

HYDRODESULFURIZATION CATALYST FOR HYDROCARBON OIL

Technical Field

[0001] The present invention relates to a hydrodesulfurization catalyst for hydrocarbon oils.

Background Art

[0002] Conventionally, a catalyst comprising metal components selected from VIA and VIII groups of the periodic table, supported on a support comprising porous inorganic oxides such as alumina, alumina-silica, titania, and alumina-titania has been used widely for the purpose of hydrotreating of hydrocarbon oils.

Currently, regulations on the sulfur contents of fuel oils have been tightened from the viewpoint of environmental protection. In particular, the sulfur content of gas oil has been more severely regulated to be 10 ppm by mass or less. Under these circumstances, development of gas oil ultra-deep desulfurization catalysts has been proceeded so as to cope with these regulations.

Patent Literature 1 discloses catalyst comprising metal components selected from VIA and VIII groups of the periodic table, supported on a silica-titania-alumina support. This catalyst has

accomplished a high hydrodesulfurization activity by adjusting the content and crystalline structure of titania and the specific surface area and pore volume of the support. However, a further enhancement in the hydrodesulfurization activity has been demanded.

Citation List

Patent Literature

[0003] Patent Literature 1: Japanese Patent Application Laid-Open Publication No. 2011-072928

Summary of Invention

Technical Problem

[0004] The present invention has an object to provide a hydrodesulfurization catalyst with higher performances than those of conventional catalysts, particularly for gas oil fractions and a process for producing the catalyst.

Solution to Problem

[0005] As the results of extensive study and research, it has been found that the use of a support having specific properties for a catalyst significantly improves the hydrodesulfurization activity thereof and thus enables the above object to be achieved.

[0006] That is, the present invention relates to a hydrodesulfurization catalyst comprising at least one

type of metal component selected from VIA and VIII groups of the periodic table, supported on a support having a diffraction peak area indicating a crystal structure of boehmite (020) planes measured by an X-ray diffraction analysis that is 1/10 or greater of a diffraction peak area indicating the aluminum crystalline structure assigned to γ -alumina (440) planes, the molar ratio of the metal component selected from VIII group to the metal component selected from VIA group being from 0.13 to 0.22.

[0007] The present invention also relates to a method for producing a hydrodesulfurization catalyst comprising: a first step of mixing a mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt and a basic aluminum salt aqueous solution in the presence of silicate ions so that the pH is from 6.5 to 9.5 to produce a hydrate; a second step of washing, extruding, drying and calcining the hydrate in turn to produce a support; and a third step of loading at least one type of metal component selected from VIA and VIII groups of the periodic table on the support.

Advantageous Effect of Invention

[0008] The hydrodesulfurization catalyst of the present invention has more excellent performance than

conventional catalysts and are particularly suitable for hydrodesulfurization of gas oil fractions.

Brief Description of Drawings

[0009] Fig. 1 is a graph indicating X-ray diffraction spectra of support a and support e produced in Example 1 and Comparative Example 1, respectively.

Fig. 2 is a graph indicating transmission type Fourier transform infrared absorption spectra of support a and support e produced in Example 1 and Comparative Example 1, respectively.

Fig. 3 is a graph indicating the maximal peak positions of the absorption spectra caused by the acidic OH group and weakly basic OH group of a support.

Description of Embodiments

[0010] The present invention will be described in detail below.

The hydrodesulfurization catalyst of the present invention is characterized in that the support comprises at least both boehmite and γ -alumina and has a diffraction peak area indicating the crystal structure of boehmite (020) planes measured by an X-ray diffraction analysis that is 1/10 or greater of the diffraction peak area indicating the aluminum crystalline structure assigned to γ -alumina (440) planes.

[0011] The support contains boehmite and γ -alumina each in the form of Al_2O_3 in the total amount of preferably 50 to 96 percent by mass, more preferably 58 to 83 percent by mass, more preferably 70 to 83 percent by mass. 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.

[0012] The support may contain any compound other than boehmite and γ -alumina, such as silica, titania, boria, diphosphorus pentaoxide, and zirconia and contains particularly preferably silica and titania.

