfided). By presulfiding under carefully controlled conditions, coke formation, which leads to catalyst deactivation by plugging the catalyst pores, is minimized.

There has already been proposed a presulfiding agent which is a dialkyl polysulfide of the formula: $R(S)_xR'$ wherein R and R' are C_1 - C_{20} alkyl groups and x an average number is in the range of 2 to 8. The process of presulfiding the oxidic hydrotreating catalyst requires that no reducing agent be introduced into the presulfiding procedure.

Pretreatment of an oxidic hydrotreating catalyst is well known in the art of petroleum refining. US-A-4,443,330 discloses the upgrading of a coal liquid by feeding said liquid along with hydrogen and a sulfur-containing liquid to a catalytic reactor. The catalyst in the reactor is a metal oxide which is converted to the sulfided state by sulfur or hydrogen sulfide in the reactor. The catalyst is kept in a highly sulfided state by the reaction with the sulfur-containing liquid passed through the reactor. The sulfur-containing liquid may be a high boiling hydrocarbon sulfur compound of the formula RSR_1 where R and R_1 are alkyl groups having from 2 to 20 carbon atoms (methyl disulfide, dodecyl disulfide and diphenyl disulfide are also mentioned).

US-A-4,530,917 discloses the presulfiding (*ex situ*) in the absence of hydrogen of a metal oxide hydrotreating catalyst by means of a sulfurization agent having the formula: $R-S_n-R_1$ wherein n is 3 to 20 and R and R_1 are each an organic radical which may be a C_1 - C_{150} alkyl. The sulfurization agent may be diluted with a solvent therefor.

This invention provides a presulfiding agent comprising a blend of from at least 10 to about 90 weight percent dialkyl sulfide of the formula $R_1S_xR_2$ wherein R_1 and R_2 are independently alkyl groups having from 1 to 12 carbon atoms and x is 1 or 2, and from no more than 90 to about 10 weight percent of a dialkyl polysulfide of the formula $R_3S_yR_4$ wherein R_3 and R_4 are independently alkyl groups having from 1 to 20 carbon atoms and y, the sulfur rank of the polysulfide (average number of sulfur atoms per molecule), is 2 to 8 provided that the total number of carbon atoms in R_3 and R_4 do not exceed 30 and y is greater than x.

This invention also provides a process of presulfiding a oxidic hydrotreating catalyst to form a sulfided hydrotreating catalyst which comprises passing at an elevated temperature and pressure a presulfiding solution and hydrogen gas in contact with an inert, solid, porous catalyst support bearing molybdenum oxide in an amount ranging from 5 to 50 percent, based on the combined weight of the support and oxide, and cobalt oxide in an amount ranging from 0 to 20 percent, based on the combined weight of the support and oxides, said presulfiding solution comprising a liquid hydrocarbon solvent containing the presulfiding agent as defined above in an amount sufficient to provide a total sulfur content of from 0.5 to 5 percent based on the weight of said solution, said contact with said support continuing for a time sufficient to materially presulfide said metal oxides.

This invention also provides the sulfided hydrotreating catalyst prepared in accordance with the above described process.

The invention provides an improved presulfiding agent for sulfiding oxidic hydrotreating catalysts, said presulfiding agent being a blend of a dialkyl sulfide or dialkyl disulfide with one or more polysulfides, said presulfiding agent affording a catalyst composition of surprisingly high activity when used to presulfide an oxidic hydrotreating catalyst by contacting a solution of said presulfiding agent in a hydrocarbon carrier with said oxidic hydrotreating catalyst in the presence of hydrogen at elevated temperatures and pressures.

A preferred presulfiding agent of this invention is a blend of 25 to 75 weight percent of a dialkyl sulfide or a dialkyl disulfide wherein the alkyl group or groups have from 1 to 6 carbon atoms and from 75 to 25 weight percent of a dialkyl disulfide or polysulfide wherein the alkyl groups have from 1 to 9 carbon atoms. Typically, the alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, t-octyl, nonyl, t-nonyl, decyl, undecyl, dodecyl, t-dodecyl, hexadecyl, heptadecyl, octadecyl, eicosanyl and homologs of these.

A more preferred presulfiding agent is a blend of dimethyl sulfide with a dialkyl polysulfide which is one or more of the compounds selected from the group of dimethyl disulfide, dimethyl polysulfide and ditertiary nonyl polysulfide. A most preferred presulfiding agent is a blend of dimethyl disulfide and either dimethyl polysulfide or ditertiary nonyl polysulfide.

The inert solid, porous catalyst support is preferably alumina (α - Al_2O_3) or silica (SiO_2) or a mixture of

these materials. However, other solid catalyst supports including clays and carbon may be used.

The oxidic hydrotreating catalyst borne by the support is molybdenum oxide (MoO_3) or a combination of MoO_3 and cobalt oxide (CoO) where the MoO_3 is present in the greater amount. The MoO_3 is present on the catalyst support in an amount ranging from 5 to 50 percent, preferably from about 10 to 25 percent, based on the combined weight of the support and MoO_3 . When CoO is present it will be in amounts ranging up to 20 percent, preferably from 2 to 10 percent, based on the combined weight of the catalyst support and metal oxides.

