

(19) **DANMARK**



Patent- og
Varemærkestyrelsen

(10) **DK/EP 2484745 T3**

(12) **Oversættelse af
europæisk patentskrift**

-
- (51) Int.Cl.: **B 01 J 21/06 (2006.01)** **B 01 J 21/08 (2006.01)** **B 01 J 21/12 (2006.01)**
B 01 J 23/24 (2006.01) **B 01 J 23/74 (2006.01)** **B 01 J 23/85 (2006.01)**
B 01 J 23/882 (2006.01) **B 01 J 23/883 (2006.01)** **B 01 J 27/19 (2006.01)**
B 01 J 35/00 (2006.01) **B 01 J 35/10 (2006.01)** **B 01 J 37/28 (2006.01)**
C 10 G 45/04 (2006.01) **C 10 G 45/06 (2006.01)** **C 10 G 45/08 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2021-01-25**
- (80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2020-11-18**
- (86) Europæisk ansøgning nr.: **10820343.1**
- (86) Europæisk indleveringsdag: **2010-09-14**
- (87) Den europæiske ansøgnings publiceringsdag: **2012-08-08**
- (86) International ansøgning nr.: **JP2010065785**
- (87) Internationalt publikationsnr.: **WO2011040224**
- (30) Prioritet: **2009-09-30 JP 2009227465** **2009-09-30 JP 2009227464**
- (84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR**
- (73) Patenthaver: **JX Nippon Oil & Energy Corporation, 6-3, Otemachi 2-chome, Chiyoda-ku, Tokyo 100-8162, Japan**
JGC Catalysts And Chemicals Ltd., 16th Floor, Solid Square East Tower , 580 Horikawa-cho , Saiwai-ku, Kawasaki-shi, Kanagawa 212-0013, Japan
- (72) Opfinder: **TAGAWA, Shogo, c/o JGC Catalysts and Chemicals Ltd., 13-2 Kitaminato-machi, Wakamatsu-ku, Kitakyushu-shi, Fukuoka 808-0027, Japan**
KAGAWA, Tomoyasu, c/o JGC Catalysts and Chemicals Ltd., 13-2 Kitaminato-machi, Wakamatsu-ku, Kitakyushu-shi, Fukuoka 808-0027, Japan
SEKI, Hiroyuki, c/o JX Nippon Oil & Energy Corporation, 6-3, otemachi 2-chome, Chiyoda-ku, Tokyo 100-8162, Japan
FUKUI, Yoshiaki, c/o JX Nippon Oil & Energy Corporation, 6-3, Otemachi 2-chome, Chiyoda-ku, Tokyo 100-8162, Japan
YOSHIDA, Masanori, c/o JX Nippon Oil & Energy Corporation, 6-3, Otemachi 2-chome, Chiyoda-ku, Tokyo 100-8162, Japan
- (74) Fuldmægtig i Danmark: **RWS Group, Europa House, Chiltern Park, Chiltern Hill, Chalfont St Peter, Bucks SL9 9FG, Storbritannien**
- (54) Benævnelse: **HYDROAFSVOVLINGSKATALYSATOR FOR EN CARBONHYDRIDOLIE, FREMGANGSMÅDE TIL FREMSTILLING HERAF OG FREMGANGSMÅDE TIL HYDRORAFFINERING**
- (56) Fremdragne publikationer:
JP-A- 5 184 921
JP-A- 10 118 495

Fortsættes ...

JP-A- 11 319 554

JP-A- 54 104 495

JP-A- 2005 254 141

JP-A- 2005 262 173

JP-A- 2005 336 053

US-A1- 2006 249 429

HIROMICHI KOSHIKA ET AL.: 'Keiyu Choshindo Datsuryu Shokubai no Kaihatsu -Dai San Seibun Tenka Koka'

IDEMITSU GIHO vol. 47, no. 3, 2004, pages 301 - 307, XP008157438

**GARDNER ET AL.: 'PERFORMANCE OF TITANIA- SUPPORTED NIMO CATALYST COATINGS ON ALUMINA
EXTRUDATES FOR ADVANCED HYDROPROCESSING APPLICATIONS' PREPR.AM.CHEM.SOC.DIV.PET.CHEM.**

vol. 47, no. 1, 2002, pages 73 - 76, XP008157418

DESCRIPTION

Technical Field

[0001] The present invention relates to a hydrodesulfurization catalyst for hydrocarbon oil, a process of producing the catalyst, and a method for hydrorefining hydrocarbon oils, more specifically to a hydrodesulfurization catalyst having a high desulfurization activity, comprising an active component supported on a silica-titania-alumina support, used for hydrotreating hydrocarbon oils in particular gas oil fractions, a process of producing such a catalyst, and a method for hydrorefining hydrocarbon oils using the catalyst.

Background Art

[0002] Recently, a demand has been rapidly increased for a clean liquid fuel with a low sulfur content. In response to this demand, various methods for producing clean fuels have already been studied in the fuel oil industry. Due to a regulation requiring diesel fuel in particular to contain 10 ppm by mass or less of sulfur, petroleum companies have, therefore, created systems to produce a clean fuel with improved catalysts or installation of more facilities.

[0003] The main base oil of diesel fuel is generally a gas oil fraction distilling from an atmospheric distillation tower or a cracker. Production of a low sulfur content clean diesel fuel thus requires the sulfur to be removed with a hydrorefining unit.

[0004] Typically, gas oil is hydrorefined in a hydrogen flow in a fixed-bed reactor filled with a desulfurization catalyst under high temperature and pressure conditions.

[0005] Conventionally, a catalyst comprising an active metal component selected from Groups VIA and VIII in the periodic table supported on a support of a porous inorganic oxide such as alumina, alumina-silica, titania, or alumina-titania has been widely used as a catalyst used for the purpose of hydrotreating a hydrocarbon oil.

[0006] The titania support is known to exhibit a higher desulfurization performance than the alumina support but has a problem that it has a small specific surface area and low thermal stability at elevated temperatures. A titania-containing catalyst is known to be produced by a process wherein a titania support is prepared using titania gel (see Patent Literature 1 below) or wherein an alumina-titania support is prepared by loading a water-soluble titania compound on an alumina support (see Patent Literature 2 below) . The catalyst described in Patent Literature 1 contains a large amount of titania, which is expensive and increase the production cost and bulk density compared with a catalyst comprising a conventional alumina support. Since the catalyst described in Patent Literature 2 can support titania only in an amount corresponding the water absorption rate of titania, it is expensive to be produced industrially

because loading step is necessarily repeated so as to load titania in a large amount on a support. A method has been proposed wherein titania is mixed and highly dispersed in alumina upon preparation of thereof (see Patent Literature 3). This method enables titania to be highly dispersed in alumina but has disadvantages that as the content of titania increases, crystallization thereof is likely to accelerate, resulting in a catalyst with a decreased specific surface area and a deteriorated sharpness of the pore distribution. Furthermore, the catalyst is not a catalyst having sufficient properties that can cope with a regulation of 10 ppm sulfur content.

[0007] As described above, an improvement in a desulfurization catalyst has been vigorously carried out to produce a clean fuel. Despite of research and development for a long period of time, a catalyst technology satisfying a higher desulfurization activity has not been achieved yet. It may be because a plurality of desulfurization passages and active site structure effective therefor are not clear and variation in support composition affects differently desulfurization activity.

Citation List

Patent Literature

[0008]

Patent Literature 1: Japanese Patent Laid-Open Publication No. 2005-336053

Patent Literature 2: Japanese Patent Laid-Open Publication No. 2005-262173

Patent Literature 3: Japanese Patent Laid-Open Publication No. 10-118495

Patent Literature 4: US 2006/249429

Patent Literature 5: JP 2005254141

Summary of Invention

Technical Problem

[0009] The present invention has an object to provide an inexpensive and high-performance hydrodesulfurization catalyst comprising a support containing mainly alumina, and silica and titania, with a high specific surface area and a process of producing such a catalyst as well as

a method for hydrotreating a hydrocarbon oil using the hydrodesulfurization catalyst.

Solution to Problem

[0010] As the results of extensive study and research, the present invention was accomplished on the basis of the finding that a hydrodesulfurization catalyst comprising a silica-titania-alumina support having a specific structure, and having specific properties was significantly improved in desulfurization performance for a hydrocarbon oil.