[0013] The support contains silica in the form of SiO_2 in an amount of preferably 1 to 10 percent by mass, more preferably 2 to 7 percent by mass, more preferably 2 to 5 percent by mass on the support basis. A silica content of less than 1 percent by mass decreases the specific surface areas of the resulting support 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 measured by an X-ray diffraction analysis. When

titania particles aggregate, the resulting support is small in the specific surface area and thus the content of a metal component of Group VIA of the periodic table and a metal component of Group VIII of the periodic table is less and cause the activity to be reduced. 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 hydrodesulfurization activity.

[0014] The support contains titania in the form of TiO_2 in an amount of preferably 3 to 40 percent by mass, more preferably 15 to 35 percent by mass, more preferably 15 to 25 percent by mass on the support basis. 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 hydrodesulfurization 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 decreased 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 hydrodesulfurization performance corresponding to the economic efficiency

according to the increased amount of titania.

[0015] The hydrodesulfurization catalyst of the present invention comprises at least one or more types of metal components selected from Group VIA (IUPAC Group 6) and Group VIII (IUPAC Groups 8 to 10) of the periodic table supported on the support.

[0016] Examples of metal components of Group VIA of the periodic table to be used in the present invention include molybdenum (Mo) and tungsten (W) while examples of metal components of Group VIII of the periodic table include cobalt (Co) and nickel (Ni). These metal components may be used alone or in combination. In view of catalyst properties, the metal components are preferably a combination of nickel-molybdenum, cobalt-molybdenum, nickel-molybdenum-cobalt, nickel-tungsten, cobalt-tungsten, or nickel-tungsten-cobalt, in particular more preferably a combination of nickel-molybdenum, cobalt-molybdenum, or nickel-molybdenum-cobalt.

[0017] The total content of the metal component(s) is preferably from 1 to 35 percent by mass, more preferably from 15 to 30 percent by mass in the form of oxide on the catalyst basis. In particular, the content of the metal component of Group VIA of the periodic table is preferably from 10 to 30 percent by

mass, more preferably from 13 to 24 percent by mass in the form of oxide while the content of the metal component of Group VIII of the periodic table is preferably from 2.6 to 4.4 percent by mass, more preferably from 2.8 to 4.2 percent by mass in the form of oxide.

[0018] The molar ratio of the metal component selected from VIII group of the periodic table to the metal component selected from VIA group of the periodic table is necessarily 0.13 to 0.22, preferably 0.14 to 0.21, more preferably 0.16 to 0.18. A structure wherein a metal of VIII group of the periodic table coordinates to the edge sights of a sulfide of metal of VIA group of the periodic table (for Co and Mo, CoMoS phase) is referred to as "high active species". If the molar ratio of the metal component selected from VIII group of the periodic table to the metal component selected from VIA group of the periodic table is less than 0.13, the CoMoS phase is not sufficiently formed. Whilst, if the molar ratio of the metal component selected from VIII group of the periodic table to the metal component selected from VIA group of the periodic table exceeds 0.22, the CoMoS phase is covered with inactive cobalt sulfide.

[0019] When the metal component of Group VIA of the

periodic table is loaded on/contained in the support of the hydrodesulfurization catalyst of the present invention, the metal components are preferably dissolved with an acid. The acid is preferably phosphoric acid and/or an organic acid.

[0020] In the case of using phosphoric acid, it is supported in an amount of preferably 3 to 25 percent by mass, more preferably 10 to 15 percent by mass of phosphorus on an oxide basis with respect to 100 percent by mass of the metal components of Group VIA of the periodic table. If the amount exceeds 25 percent by mass, the catalyst performance tends to be degraded whilst if the amount is less than 3 percent by mass, a solution of the metal to be supported is poor in stability.

[0021] No particular limitation is imposed on the method for loading and including the above-described metal components or the above-described metal components and further phosphorous into the support. Any conventional method such as impregnation (equilibrium adsorption, pore filling, incipient wetness impregnation methods) or ion-exchange may be used. Impregnation referred herein is a method wherein the support is impregnated with an impregnating solution containing active metals and then dried and

calcined.