The liquid hydrocarbon solvent for the presulfiding agent of this invention is preferably a low cut, liquid paraffinic hydrocarbon stock, more preferably a naphtha, kerosine or diesel cut having an end boiling point below 399°C (750°F). The solvent should contain minimum amounts of sulfur, nitrogen, aromatics and unsaturates.

In the process for preparing the sulfided hydrotreating catalyst, the presulfiding agent and the liquid hydrocarbon solvent are mixed together to form a solution containing at least 0.5 and up to 5 percent of sulfur, based on the weight of the solution. This solution is brought into contact with the oxidic hydrotreating catalyst bearing support in the presence of hydrogen. The preferred hydrogen flow rate is at least 50% by volume and more preferably, at least 90% of the maximum once-through hydrogen flow rate of the system. Maximum once-through hydrogen flow rate is determined by the maximum gas capacity of a given process reactor at given temperature and pressure conditions. The catalyst bearing support bed in the process reactor is heated to a temperature in the range of from at least 175°C (350°F) up to 230°C (450°F) and the presulfiding solution is preferably passed through or over the catalyst bed at a liquid hourly space velocity (LHSV) between 0.5 and 5 hr^{-1} at a pressure preferably ranging between 13 and 102 bars (200 - 1500 psig). The presulfiding solution/hydrogen gas feed is continued until the metal oxide catalyst is materially presulfided, i.e., when the catalyst has taken up at least 50 percent of the theoretical amount of sulfur required to effect stoichiometric conversion of the metal oxides (MoO_3 and CoO) to their respective reduced sulfides (MoS_2 and Co_9S_8) or until a sharp rise in the effluent concentration of H_2S is noted.

Optionally, rather than carrying out the presulfiding at one temperature, the initial presulfiding is carried out as above and, upon completion of the initial presulfiding, the temperature of the bed is raised by at least about 25°C (70°F) and the presulfiding solution is passed over the catalyst in the presence of hydrogen until the catalyst is materially presulfided or until a sharp rise in the effluent concentration of H_2S is noted.

Thus, the sulfided hydrotreating catalyst of this invention comprises a composition prepared in accordance with the above described process.

After the presulfiding operation is complete, the formed hydrotreating catalyst is used to refine petroleum or other hydrocarbon feedstock by contacting said catalyst with said feedstock in the presence of hydrogen at elevated temperature and pressure. The feedstock is preferably passed through the catalyst at a liquid hourly space velocity (LHSV) of from about 1 to 4 hr^{-1} . The temperature of the reaction preferably ranges from 287 to 482°C (550 to 900°F) while the pressure is preferably from 13 to 165 bars (200 - 2400 psig). The following example is set forth to illustrate this invention.

Example

Dimethyl Disulfide Presulfiding Agent

91 ml (73g) of a solid, particulate catalyst bearing molybdenum oxide (MoO_3) and cobalt oxide (CoO) was calcined at 455°C (850°F) for one hour. This oxidic hydrotreating catalyst, sold by Akzo Chemie as KF-165-1/16, comprised 18 weight % MoO_3 , 5 weight % CoO and a remainder of alumina ($\alpha\text{-Al}_2\text{O}_3$) as the support. The catalyst was diluted by mixing with an equal volume of alumina and the mass charged into a 200 ml. trickle-bed reactor (elongated catalyst-packed tube). The reactor was purged with nitrogen and heated to 230°C (450°F) in a molten solder bath. To 7460g. of a diesel oil [API gravity = 37.7° ; total sulfur = 0.24%; total nitrogen = 84 ppm; distillation range = $203\text{--}355^\circ\text{C}$ ($398\text{--}672^\circ\text{F}$)] was added 110g of dimethyl disulfide (DMDS) to give a solution containing 1.0 wt% sulfur contributed by the presulfiding agent and a total sulfur content of 1.2 wt%. After a hydrogen flow rate of 2 SCFH at 34 bars (500 psig) total pressure was established, the presulfiding solution was fed at a rate of 206g/hour (LHSV = 2.7 hr^{-1}) for twelve hours, exposing the catalyst to a total of 30g of sulfur. The bath temperature was held at 230°C (450°F) for four hours, raised to 315°C (600°F) at 14°C (25°F) /hour over a six hour period and held at 315°C (600°F) for two hours to thereby produce a hydrotreating catalyst.

The bath temperature was then raised to 338°C (640°F) over a two hour period while the feed was switched from the presulfiding solution to a vacuum gas oil [API gravity = 22.5° ; total sulfur = 1.37%; total nitrogen = 822 ppm; distillation range = $270\text{--}524^\circ\text{C}$ ($518\text{--}975^\circ\text{F}$)]. The feedstock LHSV was 2.5 hr^{-1} and

the flow was maintained for 72 hours, with liquid product samples being taken every 24 hours.