[0011] That is, the present invention relates to a hydrodesulfurization catalyst for a hydrocarbon oil comprising at least one type of metal component selected from Groups VIA and VIII in the periodic table, supported on a silica-titania-alumina support where the total of the diffraction peak area indicating the crystal structure of anatase titania (101) planes and the diffraction peak area indicating the crystal structure of rutile titania (110) planes is 1/4 or less of the diffraction peak area indicating the aluminum crystal structure ascribed to γ -alumina (400) planes, as measured by X-ray diffraction analysis, the catalyst having (a) a specific surface area (SA) of 150 m²/g or greater, (b) a total pore volume (PVo) of 0.30 ml/g or greater, (c) an average pore diameter (PD) of 6 to 15 nm (60 to 150 Å), and (d) the ratio of the pore volume (PVp) of pores having diameters within ± 30 percent of the average pore diameter (PD) being 70 percent or greater of the total pore volume (PVo).

[0012] The present invention also relates to a process of producing the foregoing catalyst comprising:

a first step of producing a hydrate by mixing a basic aluminum salt aqueous solution and a mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt such that the pH is from 6.5 to 9.5;

a second step of producing a support by in turn washing, extruding, drying and calcining the hydrate; and

a third step of loading at least one type of metal component selected from Groups VIA and VIII in the periodic table, on the support.

[0013] The present invention also relates to a method for hydrotreating a hydrocarbon oil, comprising hydrotreating a hydrocarbon oil under a hydrogen atmosphere using the foregoing hydrodesulfurization catalyst.

Advantageous Effects of Invention

[0014] The catalyst of the present invention is extremely advantageous because it exhibits a high desulfurization activity in hydrotreatment of a hydrocarbon oil, in particular gas oil fraction. The process of producing a catalyst according to the present invention can highly disperse titanium in a support and thus can produce an inexpensive catalyst with high performances even with a small amount of titanium, which is more expensive than alumina and silica. The method for hydrotreating of the present invention can remove large amounts of sulfur and nitrogen from a hydrocarbon oil.

Brief Description of Drawing

[0015] Fig.1 is a graph showing the X-ray diffraction analysis results of support a in Example 1.

Description of Embodiments

[0016] The present invention will be described in detail below.

[0017] The catalyst of the present invention comprises at least one type of metal component selected from Groups VIA and VIII in the periodic table, supported on a silica-titania-alumina support where the total of the diffraction peak area indicating the crystal structure of anatase titania (101) planes and the diffraction peak area indicating the crystal structure of rutile titania (110) planes is 1/4 or less of the diffraction peak area indicating the aluminum crystal structure ascribed to γ -alumina (400) planes, as measured by X-ray diffraction analysis, the catalyst having (a) a specific surface area (SA) of 150 m²/g or greater, (b) a total pore volume (PVo) of 0.30 ml/g or greater, (c) an average pore diameter (PD) of 6 to 15 nm (60 to 150 Å), and (d) the ratio of the pore volume (PVp) of pores having diameters within ± 30 percent of the average pore diameter (PD) being 70 percent or greater of the total pore volume (PVo).

[0018] The silica-titania-alumina support of the hydrodesulfurization catalyst of the present invention contains silica in the form of SiO₂ in an amount of 2 to 5 percent by mass on the support basis. A silica content of less than one percent by mass decreases the specific surface areas of the resulting catalyst and causes titania particles to be likely to aggregate upon calcination of the support, resulting in larger diffraction peak areas indicating the crystal structures of anatase titania and rutile titania. A silica content of more than 10 percent by mass causes the resulting support to be poor in sharpness of the pore distribution and thus possibly to fail to obtain a desired desulfurization activity.

[0019] In the present invention, the silica-titania-alumina support contains titania in the form of TiO₂ in an amount of 15 to 25 percent by mass on the basis of the weight of the support. A titania content of less than 3 percent by mass is too less in effect achieved by addition of titania, resulting in a catalyst that may not obtain a sufficient desulfurization activity. A titania content of more than 40 percent by mass is not preferable because not only the mechanical

strength of the resulting catalyst is reduced but also the specific surface area is reduced due to the increased tendency for titania particles to accelerate in crystallization upon calcination of the support and thus the resulting catalyst may not exhibit a desulfurization performance corresponding to the economic efficiency according to the increased amount of titania, and may not be a catalyst, which is cheap and has high performances intended by the present invention.

[0020] The silica-titania-alumina support contains alumina in the form of Al_2O_3 in an amount of 70 to 83 percent by mass on the basis of the weight of the support. An alumina content of less than 50 percent by mass is not preferable because the resulting catalyst tends to degrade significantly. An alumina content of more than 96 percent by mass is also not preferable because the catalyst performances tend to deteriorate.

[0021] The hydrodesulfurization catalyst of the present invention comprises one or more type of metal component selected from Group VIA (IUPAC Group 6) and Group VIII (IUPAC Groups 8 to 10) in the periodic table, supported on the above-described support.

[0022] Examples of metal components of Group VIA in the periodic table include molybdenum (Mo) and tungsten (W). Examples of metal components of Group VIII in the periodic table include cobalt (Co) and nickel (Ni). These metal components may be used alone or in combination. In view of catalyst performances, the metal components are preferably combinations such as nickel-molybdenum, cobalt-molybdenum, nickel-molybdenum-cobalt, nickel-tungsten, cobalt-tungsten, and nickel-tungsten-cobalt, more preferably combinations such as nickel-molybdenum, cobalt-molybdenum, and nickel-molybdenum-cobalt.

[0023] The metal component (s) are supported in the form of oxide in an amount of preferably 1 to 35 percent by mass, more preferably 15 to 30 percent by mass on the catalyst basis. The metal component of Group VIA in the periodic table is supported in the form of oxide in an amount of preferably 10 to 30 percent by mass, more preferably 13 to 24 percent by mass while the metal component of Group VIII in the periodic table is supported in the form of oxide in an amount of preferably 1 to 10 percent by mass, more preferably 2 to 6 percent by mass.

[0024] In the case where the hydrodesulfurization catalyst of the present invention contains a metal component of Group VIA in the periodic table, the metal component is preferably dissolved in acid. The acid is preferably an inorganic acid and/or an organic acid. Examples of the inorganic acid include phosphoric acid and nitric acid. More preferred is phosphoric acid. The organic acid is preferably a carboxylic acid. Examples of the carboxylic acid include citric acid, malic acid, tartaric acid, and gluconic acid.

[0025] In the case of using phosphoric acid, it is contained in an amount of preferably 3 to 25 percent by mass, more preferably 10 to 15 percent by mass on an oxide basis, of 100 percent by mass of the metal component of Group VIA in the periodic table. A content of more than 25 percent by mass is not preferable because catalyst performances would be poor. A content of less than 3 percent by mass is also not preferable because stability of the resulting metal

component solution to be loaded would be deteriorated.

[0026] In the case of using an organic acid, it is contained in an amount of preferably 35 to 75 percent by mass, more preferably 55 to 65 percent by mass of the metal component of Group VIA in the periodic table. A content of more than 75 percent by mass is not preferable because a solution containing the metal component (hereinafter may be referred to as "metal-containing solution for loading") is increased in viscosity and thus renders it difficult to be impregnated during the process. A content of less than 35 percent by mass is also not preferable because the stability of the metal-containing solution for loading would be poor and catalyst performances tends to deteriorate.

[0027] No particular limitation is imposed on the method for including the above-described metal component or further an inorganic acid (phosphoric acid or the like) and/or an organic acid solution in the above-described support. Any conventional method may be used such as impregnation (equilibrium adsorption, pore-filling, incipient-wetness methods) and ion exchange method using a compound containing the metal component or further using an inorganic acid (phosphoric acid) and/or an organic acid. Impregnation used herein refers to a method wherein a support is impregnated with a solution of a metal component, dried and then calcined.

[0028] In impregnation, metal components of Groups VIA and VIII in the periodic tables are preferably loaded simultaneously. Separate loading of the metal components would result in insufficient desulfurization and denitrogenation activities. Loading by impregnation is carried out in the coexistence of acid, preferably an inorganic acid and/or an organic acid, more preferably phosphoric acid and/or an organic acid because the resulting catalyst will be enhanced in desulfurization and denitrogenation activities as the metal component of Group VIA in the periodic table is highly dispersed on the support. Thereupon, phosphoric acid and/or an organic acid are preferably added in an amount of 3 to 25 percent by mass (an oxide basis) and an amount of 35 to 75 percent by mass, respectively of 100 percent by mass of the metal component of Group VIA in the periodic table. Examples of the organic acid include carboxylic acid compounds, specifically citric acid, malic acid, tartaric acid, and gluconic acid.