[0022] In the impregnation method, a metal component of Group VIA of the periodic table and a metal component of Group VIII of the periodic table are preferably loaded at the same time. When metal components are loaded separately, the resulting catalyst would be insufficient in desulfurization activity or denitrogenation activity. In the case where the metal components are loaded by an impregnation method, they are loaded in the coexistence of an acid, preferably phosphoric acid or an organic acid because the metal component of Group VIA of the periodic table is highly dispersed on the support and thus the resulting catalyst is further enhanced in desulfurization activity and denitrogenation activity. Whereupon, phosphoric acid is preferably added in an amount of 3 to 25 percent by mass based on 100 percent by mass of the metal component of Group VIA of the periodic table.

[0023] The hydrodesulfurization catalyst of the present invention has a specific surface area (SA) measured by BET method of preferably $150 \text{ m}^2/\text{g}$ or larger, more preferably $170 \text{ m}^2/\text{g}$ or larger. If the specific surface area (SA) is smaller than $150 \text{ m}^2/\text{g}$, the catalyst has fewer active sites for hydrodesulfurization

reaction and thus is degraded in hydrodesulfurization activity. Whilst, no particular limitation is imposed on the upper limit. However, when the specific surface area (SA) exceeds $300 \text{ m}^2/\text{g}$, the catalyst strength tends to be reduced and thus the upper limit is preferably $300 \text{ m}^2/\text{g}$ or smaller, more preferably $280 \text{ m}^2/\text{g}$ or smaller.

[0024] The support of the hydrodesulfurization catalyst of the present invention has a diffraction peak area indicating the crystal structure of boehmite (020) planes measured by an X-ray diffraction analysis that is necessarily $1/10$ or greater, preferably $1/5$ or greater, more preferably $1/4$ or greater of the diffraction peak area indicating the aluminum crystalline structure assigned to γ -alumina (440) planes. No particular limitation is imposed on the upper limit, which is, however, preferably 1 or less, more preferably $4/5$ or less. If the diffraction peak area indicating the crystal structure of boehmite (020) planes measured by an X-ray diffraction analysis is less than $1/10$ of the diffraction peak area indicating the aluminum crystalline structure assigned to γ -alumina (440) planes, the metal component of Group VIA of the periodic table and the metal component of Group VIII of the periodic table are less dispersed and as the result sufficient activity cannot be obtained.

Whilst, the upper limit exceeds 1, the ratio of boehmite is too large and thus the resulting catalyst is reduced in strength.

The diffraction peak indicating the crystal structure of boehmite (020) planes is measured at $2\theta=14^\circ$ while the diffraction peak indicating the aluminum crystal structure assigned to γ -alumina (440) planes is measured at $2\theta=67^\circ$.

[0025] 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 ($1/2W$) thereby defining the product of the full width at half maximum and peak intensity as a diffraction peak area.

"Boehmite diffraction peak area/alumina diffraction peak area" is derived from each of the diffraction peak areas thus obtained.

[0026] In the support of the hydrodesulfurization catalyst of the present invention, the ratio of the absorbance per unit surface area of the support caused by the acidic OH group to the absorbance per unit surface

area of the support caused by the weakly basic OH group, both measured with a transmission type Fourier transform infrared absorption spectrum apparatus (FT-IR) is preferably 0.9 or greater, more preferably 1.0 or greater, more preferably 1.1 or greater. It is preferred that the ratio of the acidic OH group increase because the metal component of Group VIA of the periodic table and the metal component of Group VIII of the periodic table are highly dispersed on the support, and as the result the number of active sites increases and the activity is enhanced.

The wavenumber of maximal peak position of the absorption spectrum caused by the acidic OH group is within the range of 3670 to 3695 cm^{-1} while the wavenumber of maximal peak position of the absorption spectrum caused by the weakly basic OH group is within the range of 3720 to 3740 cm^{-1} (see Figure 3).

The above-mentioned measurement with FT-IR will be described later.

[0027] The hydrodesulfurization catalyst of the present invention is suitably used for hydrotreating hydrocarbon oils, in particular gas oil fractions. Hydrodesulfurization using the catalyst is carried out under a hydrogen atmosphere at a high temperature and a high pressure after charging the catalyst into a fixed

bed reactor.