The average sulfur analysis of the samples was 0.779 wt% and the hydrosulfurization rate constant, k , was calculated using the following relationship:

$$k = (\text{LHSV}) \times \frac{1}{n-1} \left[\frac{1}{S^{n-1}} - \frac{1}{S_0^{n-1}} \right]$$

where LHSV is the feedstock liquid hourly space velocity, n is the catalyst HDS (hydrodesulfurization) reaction order ($n=1.65$ for the above identified MoO_3 , CoO , alumina hydrotreating catalyst), S is the average weight % sulfur in the product samples and S_0 is the weight % sulfur in the feedstock. The calculated k for the above run was 1.41 and this value was used as the basis for calculating the relative volume activities (RVA's) of catalysts sulfided with test sulfiding agents.

A sample of the spent catalyst was taken, extracted with toluene and analyzed for total carbon, hydrogen and sulfur, and the pore volume and surface area were determined by mercury perfusion at 4880 bars (60,000 psi). The results are shown in Table 1 below.

Dimethyl Polysulfide Presulfiding Agent

The above procedure was followed except that pure dimethyl polysulfide (DMPS) containing 76 weight % total sulfur was used in place of DMDS as the presulfiding agent. 110g of DMPS was blended with 7490g of diesel oil to give a solution containing 1.0 wt% sulfur contributed by the DMPS. The RVA (relative volume activity) of the catalyst was calculated using the formula:

$$\text{RVA}_T = (k_T/k_R) \times 100$$

where RVA_T is the RVA of a catalyst sulfided with test agent T, k_T is the HDS-rate constant for a catalyst sulfided with test agent T calculated as described above for k , and k_R is the HDS-rate constant for a catalyst sulfided with DMDS, calculated above to be 1.41.

The results, including spent catalyst analysis, for duplicate runs where DMPS was used as the sulfiding agent, are given in Table 1 below. The average RVA of 140 is significantly greater than that for DMDS.

DMDS/DMPS Blend Presulfiding Agent

The procedure shown for DMDS above was repeated except that a 1:1 weight blend of DMDS and DMPS was used as the presulfiding agent and 55g of the 1:1 blend was dissolved in 3905g of diesel oil to give a solution containing 1.0 wt% sulfur contributed by the blend. The results are given in Table 1 below.

TABLE 1

Spent Catalyst Analysis						
Presulfiding Agent	RVA (HDS)	%C	%H	%S	Pore Volume (ml./g.)	Surface Area M ² /g
Catalyst Prior to Sulfurization	--	--	--	--	0.52 ¹	268 ¹
DMDS	100 ²	8.19 ³	1.32	5.32	0.27	215
DMPS	143) 140 ⁴	10.56 ⁵	1.79	5.51	0.2	196
DMPS	137)	--	--	--	--	--
DMDS/DMPS Blend	155	9.07 ³	1.55	5.39	0.33	287

1. Actual lot analysis - manufacturer's data
2. By definition
3. Single sample
4. Average of duplicate runs
5. Average of analyses of duplicate samples

As can be seen from the above table, the RVA of 155 for the blend of DMDS and DMPS is significantly greater than that observed of DMDS and DMPS and such RVA is also significantly greater than that expected on the basis of the individual RVA values for DMDS and DMPS.

Claims

Claims for the following Contracting States : BE, DE, GB, IT, NL

TABLE 1

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As can be seen from the above table, the RVA of 155 for the blend of DMDS and DMPS is significantly greater than that observed of DMDS and DMPS and such RVA is also significantly greater than that expected on the basis of the individual RVA values for DMDS and DMPS.

Claims

Claims for the following Contracting States : BE, DE, GB, IT, NL



1. A presulfiding agent comprising a blend of a dialkyl sulfide of the formula $R_1S_xR_2$ wherein R_1 and R_2 are independently alkyl groups having from 1 to 12 carbon atoms and x is 1 or 2, and a dialkyl polysulfide of the formula $R_3S_yR_4$ wherein R_3 and R_4 are independently alkyl groups having from 1 to 20 carbon atoms and y is 2 to 8, provided that the total number of carbon atoms in R_3 and R_4 do not exceed 30 and y is greater than x , the dialkyl sulfide being present in the blend in an amount ranging from 25 to 75 weight percent and said dialkyl polysulfide being present in the blend in an amount ranging from 75 to 25 weight percent.
2. The presulfiding agent of claim 1 wherein said dialkyl sulfide has from 1 to 6 carbon atoms in each alkyl group and said dialkyl polysulfide has from 1 to 9 carbon atoms in each alkyl group.
3. The presulfiding agent of claim 1 dissolved or dispersed in a liquid hydrocarbon carrier therefor.
4. The presulfiding agent of claim 1 wherein x is 2.
5. The presulfiding agent of claim 4 wherein said dialkyl sulfide has from 1 to 6 carbon atoms in each alkyl group and said dialkyl polysulfide has from 1 to 9 carbon atoms in each alkyl group.
6. The presulfiding agent of claim 5 wherein said dialkyl sulfide is dimethyl disulfide and said dialkyl polysulfide is dimethyl polysulfide or di-t-nonyl polysulfide.
7. A process of presulfiding an oxidic hydrotreating catalyst to form a sulfided hydrotreating catalyst which comprises passing at an elevated temperature and pressure a presulfiding solution and hydrogen gas in contact with an inert solid, porous catalyst support bearing molybdenum oxide in an amount ranging from 5 to 50 percent and cobalt oxide in an amount ranging from 0 to 20 percent, said amounts based on the combined weight of the support and oxides, said presulfiding solution comprising a liquid hydrocarbon solvent containing the presulfiding agent of claim 1 in an amount sufficient to provide a total sulfur content of from 0.5 to 5 percent based on the weight of said solution, the contact of said presulfiding agent and hydrogen with the catalyst bearing support continuing for a time sufficient to materially presulfide said metal oxides.
8. The process of claim 7 wherein said presulfiding agent is the agent of claim 2.
9. The process of claim 8 wherein the molybdenum oxide is present in an amount of from 10 to 25 percent and said cobalt oxide is present in an amount of from 2 to 20 percent.
10. The process of claim 9 wherein the presulfiding solution is passed in contact with said catalyst bearing support at a liquid hourly space velocity of between 0.5 and 5, the hydrogen gas is passed in contact with the support at the rate of about at least 50% by volume of the maximum once-through hydrogen flow rate of the process system, and the pressure in the reaction zone ranges between 13 and 102 bars (200 - 1500 psig).
11. The process of claim 7 wherein the presulfiding agent is the agent of claim 4.
12. The process of claim 11 wherein the presulfiding agent is the agent of claim 5.
13. The process of claim 12 wherein the presulfiding agent is the agent of claim 6.
14. A sulfided hydrotreating catalyst prepared in accordance with the process of claim 7.
15. A sulfided hydrotreating catalyst prepared in accordance with the procedure of claim 11.
16. A sulfided hydrotreating catalyst prepared in accordance with the procedure of claim 12.
17. A sulfided hydrotreating catalyst prepared in accordance with the procedure of claim 13.