[0029] The desulfurization catalyst of the present invention has necessarily a specific surface area (SA) of 150 m²/g or greater, preferably 170 m²/g or greater, as measured by BET method. A specific surface area (SA) of smaller than 150 m²/g is not preferable because the number of active site for desulfurization would be decreased. Whilst, no particular limitation is imposed on the upper limit. However, a specific surface area (SA) of greater than 250 m²/g would tend to decrease the catalyst strength and thus is preferably 250 m²/g or smaller, more preferably 230 m²/g or smaller.

[0030] The hydrodesulfurization catalyst of the present invention has necessarily a total pore volume (PVo) of 0.30 ml/g or greater, preferably 0.35 ml/g or greater, as measured by mercury intrusion technique (mercury contact angle: 135 degrees, surface tension: 480 dyn/cm). No

particular limitation is imposed on the upper limit of the total pore volume, which is, however, preferably 0.60 ml/g or smaller, more preferably 0.50 ml/g or smaller because a total pore volume of greater than 0.60 ml/g would likely cause the resulting catalyst to be decreased in strength.

[0031] Furthermore, the hydrodesulfurization catalyst has necessarily an average pore diameter (PD) of 6 to 15 nm (60 to 150 Å), preferably 6.5 to 11 nm. A catalyst with an average pore diameter (PD) of less than 6 nm would have too small pores and thus be poor in reactivity with a feedstock while a catalyst with an average pore diameter of greater than 15 nm would be difficult to be produced and tend to be poor in catalyst performances because of its too small specific surface area. The total pore volume (PVo) refers to pores with a pore diameter of 4.1 nm (41 Å) or greater, which is the quantitative limit in measurement while the average pore diameter (PD) refers to a pore diameter corresponding to 50 percent of the total pore volume (PVo).

[0032] In the hydrodesulfurization catalyst, the ratio (PVp/PVo) of the pore volume of the pores having a pore diameter within ± 30 percent of the average pore diameter (PVp) in the total pore diameter (PVo) is necessarily 70 percent or more, preferably 80 percent or more, and the pore distribution is sharp. When the PVp/PVo is less than 70 percent, the pore distribution is too broad and thus the resulting catalyst may not obtain a desired desulfurization performance.

[0033] For the support of the hydrodesulfurization catalyst of the present invention, the total of the diffraction peak area indicating the crystal structure of anatase titania (101) planes and the diffraction peak area indicating the crystal structure of rutile titania (110) planes (hereinafter also referred to as "titania diffraction peak area") is necessarily $1/4$ or less, preferably $1/5$ or less, more preferably $1/6$ or less of the diffraction peak area indicating the aluminum crystal structure ascribed to γ -alumina (400) planes, as measured by X-ray diffraction analysis. When the titania diffraction peak area to the alumina diffraction peak area (titania diffraction peak area/alumina diffraction peak area) is greater than $1/4$, crystallization of titania accelerates and thus the number of the pores effective for the reaction is decreased. Therefore, even if the amount of titania is increased, the resulting catalyst can not exhibit a desulfurization performance as balanced with the economy and fails to be an inexpensive catalyst with high performances intended by the present invention.

[0034] The diffraction peak indicating the crystal structure of anatase titania (101) planes is measured at $2\theta=25.5^\circ$ while the diffraction peak indicating the crystal structure of rutile titania (110) planes is measured at $2\theta=27.5^\circ$. The diffraction peak indicating the aluminum crystal structure ascribed to γ -alumina (400) planes is measured at $2\theta=45.9^\circ$.

[0035] Each of the diffraction peak areas is calculated by fitting a graph obtained through X-ray diffraction analysis with an X-ray diffraction device, with a least square method, followed by baseline correction, and finding the height (peak intensity W) from the maximum peak value to the baseline so as to derive the peak width (full width at half maximum) when the resulting peak strength is half ($W/2$) thereby defining the product of the full width at half maximum and

peak intensity as a diffraction peak area. "Titania diffraction peak area/alumina diffraction peak area" is derived from each of the diffraction peak areas thus obtained.

[0036] A process of producing the hydrodesulfurization catalyst of the present invention will be described next.

[0037] The process of producing the hydrodesulfurization catalyst of the present invention comprises: a first step of producing a hydrate by mixing a mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt (hereinafter simply referred to as "mixed aqueous solution") with a basic aluminum salt aqueous solution in the presence of silicate ion such that the pH is form 6.5 to 9.5; a second step of producing a support by in turn washing, extruding, drying and calcining the hydrate; and a third step of loading at least one type of metal component selected from Groups VIA (IUPAC Group 6) and VIII (IUPAC Groups 8 to 10) in the periodic table on the support. Each of the steps will be described below.

(First Step)

[0038] First of all, in the presence of silicate ion, a mixed solution of a titanium mineral acid salt and an acidic aluminum salt (this is an acidic aqueous solution) is mixed with a basic aluminum salt aqueous solution (this is an alkaline aqueous solution) such that the pH is form 6.5 to 9.5, preferably from 6.5 to 8.5, more preferably from 6.5 to 7.5 thereby producing a hydrate containing silica, titania and alumina.

[0039] In this step, there are two alternative cases (1) where a mixed aqueous solution is added to a basic aluminum salt aqueous solution containing silicate ion and (2) where a basic aluminum salt aqueous solution is added to a mixed solution containing silicate ion.

[0040] In case (1), silicate ion contained in a basic aluminum aqueous solution may be basic or neutral. Basic silicate ion sources may be silicic acid compounds such as sodium silicate, which can generate silicate ions in water. In case (2), silicate ion contained in a mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt aqueous solution may be acidic or neutral. Acidic silicate sources may be silicic acid compounds such as silicic acid, which can generate silicate ions in water.

[0041] Examples of the basic aluminum salt include sodium aluminate and potassium aluminate. Examples of the acidic aluminum salt include aluminum sulfate, aluminum chloride, and aluminum nitrate. Examples of the titanium mineral acid salt include titanium tetrachloride, titanium trichloride, titanium sulfate, and titanium nitrate. In particular, titanium sulfate is preferably used because it is inexpensive.

[0042] For example, a predetermined amount of a basic aluminum salt aqueous solution containing basic silicate ion is charged into a tank with a stirrer and heated and maintained to a temperature of usually 40 to 90°C, preferably 50 to 70°C, and to the solution was continuously

added a predetermined amount of a mixed aqueous solution of a titanium mineral acid salt and acidic aluminum salt aqueous solution heated to a temperature of $\pm 5^{\circ}\text{C}$, preferably $+2^{\circ}\text{C}$, more preferably $\pm 1^{\circ}\text{C}$ of the basic aluminum salt aqueous solution for usually from 5 to 20 minutes, preferably from 7 to 15 minutes so that the pH is from 6.5 to 9.5, preferably from 6.5 to 8.5, more preferably from 6.5 to 7.5 to produce a precipitate, which is a slurry of hydrate. It is noted that since addition of the basic aluminum salt aqueous solution to the mixed solution for a too long period of time would cause the production of crystals of pseudoboehmite, bayerite or gibbsite, which are not preferable, the addition is carried out for desirously 15 minutes or shorter, more desirously 13 minutes or shorter. Bayerite and gibbsite are not preferable because they reduce the specific surface area after calcination.

(Second Step)

[0043] The hydrate slurry produced in the first step is aged if necessary and then washed to remove the by-produced salts thereby producing a hydrate slurry containing silica, titania and alumina. The resulting hydrate slurry is further heated and aged if necessary and then formed into an extrudable kneaded product by a conventional method, such as heat-kneading. The extrudable product is extruded into a desired shape by extrusion and then dried at a temperature of 70 to 150°C , preferably 90 to 130°C and calcined at a temperature of 400 to 800°C , preferably 450 to 600°C for 0.5 to 10 hours, preferably 2 to 5 hours thereby producing a silica-titania-alumina support.

(Third Step)

[0044] On the resulting silica-titania-alumina support is loaded at least one type of metal component selected from Groups VIA and VII in the periodic table with a conventional manner (impregnation, immersion) as described above. The support with the metal component loaded thereon is then calcined at a temperature of usually 400 to 800°C , preferably 450 to 600°C for 0.5 to 10 hours, preferably 2 to 5 hours thereby producing a hydrodesulfurization catalyst according to the present invention.

[0045] Raw materials of the metal component are preferably nickel nitrate, nickel carbonate, cobalt nitrate, cobalt carbonate, molybdenum trioxide, ammonium molybdate, and ammonium paratungsten.

[0046] Next, an explanation will be given of a method for hydrorefining a hydrocarbon oil according to the present invention.