Examples of the gas oil fraction used in the present invention include straight-run gas oil produced through an atmospheric distillation unit for crude oil; vacuum gas oil produced through a vacuum distillation unit by distilling straight heavy oil or residue obtained from an atmospheric distillation unit; light cycle gas oil produced by fluid catalytic-cracking vacuum heavy gas oil or desulfurized heavy oil; and hydrocracked gas oil produced by hydrocracking vacuum heavy gas oil or desulfurized heavy oil.

[0028] The reaction pressure (hydrogen partial pressure) is preferably from 3 to 15 MPa, more preferably from 4 to 10 MPa. At a reaction pressure of lower than 3 MPa, desulfurization and denitrogenation activities tend to significantly degrade. A reaction pressure of higher than 15 MPa is not preferable because hydrogen consumption increases, resulting in a higher running cost.

[0029] The reaction temperature is preferably from 300 to 420°C, more preferably 320 to 380°C. A reaction temperature of lower than 300°C is not practical because desulfurization and denitrogenation activities tend to significantly degrade. A reaction

temperature of higher than 420°C is not preferable because the catalyst is drastically degraded and the temperature is close to the service temperature limit (usually 425°C) of the reactor.

[0030] No particular limitation is imposed on the liquid-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-space velocity of less than 0.5 h⁻¹ is not practical because the productivity is reduced due to the reduced amount of the throughput. A liquid-space velocity of greater than 4.0 h⁻¹ is not preferable because the reaction temperature is increased, and as the result the decomposition of the catalyst accelerates.

[0031] The hydrogen/oil ratio 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 hydrodesulfurization rate decreases. A hydrogen/oil ratio of greater than 420 NL/L is not also preferable because it cannot change the hydrodesulfurization activity to a large extent and only increases the running cost.

[0032] Next, the process for producing the hydrodesulfurization catalyst of the present invention will be described.

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

[0033] (First Step)

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 from 6.5 to 9.5, preferably from 6.5 to 8.5, more preferably from 6.5 to 7.5 to produce a hydrate containing silica, titania and alumina.

[0034] In this step, there are two alternative cases (1) where the mixed aqueous solution is added to the

basic aluminum salt aqueous solution containing silicate ion and (2) where the basic aluminum salt aqueous solution is added to the mixed solution containing silicate ion.

In case (1), silicate ion contained in the basic aluminum aqueous solution may be basic or neutral. The basic silicate ion source may be a silicic acid compound such as sodium silicate, which can generate silicate ions in water. In case (2), silicate ion contained in the mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt aqueous solution may be acidic or neutral. The acidic silicate source may be a silicic acid compound such as silicic acid, which can generate silicate ions in water.

[0035] 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.

[0036] 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 at 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 $\pm 2^{\circ}\text{C}$, more preferably $\pm 1^{\circ}\text{C}$ of the heated basic aluminum salt aqueous solution for usually 5 to 20 minutes, preferably 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.

[0037] (Second Step)

The hydrate slurry produced in the first step is aged if necessary and then washed to remove 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 preferably 400 to 500°C, more preferably 400 to 480°C, more preferably 430 to 470°C, most preferably 440 to 460°C for 0.5 to 10 hours, preferably 2 to 5 hours thereby producing a silica-titania-alumina support.

During the second step, adjustment of conditions for calcination, in particular calcining temperature enables the preparation of a support having a diffraction peak area indicating the crystal structure of boehmite (020) planes measured by an X-ray diffraction analysis that is 1/10 or greater of the diffraction peak area indicating the aluminum crystalline structure assigned to γ -alumina (440) planes.

[0038] (Third Step)

On the resulting silica-titania-alumina support is loaded by a conventional manner (impregnation, immersion) at least one type of metal component selected from VIA and VIII groups of the periodic table as described above, followed by

calcination at preferably 400 to 500°C, more preferably 400 to 480°C, more preferably 430 to 470°C for usually 0.5 to 10 hours, preferably 2 to 5 hours to produce the hydrodesulfurization catalyst of the present invention.

Raw materials of the metal component are preferably for example, nickel nitrate, nickel carbonate, cobalt nitrate, cobalt carbonate, molybdenum trioxide, ammonium molybdate, and ammonium paratungstate.