Claims for the following Contracting States : ES, FR, SE



1. A presulfiding agent comprising a blend of from at least 10 to about 90 weight percent dialkyl sulfide of the formula $R_1S_xR_2$ wherein R_1 and R_2 are independently alkyl groups having from 1 to 12 carbon atoms and x is 1 or 2, and from no more than 90 to 10 weight percent of a dialkyl polysulfide of the formula $R_3S_yR_4$ wherein R_3 and R_4 are independently alkyl groups having from 1 to 20 carbon atoms and y is 2 to 8, provided that the total number of carbon atoms in R_3 and R_4 do not exceed 30 and y is greater than x .
2. The presulfiding agent of claim 1 wherein said dialkyl sulfide is present in the blend in an amount ranging from 25 to 75 weight percent and said dialkyl polysulfide is present in the blend in an amount ranging from 75 to 25 weight percent.
3. The presulfiding agent of claim 2 wherein said dialkyl sulfide has from 1 to 6 carbon atoms in each alkyl group and said dialkyl polysulfide has from 1 to 9 carbon atoms in each alkyl group.
4. The presulfiding agent of claim 1 dissolved or dispersed in a liquid hydrocarbon carrier therefor.
5. The presulfiding agent of claim 1 wherein x is 2.
6. The presulfiding agent of claim 5 wherein said dialkyl sulfide has from 1 to 6 carbon atoms in each alkyl group and said dialkyl polysulfide has from 1 to 9 carbon atoms in each alkyl group.
7. The presulfiding agent of claim 5 wherein said dialkyl sulfide is present in the blend in an amount ranging from 25 to 75 weight percent and said dialkyl polysulfide is present in the blend in an amount ranging from 75 to 25 weight percent.
8. The presulfiding agent of claim 6 wherein said dialkyl sulfide is dimethyl disulfide and said dialkyl polysulfide is dimethyl polysulfide or di-t-nonyl polysulfide.
9. A process of presulfiding an oxidic hydrotreating catalyst to form a sulfided hydrotreating catalyst which comprises passing at an elevated temperature and pressure a presulfiding solution and hydrogen gas in contact with an inert solid, porous catalyst support bearing molybdenum oxide in an amount ranging from 5 to 50 percent and cobalt oxide in an amount ranging from 0 to 20 percent, said amounts based on the combined weight of the support and oxides, said presulfiding solution comprising a liquid hydrocarbon solvent containing the presulfiding agent of claim 1 in an amount sufficient to provide a total sulfur content of from 0.5 to 5 percent based on the weight of said solution, the contact of said presulfiding agent and hydrogen with the catalyst bearing support continuing for a time sufficient to materially presulfide said metal oxides.
10. The process of claim 9 wherein said presulfiding agent is the agent of claim 3.
11. The process of claim 10 wherein the molybdenum oxide is present in an amount of from 10 to 25 percent and said cobalt oxide is present in an amount of from 2 to 20 percent.
12. The process of claim 11 wherein the presulfiding solution is passed in contact with said catalyst bearing support at a liquid hourly space velocity of between 0.5 and 5, the hydrogen gas is passed in contact with the support at the rate of about at least 50% by volume of the maximum once-through hydrogen flow rate of the process system, and the pressure in the reaction zone ranges between 13 and 102 bars (200 - 1500 psig).
13. The process of claim 9 wherein the presulfiding agent is the agent of claim 5.
14. The process of claim 13 wherein the presulfiding agent is the agent of claim 6.
15. The process of claim 14 wherein the presulfiding agent is the agent of claim 8.
16. A sulfided hydrotreating catalyst prepared in accordance with the process of claim 9.
17. A sulfided hydrotreating catalyst prepared in accordance with the procedure of claim 13.