[0047] In this method, a hydrocarbon oil is hydrotreated under hydrogen atmosphere and high temperature and pressure conditions using the above-described hydrodesulfurization catalyst, which is filled into a fixed-bed reactor.

[0048] Hydrocarbon oils used in the present invention are preferably gas oil fractions. Examples of the gas oil fractions include straight-run gas oil produced through an atmospheric distillation unit for crude oil; vacuum gas oil produced by distilling straight heavy oil or residue obtained from an atmospheric distillation unit, in a vacuum distillation unit; light cycle oil produced by fluid catalytic-cracking vacuum heavy gas oil or desulfurized heavy oil; hydrocracked gas oil produced by hydrocracking vacuum heavy gas oil or desulfurized heavy oil; and thermal-cracked gas oil obtained through a thermal cracking unit such as a coker, all of which are fractions containing 70 percent by volume or more of a fraction whose boiling point is from 260 to 360°C. No particular limitation is imposed on oils to be treated in an atmospheric distillation unit. Examples of such oils include petroleum crude oil, synthetic crude oil derived from oil sand, liquefied coal oil, and bitumen reformed oil.

[0049] The value of the distillation characteristics (boiling point) referred herein is measured in accordance with the method described in JIS K2254 "Petroleum products-Determination of distillation characteristics".

[0050] The method for hydrorefining a hydrocarbon oil according to the present invention is preferably carried out under the following reaction conditions.

[0051] No particular limitation is imposed on the reaction temperature, which is, however, preferably from 300 to 420°C, more preferably from 320 to 380°C. A reaction temperature of lower than 300°C is not practical because desulfurization and denitrogenation activities tend to significantly deteriorate. A reaction temperature of higher than 420°C is not preferable because the catalyst is drastically decomposed and the reaction temperature is close to the operating temperature limit (usually 425°C) of the reactor.

[0052] No particular limitation is imposed on the reaction pressure (hydrogen partial pressure), which is, however, preferably from 3.0 to 15.0 MPa. At a reaction pressure of lower than 3.0 MPa, desulfurization and denitrogenation activities tend to significantly decrease. The reaction pressure is thus preferably 3.0 MPa or higher, more preferably 4.0 MPa or higher. A reaction pressure of higher than 15.0 MPa is not preferable because hydrogen consumption increases, resulting in a higher running cost. The reaction pressure is thus preferably 15.0 MPa or lower, more preferably 10.0 MPa or lower, more preferably 7.0 MPa or lower.

[0053] No particular limitation is imposed on the liquid hourly space velocity, which is, however, preferably from 0.5 to 4.0 h⁻¹, more preferably from 0.5 to 2.0 h⁻¹. A liquid hourly space velocity of less than 0.5 h⁻¹ is not practical because the productivity is reduced due to the reduced amount of throughput. A liquid hourly space velocity of greater than 4.0 h⁻¹ is not preferable because the decomposition of the catalyst accelerates.

[0054] No particular limitation is imposed on the hydrogen/oil ratio, which is, however, is preferably from 120 to 420 NL/L, more preferably from 170 to 340 NL/L. A hydrogen/oil ratio of less than 120 NL/L is not preferable because the desulfurization rate decreases. A

hydrogen/oil ratio of greater than 420 NL/L is not also preferable because it can not change the desulfurization activity and only increases the running cost.

[0055] The oil produced by hydrotreating of hydrocarbon oil according to the present invention has a sulfur content of preferably 10 ppm by mass or less, more preferably 8 ppm by mass or less, more preferably 7 ppm by mass or less. The oil has a nitrogen content of preferably 3 ppm by mass or less, more preferably one ppm by mass. The present invention can decrease significantly the sulfur and nitrogen contents of the produced oil by hydrotreating hydrocarbon oil using the above-described specific hydrodesulfurization catalyst.

[0056] The sulfur content (sulfur concentration) referred herein is measured in accordance with the method described in JIS K2541 "Determination of sulfur content". The nitrogen content (nitrogen concentration) referred herein is measured in accordance with the method described in JIS K2609 "Determination of nitrogen content".

Examples

[0057] The present invention will be described in more details with reference to the following examples but is not limited thereto.

[Preparation of Hydrodesulfurization Catalyst a]

[0058] Into a 100 L volume tank equipped with a steam jacket were put 8.16 kg of an aqueous solution containing sodium aluminate in an amount of 22 percent by mass on an Al_2O_3 concentration basis. The solution was diluted with 41 kg of ion-exchange water, to which 1.80 kg of a solution containing sodium silicate in an amount of 5 percent by mass on an SiO_2 concentration basis were then added, stirring. The resulting mixture was heated at a temperature of 60°C thereby preparing a basic aluminum salt aqueous solution. An acidic aluminum salt aqueous solution was prepared by diluting 7.38 kg of an aqueous solution containing aluminum sulfate in an amount of 7 percent by mass on an Al_2O_3 concentration basis with 13 kg of ion-exchange water while a titanium mineral acid salt aqueous solution was prepared by dissolving 1.82 kg of 33 percent by mass on a TiO_2 concentration basis of titanium sulfate in 10 kg of ion-exchange water. These aqueous solutions were mixed and heated to a temperature of 60°C thereby preparing a mixed aqueous solution. This mixed aqueous solution was added at a constant rate (addition time: 10 minutes) into the tank containing therein the basic aluminum salt aqueous solution using a roller pump until the pH was 7.2 thereby preparing Hydrate Slurry a containing silica, titania, and alumina.

[0059] The resulting Hydrate Slurry a was aged, stirring at a temperature of 60°C for one hour, and then dewatered with a flat sheet filter and washed with 150 L of a 0.3 percent by mass ammonium aqueous solution. After washing, the resulting cake-like slurry was diluted with ion-

exchange water so that the amount of the slurry was 10 percent by mass on an Al_2O_3 concentration basis and then adjusted in pH to 10.5 with 15 percent by mass of ammonium water. The slurry was transferred to an aging tank with a reflux condenser and aged, stirring at a temperature of 95°C for 10 hours. The resulting slurry was dewatered and then concentrated and kneaded to have a certain moisture level with a double-armed kneader with a steam jacket. The resulting kneaded product was extruded into a cylindrical shape with a diameter of 1.8 mm with an extruder and dried at a temperature of 110°C . The dried extruded products were calcined at a temperature of 550°C in an electric furnace for 3 hours thereby producing Support a. Support a contained silica in an amount of 3 percent by mass on a SiO_2 concentration basis, titania in an amount of 20 percent by mass on a TiO_2 concentration basis, and aluminum in an amount of 77 percent by mass on an Al_2O_3 concentration basis, all on the support basis.

[0060] Support a was subjected to X-ray diffraction analysis with an X-ray diffraction apparatus "RINT 2100" manufactured by Rigaku Corporation (the same is applied to the following examples). The results are set forth in Fig. 1. Least square fitting was applied to the resulting graph, followed by baseline correction so as to find the full width at half maximum of the peak ascribed to the anatase titania (101) planes indicated at $2\theta=25.5^\circ$. The product of the full width at half maximum and the peak intensity from the baseline to the maximum peak was defined as an anatase titania diffraction peak area. The same procedures were carried out to find the full width at half maximum of the peak ascribed to the rutile titania (110) planes indicated at $2\theta=27.5^\circ$, and the product of the full width at half maximum and the peak intensity from the baseline was defined as a rutile titania diffraction peak area. The total of the anatase titania diffraction peak area and rutile titania diffraction peak area was defined as a titania diffraction peak area. It is noted that no rutile titania peak was not detected in Support a. Furthermore, the full width at half maximum of the peak ascribed to the γ -alumina (400) planes indicated at $2\theta=45.9^\circ$ was also found, and the product of the full width at half maximum and the peak intensity from the baseline was defined as an alumina diffraction peak area. For Support a, the diffraction peak area indicating the crystal structures of the anatase titania and rutile titania was 1/8 of the diffraction peak area of the crystal structure ascribed to aluminum (titania diffraction peak area/alumina diffraction peak area=1/8, and the same is applied to the following).

[0061] Next, 306 g of molybdenum trioxide and 68 g of cobalt carbonate were suspended in 500 ml of ion-exchanged water, and then heated at a temperature of 95°C for 5 hours, applying a suitable reflux treatment so that the volume is not decreased, followed by dissolving of 68 g of phosphoric acid in the suspension thereby preparing an impregnation solution. After 1000 g of Support a was impregnated with this impregnation solution by spray, it was dried at a temperature of 250°C and calcined at a temperature of 550°C in an electric furnace for one hour thereby producing Hydrodesulfurization Catalyst a (hereinafter also referred to as "Catalyst a" and the same is applied to the following examples). Catalyst a contained the following metal components, 22 percent by mass of MoO_3 , 3 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on the catalyst basis. Properties of Catalyst a are set forth in Table 1 below.