[0039] <Absorbance of the acidic OH group and absorbance of the weakly basic OH group>

A transmission type Fourier transform infrared spectrophotometer (FT-IR/6100 manufactured by JASCO Corporation) was used to measure the maximal peak wavenumber of the acidic OH group and the absorbance at the wavenumber and the maximal peak wavenumber of the weakly basic OH group and the absorbance at the wavenumber as described below.

[0040] (Measurement)

Into a molding container (inner diameter 20 mm) were charged 20 mg of a sample, which were then compressed by applying pressure of 4 ton/cm² (39227 N/cm²) to be molded into a thin disk-shape. This molded product was kept under a condition of a pressure of

1.0x10⁻³Pa or lower at a temperature of 400 to 500°C for 2 hours and then cooled to room temperature to measure the absorbance of the product.

Specifically, a baseline correction was carried out at a resolution of 4 cm⁻¹ and a cumulated number of 200 within the wavenumber range of 3000 to 4000 cm⁻¹ with a TGS detector, followed by correction with the specific surface area. The absorbance was converted to that per unit surface area.

Absorbance per unit surface area (m⁻²)
=(absorbance)/(molded body mass x specific surface area)

[0041] In all of the following examples and comparative examples, the wavenumber of the maximal peak position of the absorption spectrum caused by the acidic OH group was within the range of 3670 to 3695 cm⁻¹ while the wavenumber of the maximal peak position of the absorption spectrum caused by the weakly basic OH group was within the range of 3720 to 3740 cm⁻¹.

Examples

[0042] The present invention will be described in more details with reference to the following examples and comparative examples but is not limited thereto.

[0043] [Example 1: Preparation of hydrodesulfurization catalyst a]

Into a 100 L volume tank equipped with a steam jacket were put 8.16 kg of an aqueous solution containing sodium aluminate (manufactured by JGC C&C) 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 (manufactured by AGC Si-Tech. Co., Ltd.; SiO_2 concentration 24 percent by mass) 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 (manufactured by JGC C&C) in an amount of 7 percent by mass on an Al_2O_3 concentration basis with 13 kg of ion-exchanged 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 (manufactured by Tayca Corporation) in 10 kg of ion-exchanged 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.

[0044] The resulting hydrate slurry a was aged, stirring at a temperature of 60°C for one hour, and then dewatered with a flatsheet 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-exchanged 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 aqueous solution. 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 product was calcined at a temperature of 450°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 an SiO_2 concentration

basis (on the support basis), titania in an amount of 20 percent by mass on a TiO_2 concentration basis (on the support basis), and aluminum in an amount of 77 percent by mass on an Al_2O_3 concentration basis (on the support basis).

[0045] Support a was subjected to an X-ray diffraction analysis with an X-ray diffraction apparatus "RINT 2100" manufactured by Rigaku Corporation (the same applies hereafter). 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 assigned to the boehmite (020) planes indicated at $2\theta=14^\circ$. The product of the full width at half maximum and the peak intensity from the baseline to the maximum peak was defined as a boehmite diffraction peak area. The same procedures were carried out to find the full width at half maximum of the peak assigned to the γ -alumina (440) planes indicated at $2\theta=67^\circ$, and the product of the full width at half maximum and the peak intensity from the baseline was defined as a γ -alumina diffraction peak area. The diffraction peak area indicating the crystalline structure of boehmite was 1/3 of the diffraction peak area indicating the crystalline structure assigned to

γ -alumina (boehmite diffraction peak area/ γ -alumina diffraction peak area = 1/3, and the same applies hereafter).

Figure 2 shows the transmission type Fourier transform infrared absorption spectrum of support a.

[0046] Next, 268 g of molybdenum trioxide (manufactured by Climax; MoO_3 concentration 99 percent by mass) and 66 g of cobalt carbonate (manufactured by Tanaka Chemical Corporation; CoO concentration 61 percent by mass) 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 54 g of phosphoric acid (manufactured by KANTO CHEMICAL CO., INC.; P_2O_5 concentration 62 percent by mass) in the suspension thereby preparing an impregnating solution. After 1000 g of support a was impregnated with an impregnating solution by spray, it was dried at a temperature of 250°C and calcined at a temperature of 450°C for one hour in an electric furnace thereby producing hydrodesulfurization catalyst a (hereinafter, simply referred to as "catalyst a", the same applies hereafter). Properties of catalyst a are set forth in Table 1.