18. A sulfided hydrotreating catalyst prepared in accordance with the procedure of claim 14.

19. A sulfided hydrotreating catalyst prepared in accordance with the procedure of claim 15.

5 Revendications

Revendications pour les Etats contractants suivants : BE, DE, GB, IT, NL

1. Agent de présulfuration, comprenant un mélange composé d'un sulfure de dialkyle de formule $R_1S_xR_2$ dans laquelle R_1 et R_2 représentent indépendamment des groupes alkyle ayant 1 à 12 atomes de carbone et x a la valeur 1 ou 2, et d'un polysulfure de dialkyle de formule $R_3S_yR_4$ dans laquelle R_3 et R_4 représentent indépendamment des groupes alkyle ayant 1 à 20 atomes de carbone et y a une valeur de 2 à 8, sous réserve que le nombre total d'atomes de carbone dans R_3 et R_4 ne dépasse pas 30 et que y soit supérieur à x , le sulfure de dialkyle étant présent dans le mélange en une quantité allant de 25 à 75 % en poids et ledit polysulfure de dialkyle étant présent dans le mélange en une quantité allant de 75 à 25 % en poids.
2. Agent de présulfuration suivant la revendication 1, dans lequel le sulfure de dialkyle comprend 1 à 6 atomes de carbone dans chaque groupe alkyle et le polysulfure de dialkyle comprend 1 à 9 atomes de carbone dans chaque groupe alkyle.
3. Agent de présulfuration suivant la revendication 1, dissous ou dispersé dans un véhicule hydrocarboné liquide approprié.
4. Agent de présulfuration suivant la revendication 1, dans lequel x est égal à 2.
5. Agent de présulfuration suivant la revendication 4, dans lequel le sulfure de dialkyle comprend 1 à 8 atomes de carbone dans chaque groupe alkyle et le polysulfure de dialkyle comprend 1 à 9 atomes de carbone dans chaque groupe alkyle.
6. Agent de présulfuration suivant la revendication 5, dans lequel le sulfure de dialkyle est le sulfure de diméthyle et le polysulfure de dialkyle est le polysulfure de diméthyle ou le polysulfure de ditiononyle.
7. Procédé de présulfuration d'un catalyseur oxydique d'hydrotraitement pour former un catalyseur sulfuré d'hydrotraitement, qui consiste à faire passer à une température et à une pression élevées, une solution de présulfuration et de l'hydrogène gazeux au contact d'un support de catalyseur poreux solide inerte portant de l'oxyde de molybdène en une quantité allant de 5 à 50 % et de l'oxyde de cobalt en une quantité allant de 0 à 20 %, lesdites quantités étant basées sur le poids total de support et d'oxydes, la solution de présulfuration comprenant un solvant hydrocarboné liquide qui contient l'agent de présulfuration suivant la revendication 1 en une quantité suffisante pour établir une teneur totale en soufre de 0,5 à 5 % sur la base du poids de ladite solution, le contact dudit agent de présulfuration et de l'hydrogène avec le support portant le catalyseur se poursuivant pendant une durée suffisante pour présulfurer notablement lesdits oxydes métalliques.
8. Procédé suivant la revendication 7, dans lequel l'agent de présulfuration est l'agent suivant la revendication 2.
9. Procédé suivant la revendication 8, dans lequel l'oxyde de molybdène est présent en une quantité de 10 à 25 % et l'oxyde de cobalt est présent en une quantité de 2 à 20 %.
10. Procédé suivant la revendication 9, dans lequel on fait passer la solution de présulfuration au contact du support portant le catalyseur à une vitesse spatiale horaire du liquide comprise entre 0,5 et 5, on fait passer l'hydrogène gazeux au contact du support à une vitesse représentant environ au moins 50 % en volume de la vitesse maximale d'écoulement direct de l'hydrogène dans l'installation de production, et la pression dans la zone de réaction se situe dans une plage de 13 à 102 bars (200 à 1500 lb/in²) au manomètre.
11. Procédé suivant la revendication 7, dans lequel l'agent de présulfuration est l'agent de la revendication



4.

12. Procédé suivant la revendication 11, dans lequel l'agent de présulfuration est l'agent de la revendication 5.

13. Procédé suivant la revendication 12, dans lequel l'agent de présulfuration est l'agent de la revendication 6.

14. Catalyseur sulfuré d'hydrotraitement, préparé conformément au procédé de la revendication 7.

15. Catalyseur sulfuré d'hydrotraitement préparé conformément au mode opératoire de la revendication 11.

16. Catalyseur sulfuré d'hydrotraitement préparé conformément au mode opératoire de la revendication 12.

17. Catalyseur sulfuré d'hydrotraitement préparé conformément au mode opératoire de la revendication 13.

Revendications pour les Etats contractants suivants : ES, FR, SE

1. Agent de présulfuration comprenant un mélange composé d'au moins 10 à environ 90 % en poids d'un sulfure de dialkyle de formule $R_1S_xR_2$ dans laquelle R_1 et R_2 sont, indépendamment, des groupes alkyle ayant 1 à 12 atomes de carbone et x a la valeur 1 ou 2, et de pas plus de 90 à 10 % en poids d'un polysulfure de dialkyle de formule $R_3S_yR_4$ dans laquelle R_3 et R_4 sont, indépendamment, des groupes alkyle ayant 1 à 20 atomes de carbone et y a une valeur de 2 à 8, sous réserve que le nombre total d'atomes de carbone dans R_3 et R_4 ne dépasse pas 30 et que y soit supérieur à x .