[Example 2: Preparation of**Hydrodesulfurization Catalyst b - not according to the invention]**

[0062] This example is different from Example 1 in that Hydrate Slurry b was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 8.49 kg of an aqueous solution containing 22 percent by mass on an Al_2O_3 concentration basis of sodium aluminate with 37 kg of ion-exchanged water and adding thereto, stirring 1.80 kg of a solution containing 5 percent by mass on an SiO_2 concentration basis of sodium silicate, followed by heating to a temperature of 60°C (2) a mixed aqueous solution prepared by mixing an acidic aluminum salt aqueous solution prepared by diluting 10.62 kg of an aqueous solution containing 7 percent by mass on an Al_2O_3 concentration basis of aluminum sulfate with 19 kg of ion-exchanged water and a titanium mineral acid salt aqueous solution prepared by dissolving 0.91 kg of 33 percent by mass on a TiO_2 concentration basis of titanium sulfate in 5 kg of ion-exchanged water, until the pH was 7.2.

[0063] In the same manner as Example 1, Support b was prepared from Hydrate Slurry b. Support b contained silica in an amount of 3 percent by mass on an SiO_2 concentration basis, titanium in an amount of 10 percent by mass on a TiO_2 concentration basis, and aluminum in an amount of 87 percent by mass on an Al_2O_3 basis, all on the support basis.

[0064] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), no diffraction peak indicating the crystal structures of the anatase titania and rutile titania was detected, and the titania diffraction peak area/alumina diffraction peak area was less than 1/4.

[0065] As with Example 1, Catalyst b was produced using Support b. Catalyst b contained 22 percent by mass of MoO_3 , 3 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on the catalyst basis. Properties of Catalyst b are set forth in Table 1 below.

[Example 3: Preparation of Hydrodesulfurization Catalyst c - not according to the invention]

[0066] This example is different from Example 1 in that Hydrate Slurry c was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 7.82 kg of an aqueous solution containing 22 percent by mass on an Al_2O_3 concentration basis of sodium aluminate with 44 kg of ion-exchanged water and adding thereto, stirring 1.80 kg of a solution containing 5 percent by mass on an SiO_2 concentration basis of sodium silicate, followed by heating to a temperature of 60°C (2) a mixed aqueous solution prepared by mixing

an acidic aluminum salt aqueous solution prepared by diluting 4.14 kg of an aqueous solution containing 7 percent by mass on an Al_2O_3 concentration basis of aluminum sulfate with 7 kg of ion-exchanged water and a titanium mineral acid salt aqueous solution prepared by dissolving 2.73 kg of 33 percent by mass on a TiO_2 concentration basis of titanium sulfate in 15 kg of ion-exchanged water, until the pH was 7.2.

[0067] In the same manner as Example 1, Support c was prepared from Hydrate Slurry c. Support c contained silica in an amount of 3 percent by mass on an SiO_2 concentration basis, titanium in an amount of 30 percent by mass on a TiO_2 concentration basis and aluminum in an amount of 67 percent by mass on an Al_2O_3 basis, all on the support basis.

[0068] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), the titania diffraction peak area/alumina diffraction peak area was 1/5.

[0069] As with Example 1, Catalyst c was produced using Support c. Catalyst c contained 22 percent by mass of MoO_3 , 3 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on the catalyst basis. Properties of Catalyst c are set forth in Table 1 below.

[Comparative Example 1: Preparation of Hydrodesulfurization Catalyst d]

[0070] This example is different from Example 1 in that Hydrate Slurry d was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 8.82 kg of an aqueous solution containing 22 percent by mass on an Al_2O_3 concentration basis of sodium aluminate with 34 kg of ion-exchanged water and adding thereto, stirring 1.80 kg of a solution containing 5 percent by mass on an SiO_2 concentration basis of sodium silicate, followed by heating to a temperature of 60°C (2) an acidic aluminum salt aqueous solution prepared by diluting 13.86 kg of an aqueous solution containing 7 percent by mass on an Al_2O_3 concentration basis of aluminum sulfate with 25 kg of ion-exchanged water, until the pH was 7.2.

[0071] In the same manner as Example 1, Support d was prepared from Hydrate Slurry d. Support d contained silica in an amount of 3 percent by mass on an SiO_2 concentration basis, titanium in an amount of 0 percent by mass on a TiO_2 concentration basis and aluminum in an amount of 97 percent by mass on an Al_2O_3 concentration basis, all on the support basis.

[0072] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), no diffraction peak indicating the crystal structures of the anatase titania and rutile titania was detected, and the titania diffraction peak area/alumina diffraction peak area was less than 1/4.

[0073] As with Example 1, Catalyst d was produced using Support d. Catalyst d contained 22 percent by mass of MoO_3 , 3 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on

the catalyst basis. Properties of Catalyst d are set forth in Table 1 below.

[Comparative Example 2: Preparation of Hydrodesulfurization Catalyst e]

[0074] This example is different from Example 1 in that Hydrate Slurry e was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 7.09 kg of an aqueous solution containing 22 percent by mass on an Al_2O_3 concentration basis of sodium aluminate with 47 kg of ion-exchanged water and adding thereto, stirring 1.80 kg of a solution containing 5 percent by mass on an SiO_2 concentration basis of sodium silicate, followed by heating to a temperature of 60°C (2) a titanium mineral acid salt aqueous solution prepared by dissolving 4.09 kg of 33 percent by mass on a TiO_2 concentration basis of titanium sulfate in 23 kg of ion-exchange water, until the pH was 7.2.

[0075] In the same manner as Example 1, Support e was prepared from Hydrate Slurry e. Support e contained silica in an amount of 3 percent by mass on an SiO_2 concentration basis, titanium in an amount of 45 percent by mass on a TiO_2 concentration basis and aluminum in an amount of 52 percent by mass on an Al_2O_3 concentration basis, all on the support basis.

[0076] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), the titania diffraction peak area/alumina diffraction peak area was 1/3.

[0077] As with Example 1, Catalyst e was produced using Support e. Catalyst e contained 22 percent by mass of MoO_3 , 3 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on the catalyst basis. Properties of Catalyst e are set forth in Table 1 below.

[Example 4: Preparation of Hydrodesulfurization Catalyst f - not according to the invention]

[0078] This example is different from Example 1 in that Hydrate Slurry f was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 7.79 kg of an aqueous solution containing 22 percent by mass on an Al_2O_3 concentration basis of sodium aluminate with 40 kg of ion-exchanged water and adding thereto, stirring 4.20 kg of a solution containing 5 percent by mass on an SiO_2 concentration basis of sodium silicate, followed by heating to a temperature of 60°C (2) a mixed aqueous solution prepared by mixing an acidic aluminum salt aqueous solution prepared by diluting 6.81 kg of an aqueous solution containing 7 percent by mass on an Al_2O_3 concentration basis of aluminum sulfate with 12 kg of ion-exchanged water and a titanium mineral acid salt aqueous solution prepared by dissolving 1.82 kg of 33 percent by mass on a TiO_2 concentration basis of titanium sulfate in 10 kg of ion-exchanged water, until the pH was 7.2.

[0079] In the same manner as Example 1, Support f was prepared from Hydrate Slurry f. Support f contained silica in an amount of 7 percent by mass on an SiO₂ concentration basis, titanium in an amount of 20 percent by mass on a TiO₂ concentration basis and aluminum in an amount of 73 percent by mass on an Al₂O₃ concentration basis, all on the support basis.

[0080] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), the titania diffraction peak area/alumina diffraction peak area was 1/8.

[0081] As with Example 1, Catalyst f was produced using Support f. Catalyst f contained 22 percent by mass of MoO₃, 3 percent by mass of CoO, and 3 percent by mass of P₂O₅, all on the catalyst basis. Properties of Catalyst f are set forth in Table 2 below.