[0047] [Example 2: Preparation of

hydrodesulfurization catalyst b]

Support a was used and the same preparation procedures for catalyst a were followed except for using 270 g of molybdenum trioxide, 78 g of cobalt carbonate and 55 g of phosphoric acid in the preparation of the impregnation solution thereby producing catalyst b. Properties of catalyst b are set forth in Table 1.

[0048] [Example 3: Preparation of hydrodesulfurization catalyst c]

Support a was used and the same preparation procedures for catalyst a were followed except for using 272 g of molybdenum trioxide, 90 g of cobalt carbonate and 55 g of phosphoric acid in the preparation of the impregnation solution thereby producing catalyst c. Properties of catalyst c are set forth in Table 1.

[0049] [Example 4: Preparation of hydrodesulfurization catalyst d]

The same preparation procedures for catalyst a were followed except for calcining the dried extruded product at a temperature of 480°C in an electric furnace in the preparation of the support thereby producing support d. As the result of an X-ray diffraction analysis carried out as with Example 1 (not shown), the

boehmite diffraction peak area/ γ -alumina diffraction peak area was 1/9. The impregnation solution was prepared in the same manner as that for catalyst a thereby producing catalyst d. Properties of catalyst d are set forth in Table 1.

[0050] [Comparative Example 1: Preparation of hydrodesulfurization catalyst e]

The same preparation procedures for support a were followed except for calcining the dried and extruded product at a temperature of 550°C in an electric furnace thereby producing support e. As the result of X-ray diffraction analysis carried out as with Example 1, there was no boehmite diffraction peak as shown Figure 1 and the boehmite diffraction peak area/ γ -alumina diffraction peak area was 0. The impregnation solution was prepared in the same manner as that for catalyst a thereby producing catalyst e. Properties of catalyst e are set forth in Table 1.

[0051] [Comparative Example 2: Preparation of hydrodesulfurization catalyst f]

Support e was used and the impregnation solution used for catalyst b was used thereby producing catalyst f. Properties of catalyst f are set forth in Table 1.

[0052] [Comparative Example 3: Preparation of

hydrodesulfurization catalyst g]

Support e was used and the impregnation solution used for catalyst c was used thereby producing catalyst g. Properties of catalyst g are set forth in Table 1.

[0053] [Comparative Example 4: Preparation of hydrodesulfurization catalyst h]

Support a was used and the same preparation procedures for catalyst a were followed except for using 267 g of molybdenum trioxide and 55 g of cobalt carbonate in the preparation of the impregnation solution thereby producing catalyst h. Properties of catalyst h are set forth in Table 1.

[0054] [Comparative Example 5: Preparation of hydrodesulfurization catalyst i]

Support a was used and the same preparation procedures for catalyst a were followed except for using 274 g of molybdenum trioxide, 101 g of cobalt carbonate and 56 g of phosphoric acid in the preparation of the impregnation solution thereby producing catalyst i. Properties of catalyst i are set forth in Table 1.

[0055] [Hydrodesulfurization test]

Feedstock having the following properties was hydrotreated with a hydrodesulfurization unit

manufactured by ZYTEL Co. using catalysts a to i. Hydrotreating reaction was carried out under the following conditions. For each catalyst, the reaction rate constants at reaction temperatures of 330°C and 340°C were determined and an average of the reaction rate constants relative to the reaction rate constants of catalyst c at temperatures of 330°C and 340°C taken as 100 is defined as a relative hydrodesulfurization activity and set forth in Table 1.