2. Agent de présulfuration suivant la revendication 1, dans lequel le sulfure de dialkyle est présent dans le mélange en une quantité allant de 25 à 75 % en poids et le polysulfure de dialkyle est présent dans le mélange en une quantité allant de 75 à 25 % en poids.

3. Agent de présulfuration suivant la revendication 2, dans lequel le sulfure de dialkyle comprend 1 à 6 atomes de carbone dans chaque groupe alkyle et le polysulfure de dialkyle comprend 1 à 9 atomes de carbone dans chaque groupe alkyle.

4. Agent de présulfuration suivant la revendication 1, dissous ou dispersé dans un véhicule hydrocarboné liquide approprié.

5. Agent de présulfuration suivant la revendication 1, dans lequel x est égal à 2.

6. Agent de présulfuration suivant la revendication 5, dans lequel le sulfure de dialkyle comprend 1 à 6 atomes de carbone dans chaque groupe alkyle et le polysulfure de dialkyle comprend 1 à 9 atomes de carbone dans chaque groupe alkyle.

7. Agent de présulfuration suivant la revendication 5, dans lequel le sulfure de dialkyle est présent dans le mélange en une quantité allant de 25 à 75 % en poids et le polysulfure de dialkyle est présent dans le mélange en une quantité allant de 75 à 25 % en poids.

8. Agent de présulfuration suivant la revendication 6, dans lequel le sulfure de dialkyle est le sulfure de diméthyle et le polysulfure de dialkyle est le polysulfure de diméthyle ou le polysulfure de di-tertionyle.

9. Procédé de présulfuration d'un catalyseur oxydique d'hydrotraitement pour former un catalyseur d'hydrotraitement sulfuré, qui consiste à faire passer, à une température et une pression élevées, une solution de présulfuration et de l'hydrogène gazeux au contact d'un support de catalyseur poreux solide inerte portant de l'oxyde de molybdène en une quantité allant de 5 à 50 % et de l'oxyde de cobalt en une quantité allant de 0 à 20 %, lesdites quantités étant basées sur le poids total du support et des oxydes, la solution de présulfuration comprenant un solvant hydrocarboné liquide contenant l'agent de présulfuration de la revendication 1 en une quantité suffisante pour établir une teneur totale en soufre de 0,5 à 5 % sur la base du poids de ladite solution, le contact dudit agent de présulfuration et de



l'hydrogène avec le support portant le catalyseur se poursuivant pendant une durée suffisante pour présulfurer notablement lesdits oxydes métalliques.

10. Procédé suivant la revendication 9, dans lequel l'agent de présulfuration est l'agent suivant la revendication 3.

11. Procédé suivant la revendication 10, dans lequel l'oxyde de molybdène est présent en une quantité de 10 à 25 % et l'oxyde de cobalt est présent en une quantité de 2 à 20 %.

12. Procédé suivant la revendication 11, dans lequel on fait passer la solution de présulfuration au contact dudit support portant le catalyseur à une vitesse spatiale horaire du liquide entre 0,5 et 5, on fait passer l'hydrogène gazeux au contact du support à une vitesse d'au moins environ 50 % en volume de la vitesse maximale d'écoulement direct de l'hydrogène de l'installation de production, et la pression dans la zone de réaction se situe dans une plage de 13 à 102 bars (200 à 1500 lb/in²) au manomètre.

13. Procédé suivant la revendication 9, dans lequel l'agent de présulfuration est l'agent suivant la revendication 5.

14. Procédé suivant la revendication 13, dans lequel l'agent de présulfuration est l'agent suivant la revendication 6.

15. Procédé suivant la revendication 14, dans lequel l'agent de présulfuration est l'agent suivant la revendication 8.

16. Catalyseur sulfuré d'hydrotraitement, préparé conformément au procédé suivant la revendication 9.

17. Catalyseur sulfuré d'hydrotraitement préparé conformément au mode opératoire de la revendication 13.

18. Catalyseur sulfuré d'hydrotraitement préparé conformément au mode opératoire de la revendication 14.

19. Catalyseur sulfuré d'hydrotraitement préparé conformément au mode opératoire de la revendication 15.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, DE, GB, IT, NL

1. Vorschwefelungsmittel, dadurch **gekennzeichnet**, daß es ein Gemisch aus einem Dialkylsulfid der Formel $R_1S_xR_2$, worin R_1 und R_2 unabhängig voneinander Alkylgruppen mit 1 bis 12 Kohlenstoffatomen bedeuten und x für 1 oder 2 steht, und ein Dialkylpolysulfid der Formel $R_3S_yR_4$, worin R_3 und R_4 unabhängig voneinander Alkylgruppen mit 1 bis 20 Kohlenstoffatomen bedeuten und y eine Zahl zwischen 2 und 8 ist, mit der Maßgabe, daß die Gesamtzahl der Kohlenstoffatome in R_3 und R_4 30 nicht übersteigt und y größer als x ist, umfaßt, wobei das Dialkylsulfid in einer Menge von 25 bis 75 Gew.-% und das Dialkylpolysulfid in einer Menge von 75 bis 25 Gew.-% in dem Gemisch vorliegen.