[Example 5: Preparation of Hydrodesulfurization Catalyst g - not according to the invention]

[0082] This example is different from Example 1 in that Hydrate Slurry g was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 7.52 kg of an aqueous solution containing 22 percent by mass on an Al₂O₃ concentration basis of sodium aluminate with 40 kg of ion-exchanged water and adding thereto, stirring 6.00 kg of a solution containing 5 percent by mass on an SiO₂ concentration basis of sodium silicate, followed by heating to a temperature of 60°C (2) a mixed aqueous solution prepared by mixing an acidic aluminum salt aqueous solution prepared by diluting 6.38 kg of an aqueous solution containing 7 percent by mass on an Al₂O₃ concentration basis of aluminum sulfate with 11 kg of ion-exchanged water and a titanium mineral acid salt aqueous solution prepared by dissolving 1.82 kg of 33 percent by mass on a TiO₂ concentration basis of titanium sulfate in 10 kg of ion-exchanged water, until the pH was 7.2.

[0083] In the same manner as Example 1, Support g was prepared from Hydrate Slurry g. Support g contained silica in an amount of 10 percent by mass on an SiO₂ concentration basis, titanium in an amount of 20 percent by mass on a TiO₂ concentration basis and aluminum in an amount of 70 percent by mass on an Al₂O₃ concentration basis, all on the support basis.

[0084] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), the titania diffraction peak area/alumina diffraction peak area was 1/8.

[0085] As with Example 1, Catalyst g was produced using Support g. Catalyst g contained 22 percent by mass of MoO₃, 3 percent by mass of CoO, and 3 percent by mass of P₂O₅, all on the catalyst basis. Properties of Catalyst g are set forth in Table 2 below.

[Comparative Example 3: Preparation of Hydrodesulfurization Catalyst h]

[0086] This example is different from Example 1 in that Hydrate Slurry h was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 8.43 kg of an aqueous solution containing 22 percent by mass on an Al_2O_3 concentration basis of sodium aluminate with 41 kg of ion-exchanged water, followed by heating to a temperature of 60°C (2) a mixed aqueous solution prepared by mixing an acidic aluminum salt aqueous solution prepared by diluting 7.81 kg of an aqueous solution containing 7 percent by mass on an Al_2O_3 concentration basis of aluminum sulfate with 14 kg of ion-exchanged water and a titanium mineral acid salt aqueous solution prepared by dissolving 1.82 kg of 33 percent by mass on a TiO_2 concentration basis of titanium sulfate in 10 kg of ion-exchanged water, until the pH was 7.2.

[0087] In the same manner as Example 1, Support h was prepared from Hydrate Slurry h. Support h contained silica in an amount of 0 percent by mass on an SiO_2 concentration basis, titanium in an amount of 20 percent by mass on a TiO_2 concentration basis and aluminum in an amount of 80 percent by mass on an Al_2O_3 concentration basis, all on the support basis.

[0088] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), the titania diffraction peak area/alumina diffraction peak area was 1/4.

[0089] As with Example 1, Catalyst h was produced using Support h. Catalyst h contained 22 percent by mass of MoO_3 , 3 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on the basis of the catalyst. Properties of Catalyst h are set forth in Table 2 below.

[Comparative Example 4: Preparation of Hydrodesulfurization Catalyst i]

[0090] This example is different from Example 1 in that Hydrate Slurry i was prepared by adding at a constant rate to (1) a basic aluminum salt aqueous solution prepared by diluting 7.07 kg of an aqueous solution containing 22 percent by mass on an Al_2O_3 concentration basis of sodium aluminate with 40 kg of ion-exchanged water and adding thereto, stirring 9.00 kg of a solution containing 5 percent by mass on an SiO_2 concentration basis of sodium silicate, followed by heating to a temperature of 60°C (2) a mixed aqueous solution prepared by mixing an acidic aluminum salt aqueous solution prepared by diluting 5.67 kg of an aqueous solution containing 7 percent by mass on an Al_2O_3 concentration basis of aluminum sulfate with 10 kg of ion-exchanged water and a titanium mineral acid salt aqueous solution prepared by dissolving 1.82 kg of 33 percent by mass on a TiO_2 concentration basis of titanium sulfate in 10 kg of ion-exchanged water, until the pH was 7.2.

[0091] In the same manner as Example 1, Support i was prepared from Hydrate Slurry i. Support i contained silica in an amount of 15 percent by mass on an SiO_2 concentration basis, titanium in an amount of 20 percent by mass on a TiO_2 concentration basis and aluminum in

an amount of 65 percent by mass on an Al_2O_3 concentration basis, all on the support basis.

[0092] As the result of X-ray diffraction analysis carried out as with Example 1 (not shown), the titania diffraction peak area/alumina diffraction peak area was 1/8.

[0093] As with Example 1, Catalyst i was produced using Support i. Catalyst i contained 22 percent by mass of MoO_3 , 3 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on the catalyst basis. Properties of Catalyst i are set forth in Table 2 below.

[Example 6: Preparation of Hydrodesulfurization Catalyst j]

[0094] Support a produced in Example 1 was used as a support.

[0095] Next, 278 g of molybdenum trioxide and 114 g of cobalt carbonate were suspended in 500 ml of ion-exchanged water, and then heated at a temperature of 95°C for 5 hours, applying thereto a suitable reflux treatment so that the volume is not decreased, followed by dissolving therein 68 g of phosphoric acid and 76 g of nitric acid thereby preparing an impregnation solution. After 1000 g of Support a was impregnated with this impregnation solution by spray, it was dried at a temperature of 250°C and calcined at a temperature of 550°C in an electric furnace for one hour thereby producing Hydrodesulfurization Catalyst j. Catalyst j contained 20 percent by mass of MoO_3 , 5 percent by mass of CoO , and 3 percent by mass of P_2O_3 , all on the catalyst basis. Properties of Catalyst j are set forth in Table 3 below.

[Example 7: Preparation of Hydrodesulfurization Catalyst k]

[0096] Support a produced in Example 1 was used as a support.

[0097] Next, 278 g of molybdenum trioxide and 114 g of cobalt carbonate were suspended in 500 ml of ion-exchanged water, and then heated at a temperature of 95°C for 5 hours, applying thereto a suitable reflux treatment so that the volume is not decreased, followed by dissolving therein 68 g of phosphoric acid and 174 g of malic acid thereby preparing an impregnation solution. After 1000 g of Support a was impregnated with this impregnation solution by spray, it was dried at a temperature of 250°C and calcined at a temperature of 550°C in an electric furnace for one hour thereby producing Hydrodesulfurization Catalyst k. Catalyst k contained 20 percent by mass of MoO_3 , 5 percent by mass of CoO , and 3 percent by mass of P_2O_5 , all on the catalyst basis. Properties of Catalyst k are set forth in Table 3 below.

[Example 8: Preparation of Hydrodesulfurization Catalyst 1]

[0098] Support a produced in Example 1 was used as a support.

[0099] Next, 267 g of molybdenum trioxide and 109 g of cobalt carbonate were suspended in 500 ml of ion-exchanged water, and then heated at a temperature of 95°C for 5 hours, applying thereto a suitable reflux treatment so that the volume was not decreased, followed by dissolving therein 167 g of malic acid thereby preparing an impregnation solution. After 1000 g of Support a was impregnated with this impregnation solution by spray, it was dried at a temperature of 250°C and calcined at a temperature of 550°C in an electric furnace for one hour thereby producing Hydrodesulfurization Catalyst 1. Catalyst 1 contained 20 percent by mass of MoO₃, 5 percent by mass of CoO, and 0 percent by mass of P₂O₅, all on the catalyst basis. Properties of Catalyst 1 are set forth in Table 3 below.

[Example 9: Preparation of Hydrodesulfurization Catalyst m]

[0100] Support a produced in Example 1 was used as a support.

[0101] Next, 306 g of molybdenum trioxide and 76 g of nickel carbonate were suspended in 500 ml of ion-exchanged water, and then heated at a temperature of 95°C for 5 hours, applying thereto a suitable reflux treatment so that the volume was not decreased, followed by addition and dissolve of 68 g of malic acid thereby preparing an impregnation solution. After 1000 g of Support a was impregnated with this impregnation solution by spray, it was dried at a temperature of 250°C and calcined at a temperature of 550°C in an electric furnace for one hour thereby producing Hydrodesulfurization Catalyst m. Catalyst m contained 22 percent by mass of MoO₃, 3 percent by mass of NiO, and 3 percent by mass of P₂O₅, all on the catalyst basis. Properties of Catalyst m are set forth in Table 3 below.