《Properties of feedstock》

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

Density@15°C: 0.8493 g/cm³

Sulfur content: 1.32 percent by mass

Nitrogen content: 105 ppm by mass

《Reaction condition》

Reaction temperatures: 330°C, 340°C

Liquid-space velocity: 1.36 hr⁻¹

Hydrogen pressure: 6.0 MPa

Hydrogen/oil ratio: 250 NL/L

[0056] Table 1

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Catalyst		a	b	c	d	e	f	g	h	i
Support components										
Si (as SiO ₂)	mass%	3	3	3	3	3	3	3	3	3
Ti (as TiO ₂)	mass%	20	20	20	20	20	20	20	20	20
Al (as Al ₂ O ₃)	mass%	77	77	77	77	77	77	77	77	77
B/A ^{*)}		1/3	1/3	1/3	1/9	0	0	0	1/3	1/3
Supported components										
MoO ₃ (catalyst basis)	mass%	20	20	20	20	20	20	20	20	20
CoO (catalyst basis)	mass%	3	3.5	4	3	3	3.5	4	2.5	4.5
P ₂ O ₅ (catalyst basis)	mass%	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Co/Mo ratio		0.15	0.175	0.2	0.15	0.15	0.175	0.2	0.125	0.225
LGO desulfurization properties										
Relative activity		107	116	100	103	93	92	81	93	92
Specific surface area		238	234	235	224	201	202	198	250	237
PV(H ₂ O)		0.43	0.43	0.41	0.43	0.44	0.43	0.42	0.44	0.40
Acidic OH group/weakly basic OH group ^{**))}		1.2	1.2	1.2	1.1	0.8	0.8	0.8	1.2	1.2

*) A: peak area of γ -alumina (440) planes ($2\theta=67^\circ$)

B: peak area of boehmite (020) planes ($2\theta=14^\circ$)

**) absorbance of maximal peak caused by acidic OH group/absorbance of maximal peak caused by weakly basic OH group

[0057] It is appreciated from the results set forth in Table 1 that when the cobalt/molybdenum ratio is within the range of 0.13 to 0.22, the catalysts are improved in hydrodesulfurization activity because the supports contain boehmite. As Boehmite is contained on the support, a relatively large number of acidic OH groups remain, and as the result, molybdenum is highly dispersedly supported. Since the active site of a hydrodesulfurization catalyst is a CoMoS structure where cobalt coordinating to edge sites of molybdenum sulfide, cobalt is highly dispersed as molybdenum is highly dispersed, and the number of CoMoS structure increases, resulting in an enhancement in the hydrodesulfurization activity. However, even though boehmite is contained, sites with less cobalt are not sufficient in the number of CoMoS structure and thus poor in the hydrodesulfurization activity, and sites with more cobalt are low in the activity because inactive cobalt species not coordinating molybdenum sulfide cover the active sites.

CLAIMS

[Claim 1] A hydrodesulfurization catalyst for hydrocarbon oils comprising at least one type of metal component selected from VIA and VIII groups of the periodic table, supported on a support having a diffraction peak area indicating a crystal structure of boehmite (020) planes measured by an X-ray diffraction analysis that is 1/10 or greater of a diffraction peak area indicating the aluminum crystalline structure assigned to γ -alumina (440) planes, the molar ratio of the metal component selected from VIII group to the metal component selected from VIA group being from 0.13 to 0.22.

[Claim 2] The hydrodesulfurization catalyst for hydrocarbon oils according to claim 1 wherein the support comprises at least one type selected from silica and titania.

[Claim 3] The hydrodesulfurization catalyst for hydrocarbon oils according to claim 1 or 2 wherein the metal component selected from VIA and VIII groups of the periodic table is selected from molybdenum, tungsten, cobalt and nickel.

[Claim 4] The hydrodesulfurization catalyst for hydrocarbon oils according to any one of claims 1 to

3 wherein the metal component selected from the VIII group is contained in an amount of 2.6 to 4.4 percent by mass in the form of oxide.

[Claim 5] A process for producing a hydrodesulfurization catalyst comprising: a first step of mixing a mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt and a basic aluminum salt aqueous solution in the presence of silicate ions so that the pH is from 6.5 to 9.5 to produce a hydrate; a second step of washing, extruding, drying and calcining the hydrate in turn to produce a support; and a third step of loading at least one type of metal component selected from VIA and VIII groups of the periodic table on the support.

[Claim 6] The process for producing a hydrodesulfurization catalyst according to claim 5 wherein the calcining temperature in the second step is from 400 to 500°C.