2. Vorschwefelungsmittel nach Anspruch 1, dadurch **gekennzeichnet**, daß das Dialkylsulfid 1 bis 6 Kohlenstoffatome in jeder Alkylgruppe hat und das Dialkylpolysulfid 1 bis 9 Kohlenstoffatome in jeder Alkylgruppe hat.

3. Vorschwefelungsmittel nach Anspruch 1, dadurch **gekennzeichnet**, daß es in einem flüssigen Kohlenwasserstoffträger dafür aufgelöst oder dispergiert ist.

4. Vorschwefelungsmittel nach Anspruch 1, dadurch **gekennzeichnet**, daß x für 2 steht.

5. Vorschwefelungsmittel nach Anspruch 4, dadurch **gekennzeichnet**, daß das Dialkylsulfid 1 bis 6 Kohlenstoffatome in jeder Alkylgruppe hat und das Dialkylpolysulfid 1 bis 9 Kohlenstoffatome in jeder Alkylgruppe hat.

6. Vorschwefelungsmittel nach Anspruch 5, dadurch **gekennzeichnet**, daß das Dialkylsulfid Dimethylsulfid und das Dialkylpolysulfid Dimethylpolysulfid oder Di-*t*-nonylpolysulfid ist.



7. Verfahren zur Vorschwefelung eines oxidischen Wasserstoffbehandlungskatalysators zur Bildung eines sulfidierten Wasserstoffbehandlungskatalysators, dadurch **gekennzeichnet**, daß bei erhöhter Temperatur und Druck eine Vorschwefelungslösung und Wasserstoffgas mit einem inerten, festen, porösen Katalysatorträger, der Molybdänoxid in einer Menge von 5 bis 50 % und Cobaltoxid in einer Menge von 0 bis 20 % trägt, in Kontakt gebracht wird, wobei die Mengen sich auf das kombinierte Gewicht von Träger und Oxiden beziehen, wobei die Vorschwefelungslösung ein flüssiges Kohlenwasserstofflösungsmittel umfaßt, das das Vorschwefelungsmittel nach Anspruch 1 in einer Menge enthält, die ausreicht, um einen Gesamtschwefelgehalt von 0,5 bis 5 %, bezogen auf das Gewicht der Lösung, zu erreichen, und wobei der Kontakt des Vorschwefelungsmittels und des Wasserstoffs mit dem den Katalysator tragenden Träger für einen ausreichenden Zeitraum anhält, um die Metalloxide in einem beträchtlichen Umfang vorzuschwefeln.
8. Verfahren nach Anspruch 7, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel das Mittel nach Anspruch 2 ist.
9. Verfahren nach Anspruch 8, dadurch **gekennzeichnet**, daß das Molybdänoxid in einer Menge von 10 bis 25 % und das Cobaltoxid in einer Menge von 2 bis 20 % vorliegen.
10. Verfahren nach Anspruch 9, dadurch **gekennzeichnet**, daß die Vorschwefelungslösung mit dem den Katalysator tragenden Träger mit einer Stundenraumgeschwindigkeit der Flüssigkeit zwischen 0,5 und 5 in Kontakt gebracht wird, das Wasserstoffgas mit dem Träger mit einer Geschwindigkeit von ungefähr mindestens 50 Vol.-% der maximalen Wasserstoff-Zwangsdurchlauf-Fließgeschwindigkeit des Verfahrenssystems in Kontakt gebracht wird, und der Druck in der Reaktionszone im Bereich zwischen 13 und 102 bar (200 bis 1500 psig) liegt.
11. Verfahren nach Anspruch 7, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel ein Mittel nach Anspruch 4 ist.
12. Verfahren nach Anspruch 11, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel ein Mittel nach Anspruch 5 ist.
13. Verfahren nach Anspruch 12, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel ein Mittel nach Anspruch 6 ist.
14. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 7.
15. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 11.
16. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 12.
17. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 13.