[Example 10: Preparation of Hydrodesulfurization Catalyst n]

[0102] This example is different from Example 1 in that Hydrate Slurry n was prepared by adding at a constant rate to (1) a mixed aqueous solution prepared by mixing an acidic aluminum salt aqueous solution prepared by diluting 7.17 kg of an aqueous solution containing 7 percent by mass on an Al₂O₃ concentration basis of aluminum sulfate with 13 kg of ion-exchanged water and a titanium mineral acid salt aqueous solution prepared by dissolving 1.82 kg of 33 percent by mass on a TiO₂ concentration basis of titanium sulfate in 10 kg of ion-exchanged water, and further 1.88 kg of a solution containing 4.8 percent by mass on a SiO₂ concentration basis of silicic acid (2) a basic aluminum salt aqueous solution prepared by diluting 8.22 kg of an aqueous solution containing 22 percent by mass on an Al₂O₃ concentration basis of sodium aluminate with 41 kg of ion-exchanged water, followed by heating to a temperature of 60°C, until the pH was 7.2.

[0103] In the same manner as Example 1, Support n was prepared from Hydrate Slurry n. Support n contained silica in an amount of 3 percent by mass on an SiO₂ concentration basis, titanium in an amount of 20 percent by mass on a TiO₂ concentration basis and aluminum in an amount of 77 percent by mass on an Al₂O₃ concentration basis, on the support basis. As the result of X-ray diffraction analysis was carried out as with Example 1 (not shown), the titania diffraction peak area/alumina diffraction peak area was 1/7.

[0104] As with Example 1, Catalyst n was produced using Support n. Catalyst n contained 22 percent by mass of MoO₃, 3 percent by mass of CoO, and 3 percent by mass of P₂O₅, all on the catalyst basis. Properties of Catalyst n are set forth in Table 3 below.

[Test 1]

[0105] Crude oil having the following properties was hydrotreated with a hydrodesulfurization unit manufactured by ZYTEL Co. using Catalysts a to n. A temperature at which the produced oil has a sulfur content of 7 ppm by mass (hereinafter referred to as "reaction temperature") is determined to compare the desulfurization performance among the catalysts. Hydrotreating reaction was carried out under the following conditions. The results are set forth in Tables 1 to 3.

[Properties of Crude Oil]

[0106]

Feedstock : straight run gas oil (boiling point range 208 to 390°C)

Density at 15°C: 0.8493 g/cm³

Sulfur content : 1.32 percent by mass

Nitrogen content: 105 ppm by mass

[Reaction Conditions]

[0107]

Liquid hourly space velocity: 1.0 hr⁻¹

Hydrogen pressure: 4.9 MPa

Hydrogen/oil ratio: 250 NL/L

[Table 1]

		Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
Catalyst		Catalyst a	Catalyst b	Catalyst c	Catalyst d	Catalyst e
Support Components						
silica	mass %	3	3	3	3	3
titania	mass %	20	10	30	0	45
alumina	mass %	77	87	67	97	52
Loaded Components						
M ₀ O ₃ (catalyst basis)	mass %	22	22	22	22	22
C ₀ O (catalyst basis)	mass %	3	3	3	3	3
P ₂ O ₅ (catalyst basis)	mass %	3	3	3	3	3
P ₂ O ₅	mass %	13.6	13.6	13.6	13.6	13.6
(basis of 100 mass % of VIA metal)						
Properties						
PV ₀	ml / g	0.43	0.45	0.4	0.47	0.26
SA	m ² / g	203	212	181	228	132
PD	Å	75	75	75	75	105
PD _p /PV ₀	%	91	89	88	90	78
Desulfurization Performance						
Reaction Temperature	°C	342	347	342	363	365

[Table 2]

		Example 1	Example 4	Example 5	Comparative Example 3	Comparative Example 4
Catalyst		Catalyst a	Catalyst f	Catalyst g	Catalyst h	Catalyst i
Support Components						
silica	mass %	3	7	10	0	15
titania	mass %	20	20	20	20	20
alumina	mass %	77	73	70	80	65
Loaded Components						
M ₀ O ₃ (catalyst basis)	mass %	22	22	22	22	22
C ₀ O (catalyst basis)	mass %	3	3	3	3	3
P ₂ O ₅ (catalyst basis)	mass %	3	3	3	3	3
P ₂ O ₅	mass %	13.6	13.6	13.6	13.6	13.6
(basis of 100 mass % of VIA metal)						
Properties						
PV ₀	ml / g	0.43	0.51	0.53	0.42	0.57
SA	m ² / g	203	221	233	171	235
PD	Å	75	90	95	90	95
PD _p / PV ₀	%	91	82	76	89	62
Desulfurization Performance						
Reaction Temperature	°C	342	350	352	361	354

[Table 3]

		Example 6	Example 7	Example 8	Example 9	Example 10
Catalyst		Catalyst j (Support a)	Catalyst k (Support a)	Catalyst l (Support a)	Catalyst m (Support a)	Catalyst n (Support n)
Support Components						
silica	mass %	3	3	3	3	3
titania	mass %	20	20	20	20	20
alumina	mass %	77	77	77	77	77
Loaded Components						
M ₀ O ₃ (catalyst basis)	mass %	20	20	20	22	22
NiO (catalyst basis)	mass %	0	0	0	3	0
C ₀ O (catalyst basis)	mass %	5	5	5	0	3
P ₂ O ₅ (catalyst basis)	mass %	3	3	0	3	3
P ₂ O ₅	mass %	15.0	15.0	0	13.6	13.6
(basis of 100 mass % of VIA metal)						
Organic Acid / Inorganic acid (excluding phosphoric acid)		nitric acid	malic acid	malic acid	none	none
Properties						
PV ₀	ml / g	0.43	0.43	0.44	0.43	0.47
SA	m ² / g	201	204	209	204	219
PD	Å	75	75	75	75	95
PD _p /PV ₀	%	91	91	91	91	82

Desulfurization Performance						
Reaction Temperature	°C	343	343	344	344	347

[0108] Table 1 sets forth the results of influences of the varied amounts of titania in the support. An increase in the titania amount in the support enhances the desulfurization performance. However, when the amount was in excess of 40 percent, the performance was deteriorated due to the poor sharpness of the pore distribution. Table 2 sets forth the results of influences of the varied amounts of silica in the support. When the silica amount in the support was in excess of 10 percent, the performance was deteriorated due to the poor sharpness of the pore distribution. Table 3 sets forth the results of influences of variations in metal components to be supported. Both nickel-molybdenum and cobalt-molybdenum exhibited an excellent desulfurization performance. The results showed that the catalysts comprising metal components together with phosphoric acid and/or an organic acid had an excellent desulfurization performance. For the support production, both the method wherein an acid solution was added to a basic solution and the method wherein a basic solution was added to an acid solution provide successfully catalysts having an excellent desulfurization performance.

[0109] From the above results, the catalysts of the present invention were found to be low in a temperature at which the sulfur content of the produced oil was 7 ppm by mass and to be excellent in desulfurization activity. The support used in the present invention comprises inexpensive alumina as the main component and thus does not increase significantly the production cost, compared with conventional alumina- or alumina-silica-based catalysts. The catalyst of the present invention is inexpensive and excellent in performances.

[Example 11]

[0110] A reaction tube (inner diameter of 20 mm) filled with catalyst a (100 ml) was installed in a fixed bed flow type hydrodesulfurization unit. Thereafter, Catalyst a was pre-sulfurized for 48 hours using a straight-run gas oil containing dimethyl disulfide, so that the sulfur content was 1.5 percent by mass, under conditions where the catalyst layer average temperature was 350°C, the hydrogen partial pressure was 5.0 MPa, the liquid hourly space velocity was 1.0 h⁻¹, and the hydrogen/oil ratio was 200 NL/L.

[0111] After pre-sulfurization, a straight run gas oil from the Middle East (properties thereof set forth in Table 4 below) was run through the catalyst under a hydrogen atmosphere for hydrotreatment under conditions where the reaction temperature was 350°C, the hydrogen partial pressure was 5.0 MPa, the liquid hourly space velocity was 1.0 h⁻¹, and the hydrogen/oil ratio was 200 NL/L. The hydrotreatment conditions and properties of the produced oil are set forth in Table 5.

[Example 12]

[0112] As with Example 11 except that the reaction temperature was 335°C, a straight-run gas oil from the Middle East (properties thereof set forth in Table 4 below) was hydrotreated. The hydrotreatment conditions and properties of the produced oil are set forth in Table 5.

[Example 13]

[0113] As with Example 11 except that the hydrogen partial pressure was 4.0 MPa, a straight-run gas oil from the Middle East (properties thereof set forth in Table 4 below) was hydrotreated. The hydrotreatment conditions and properties of the produced oil are set forth in Table 5.

[Example 14 - not according to the invention]

[0114] As with Example 11 except for using Catalyst c in place of Catalyst a, a straight-run gas oil from the Middle East (properties thereof set forth in Table 4 below) was hydrotreated. The hydrotreatment conditions and properties of the produced oil are set forth in Table 5.

[Example 15]

[0115] As with Example 11 except for using a light cycle oil (properties thereof set forth in Table 4 below) in place of the Middle East straight-run gas oil, the gas oil was hydrotreated. The hydrotreatment conditions and properties of the produced oil are set forth in Table 5.

[Comparative Example 5]

[0116] A reaction tube (inner diameter of 20 mm) filled with catalyst e (100 ml) was installed in a fixed bed flow type hydrodesulfurization unit. Thereafter, Catalyst e was pre-sulfurized for 48 hours using a straight-run gas oil containing dimethyl disulfide, so that the sulfur content was 1.5 percent by mass, under conditions where the catalyst layer average temperature was 350°C, the hydrogen partial pressure was 5.0 MPa, the liquid hourly space velocity was 1.0 h⁻¹, and the hydrogen/oil ratio was 200 NL/L.

[0117] After pre-sulfurization, a straight-run gas oil from the Middle East (properties thereof set forth in Table 4 below) was run through the catalyst under a hydrogen atmosphere for

hydrotreatment under conditions where the reaction temperature was 350°C, the hydrogen partial pressure was 5.0 MPa, the liquid hourly space velocity was 1.0 h⁻¹, and the hydrogen/oil ratio was 200 NL/L. The hydrotreatment conditions and properties of the produced oil are set forth in Table 5.

[Table 4]

Properties of Hydrocarbon Oil		Analysis Method	Hydrocarbon Oil	
			Middle East Straight Run Gas Oil	Light Cycle Oil
Ratio of fraction of 260 to 360°C boiling point	vol %	JIS K2254	80	85
10%distillation temperature	°C		270.0	264.0
90 %distillation temperature	°C		345.0	347.0
Density @15°C	g/m ³	JIS K2249	0.8493	0.8854
Sulfur Content	mass %	JIS K2541	1.32	0.3
Nitrogen Content	mass ppm	JIS K2609	105	110

[Table 5]

		Example 11	Example 12	Example 13	Example 14	Example 15	Comparative Example 5
Hydrocarbon Oil		Middle East Straight-Run Gas Oil	Middle East Straight-Run Gas Oil	Middle East Straight-Run Gas Oil	Middle East Straight-Run Gas Oil	Light Cycle Oil	Middle East Straight-Run Gas Oil
Catalyst		Catalyst a	Catalyst a	Catalyst a	Catalyst c	Catalyst a	Catalyst e
Reaction Temperature	°C	350	335	350	350	350	350
Hydrogen Partial Pressure	Mpa	5.0	5.0	4.0	5.0	5.0	5.0
Liquid Hourly Space Velocity	h ⁻¹	1.0	1.0	1.0	1.0	1.0	1.0
Hydrogen/Oil Ratio	NL/ L	200	200	200	200	200	200
Sulfur Content	mass ppm	4	10	8	6	10	85
Nitrogen Content	mass ppm	1	2	3	1	2	10

[0118] Examples 11 to 15 satisfying the requirements of the method for hydrorefining a hydrocarbon oil of the present invention are confirmed to be able to decrease sulfur and nitrogen contents at a higher level and be excellent in desulfurization activity.

Industrial Applicability

[0119] The hydrodesulfurization catalyst of the present invention has higher desulfurization activity in particular for hydrotreatment of gas oil fractions and thus are extremely used for industrial purposes.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP2005336053A [0008]
- JP2005262173A [0008]
- JP10118495A [0008]
- US2006249429A [0008]
- JP2005254141B [0008]

Patentkrav

1. Hydroafsvovlingskatalysator for en carbonhydridolie, der omfatter mindst en type metalkomponent, som er valgt fra gruppe VIA og VIII i det periodiske system, båret på en bærer af siliciumdioxid-titandioxid-aluminiumoxid, hvor det samlede areal af de diffraktionspeaks, der angiver krystalstrukturen af planerne af titanoxid i anataseform (101), og diffraktionspeaks, der angiver krystalstrukturen af planerne af titandioxid i rutilform (110), er 1/4 eller mindre af arealet af de diffraktionspeaks, der angiver det aluminiumkrystalstruktur, som tilskrives planer af γ -aluminiumoxid (400), målt ved X-røntgendiffraktionsanalyse, idet katalysatoren har (a) et specifikt overfladeareal (SA) på 150 m²/g eller mere, målt ved en BET-metode, (b) et samlet porevolumen (PVo) på 0,30 ml/g eller større, målt ved hjælp af kviksølvindtrængningsteknik med kviksølvkontaktvinkel på 135 grader og overfladespænding på 480 dyn/cm, (c) en gennemsnitlig porediameter (PD) på 6 til 15 nm (60 til 150 Å), hvor PD er en porediameter, der svarer til 50 procent af PVo, og (d) forholdet mellem porevolumen (PVp) af porer med diameter inden for ± 30 procent af den gennemsnitlige porediameter (PD) er 70 procent eller større af det samlede porevolumen (PVo),

25 hvor bæreren af silica-titandioxid-aluminiumoxid indeholder siliciumoxid i form af SiO₂ i en mængde på 2 til 5 vægtprocent, titanoxid i form af TiO₂ i en mængde på 15 til 25 vægtprocent og aluminiumoxid i form af Al₂O₃ i en mængde på 70 til 83 procent efter vægt, alt på basis af bæreren.

30

2. Hydroafsvovlingskatalysator for en carbonhydridolie ifølge krav 1, hvori den metalkomponent, der er valgt fra gruppe VIA og VIII i det periodiske system, er valgt fra gruppen bestående af molybdæn, wolfram, cobalt og nikkel.

35

3. Hydroafsvovlingskatalysator for en carbonhydridolie ifølge krav 1 eller krav 2, hvor den metalkomponent, der er valgt fra gruppe VIA og VIII i det periodiske system, bæres i

en mængde på 1 til 35 vægtprocent i form af oxid på katalysatorbasis.

4. Fremgangsmåde til fremstilling af katalysatoren ifølge et hvilket som helst af kravene 1 til 3, hvilken fremgangsmåde omfatter:

et første trin med blanding af en basisk vandig opløsning af et aluminiumsalt med en blandet vandig opløsning af et titansalt af en mineralsyre og et surt aluminiumsalt i nærvær af silicationer, således at pH-værdien ligger fra 6,5 til 9,5, for at danne et hydrat et andet trin med, i rækkefølge, vask, ekstrudering, tørring og kalcinering af hydrattet for at danne en bærer og et tredje trin med tilføring af mindst en type metalkomponent, der er valgt fra gruppe VIA og VIII i det periodiske system, på bæreren.

5. Fremgangsmåde til hydrorafinering af en carbonhydridolie, hvilken fremgangsmåde omfatter hydrogenbehandling af carbonhydridolien under en hydrogenatmosfære ved anvendelse af hydroafsvovlingskatalysatoren ifølge et hvilket som helst af kravene 1 til 3.

6. Fremgangsmåde til hydrorafinering af en carbonhydridolie ifølge krav 5, hvorved hydrogenbehandlingen udføres ved en reaktionstemperatur på 300 til 420 °C, et hydrogenpartialtryk på 3,0 til 15,0 MPa, en flydende rumhastighed på 0,5 til 4,0 h⁻¹ og et hydrogen/olie-forhold på 120 til 420 NL/L.

7. Fremgangsmåde til hydrorafinering af en carbonhydridolie ifølge krav 5 eller 6, hvorved carbonhydridolien er valgt fra gruppen bestående af gasolie fra direkte destillation, vakuumgasolie, let olie fra katalytisk krakning, hydrokrakket gasolie og termisk krakket gasolie.

8. Fremgangsmåde til hydrorafinering af en carbonhydridolie ifølge et hvilket som helst af kravene 5 til 7, hvorved carbonhydridolien indeholder 70 volumenprocent eller mere af

en fraktion med et kogepunkt på 260 til 360 °C.

9. Anvendelse af en hydroafsvovlingskatalysator ifølge et hvilket som helst af kravene 1-3 til hydrorafinering af en carbonhydridolie, der indeholder 70 volumenprocent eller mere af en fraktion med et kogepunkt på 260 til 360 °C, med henblik på at inkorporere svovl i en mængde på 10 ppm efter vægt eller mindre og nitrogen i en mængde på 3 ppm efter vægt eller mindre i den resulterende olie.

DRAWINGS

[Fig.1]