Patentansprüche für folgende Vertragsstaaten : ES, FR, SE

1. Vorschwefelungsmittel, dadurch **gekennzeichnet**, daß es ein Gemisch enthält von mindestens 10 bis ungefähr 90 Gew.-% Dialkylsulfid mit der Formel $R_1S_xR_2$, worin R_1 und R_2 unabhängig voneinander Alkylgruppen mit 1 bis 12 Kohlenstoffatomen sind und x für 1 oder 2 steht, und von nicht mehr als 90 bis 10 Gew.-% eines Dialkylpolysulfids mit der Formel $R_3S_yR_4$, worin R_3 und R_4 unabhängig voneinander Alkylgruppen mit 1 bis 20 Kohlenstoffatomen sind und y eine Zahl zwischen 2 und 8 ist, mit der Maßgabe, daß die Gesamtzahl der Kohlenstoffatome in R_3 und R_4 30 nicht übersteigt und y größer als x ist.
2. Vorschwefelungsmittel nach Anspruch 1, dadurch **gekennzeichnet**, daß das Dialkylsulfid in einer Menge von 25 bis 75 Gew.-% und das Dialkylpolysulfid in einer Menge von 75 bis 25 Gew.-% in dem Gemisch vorliegen.
3. Vorschwefelungsmittel nach Anspruch 2, dadurch **gekennzeichnet**, daß das Dialkylsulfid nicht mehr als 1 bis 6 Kohlenstoffatome in jeder Alkylgruppe hat und daß das Dialkylpolysulfid 1 bis 9 Kohlenstoff-



atome in jeder Alkylgruppe besitzt.

4. Vorschwefelungsmittel nach Anspruch 1, dadurch **gekennzeichnet**, daß es in einem flüssigen Kohlenwasserstoffträger dafür aufgelöst oder dispergiert ist.

5. Vorschwefelungsmittel nach Anspruch 1, dadurch **gekennzeichnet**, daß x für 2 steht.

6. Vorschwefelungsmittel nach Anspruch 5, dadurch **gekennzeichnet**, daß das Dialkylsulfid 1 bis 6 Kohlenstoffatome in jeder Alkylgruppe hat und das Dialkylpolysulfid 1 bis 9 Kohlenstoffatome in jeder Alkylgruppe besitzt.

7. Vorschwefelungsmittel nach Anspruch 5, dadurch **gekennzeichnet**, daß das Dialkylsulfid in einer Menge von 25 bis 75 Gew.-% und das Dialkylpolysulfid in einer Menge von 75 bis 25 Gew.-% in dem Gemisch vorliegen.

8. Vorschwefelungsmittel nach Anspruch 6, dadurch **gekennzeichnet**, daß das Dialkylsulfid Dimethydisulfid ist und das Dialkylpolysulfid Dimethylpolysulfid oder Di-t-nonylpolysulfid ist.

9. Verfahren zur Vorschwefelung eines oxidischen Wasserstoffbehandlungskatalysators zur Bildung eines sulfidierten Wasserstoffbehandlungskatalysators, dadurch **gekennzeichnet**, daß bei erhöhter Temperatur und Druck eine Vorschwefelungslösung und Wasserstoffgas in Kontakt gebracht werden mit einem inerten, festen, porösen Katalysatorträger, der Molybdänoxid in einer Menge von 5 bis 50 % und Cobaltoxid in einer Menge von 0 bis 20 % trägt, wobei die Mengen sich auf das kombinierte Gewicht des Trägers und der Oxide beziehen, und wobei die Vorschwefelungslösung ein flüssiges Kohlenwasserstofflösungsmittel umfaßt, das ein Vorschwefelungsmittel nach Anspruch 1 in einer Menge enthält, die ausreicht, um einen Gesamtschwefelgehalt von 0,5 bis 5 %, bezogen auf das Gewicht der Lösung, zu erreichen, der Kontakt des Vorschwefelungsmittels und des Wasserstoffs mit dem den Katalysator tragenden Träger für einen ausreichend langen Zeitraum anhält, um die Metalloxide in einem beträchtlichen Umfang vorzuschwefeln.

10. Verfahren nach Anspruch 9, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel ein Mittel nach Anspruch 3 ist.

11. Verfahren nach Anspruch 10, dadurch **gekennzeichnet**, daß das Molybdänoxid in einer Menge von 10 bis 25 % und das Cobaltoxid in einer Menge von 2 bis 20 % vorliegen.

12. Verfahren nach Anspruch 11, dadurch **gekennzeichnet**, daß die Vorschwefelungslösung mit dem den Katalysator tragenden Träger mit einer Stundenraumgeschwindigkeit der Flüssigkeit zwischen 0,5 und 5 in Kontakt gebracht wird, das Wasserstoffgas mit dem Träger mit einer Geschwindigkeit von ungefähr mindestens 50 Vol.-% der maximalen Wasserstoff-Zwangsdurchlauf-Fließgeschwindigkeit des Verfahrens in Kontakt gebracht wird, und der Druck in der Reaktionszone im Bereich zwischen 13 und 102 bar (200 bis 1500 psig) liegt.

13. Verfahren nach Anspruch 9, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel ein Mittel nach Anspruch 5 ist.

14. Verfahren nach Anspruch 13, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel ein Mittel nach Anspruch 6 ist.

15. Verfahren nach Anspruch 14, dadurch **gekennzeichnet**, daß das Vorschwefelungsmittel ein Mittel nach Anspruch 8 ist.

16. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 9.

17. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 13.

18. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 14.



19. Sulfidierter Wasserstoffbehandlungskatalysator, hergestellt nach dem Verfahren gemäß Anspruch 15.

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