CLAIMS

[Claim 1] A hydrodesulfurization catalyst for hydrocarbon oils, comprising a hydrodesulfurization catalyst Y comprising a support containing silica, alumina and titania and at least one type of metal component supported thereon and selected from VIA and VIII groups of the periodic table, the catalyst Y being pre-sulfurized,

the total area (titania diffraction peak area) 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 in the support, measured by X-ray diffraction analysis being 1/4 or less of the diffraction peak area (alumina diffraction peak area) indicating the aluminum crystal structure assigned to γ-alumina (400) planes,

the metal component comprising at least molybdenum,

the molybdenum being formed into molybdenum disulfide crystal and disposed in layers on the support by the pre-sulfurization and the molybdenum disulfide crystal layers having an average length of longer than 3.5 nm and 7 nm or shorter in the plane direction and

an average number of laminated layers of more than 1.0 and 1.9 or fewer.

[Claim 2] A hydrodesulfurization catalyst according to claim 1, wherein the support contains silica in the form of SiO_2 in an amount of 1 to 10 percent by mass, titania in the form of TiO_2 in an amount of 3 to 40 percent by mass and alumina in the form of Al_2O_3 in an amount of 50 percent by mass or more.

[Claim 3] A hydrodesulfurization catalyst according to claim 1 or 2, wherein the content of the metal component is from 1 to 35 percent by mass on the hydrodesulfurization catalyst Y prior to the pre-sulfurization basis, and the content of the molybdenum is from 1 to 25 percent by mass in the form of MoO_3 on the hydrodesulfurization catalyst Y prior to the pre-sulfurization basis.

[Claim 4] A hydrodesulfurization catalyst according to any one of claims 1 to 3, wherein said pre-sulfurization is carried out by contacting the hydrodesulfurization catalyst Y with a mix oil of a hydrocarbon oil and a sulfating agent or hydrogen sulfide at a temperature of 200 to 400°C.

[Claim 5] A process of producing a hydrodesulfurization catalyst for hydrocarbon oil, comprising:

(1) a first step of mixing a basic aluminum salt aqueous solution and a mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt in the presence of silicate ion so that the pH is from 6.5 to 9.5 to produce a hydrate;

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

(3) a third step of contacting the support with an impregnating solution containing at least one type of metal component selected from VIA and VIII groups of the periodic table (provided that molybdenum is indispensably contained) and a chelating agent;

(4) a fourth step of drying the support with the metal supported thereon, produced by contacting the support with the impregnating solution to produce a hydrodesulfurization catalyst Y; and

(5) a fifth step of pre-sulfurizing the hydrodesulfurization catalyst Y,

the total area (titania diffraction peak area) 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 in the support, measured by X-ray diffraction analysis being 1/4 or

less of the diffraction peak area (alumina diffraction peak area) indicating the aluminum crystal structure assigned to γ-alumina (400) planes,

the molybdenum being formed into molybdenum disulfide crystal and disposed in layers on the support by the pre-sulfurization, and the molybdenum disulfide crystal layers having an average length of longer than 3.5 nm and 7 nm or shorter in the plane direction and an average number of laminated layers of more than 1.0 and 1.9 or fewer,

the impregnating solution having a peak intensity in the range of 940 to 950cm^{-1} 2.5 times or more of the peak intensity in the range of 890 to 910 cm^{-1} in the Raman spectrum.

[Claim 6] A process of producing a hydrodesulfurization catalyst according to claim 5, wherein the pre-sulfurization of the fifth step is carried out by contacting the hydrodesulfurization catalyst Y with a mix oil of a hydrocarbon oil and a sulfating agent or hydrogen sulfide at a temperature of 200 to 400°C.

[Claim 7] A process of producing a hydrodesulfurization catalyst according to claim 5 or 6, wherein said impregnating solution further contains a phosphoric compound.

[Claim 8] A process of producing a hydrodesulfurization catalyst according to any one of claims 5 to 7, wherein said chelating agent is citric acid or malic acid.

[Claim 9] A method for hydrorefining a hydrocarbon oil comprising hydrotreating a hydrocarbon oil under a hydrogen atmosphere using the hydrodesulfurization catalyst according to claim 1.

[Claim 10] A method for hydrorefining hydrocarbon oils according to claim 9, wherein said hydrocarbon oil is selected from the group consisting of straight-run gas oil, vacuum gas oil, light cycle oil, hydrocracked gas oil, and thermal-cracked gas oil.

[Claim 11] A method for hydrorefining hydrocarbon oils according to claim 9 or 10 wherein the oil produced from the hydrotreating of a hydrocarbon oil has a sulfur content of 10 ppm by mass or less and a nitrogen content of 3 ppm by mass or less.

[Claim 12] A method for hydrorefining hydrocarbon oils according to any one of claims 9 to 11, wherein the reaction pressure is from 1 to 12 MPa, the liquid-space velocity is from 0.1 to 4.0 h^{-1}, the hydrogen/oil ratio is from 80 to 500 NL/L and the reaction temperature is from 250 to 400°C.

Claims

[Claim 1] A hydrodesulfurization catalyst for hydrocarbon oils, comprising a hydrodesulfurization catalyst Y comprising a support containing silica, alumina, and titania and at least one type of metal component supported thereon and selected from VIB and VIII groups of the periodic table, the catalyst Y being pre-sulfurized,

the total area (titania diffraction peak area) 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 in the support, measured by X-ray diffraction analysis being 1/4 or less of the diffraction peak area (alumina diffraction peak area) indicating the aluminum crystal assigned to γ-alumina (400) planes,

the metal component comprising at least molybdenum,

the molybdenum being formed into molybdenum disulfide crystal and disposed in layers on the support by the pre-sulfurization and the molybdenum disulfide crystal layers having an average length between 3.5 nm and 7 nm in the plane direction and an average number

of laminated layers between 1.0 and 1.9,

wherein the support contains silica in the form of SiO_2 in an amount of 1 to 10 percent by mass, titania in the form of TiO_2 in an amount of 15 to 40 percent by mass, and alumina in the form of Al_2O_3 in an amount of 50 percent by mass or more.

[Claim 2] A hydrodesulfurization catalyst according to claim 1, wherein the content of the metal component is from 1 to 35 percent by mass on the hydrodesulfurization catalyst Y prior to the pre-sulfurization basis, and the content of the molybdenum is from 1 to 25 percent by mass in the form of MoO_3 on the hydrodesulfurization catalyst Y prior to the pre-sulfurization basis.

[Claim 3] A hydrodesulfurization catalyst according to claim 1, wherein said pre-sulfurization is carried out by contacting the hydrodesulfurization catalyst Y with a mix oil of a hydrocarbon oil and a sulfating agent or hydrogen sulfide at a temperature of 200 to 400°C.

[Claim 4] A method for hydrorefining a hydrocarbon oil comprising hydrotreating a hydrocarbon oil under a hydrogen atmosphere using the hydrodesulfurization catalyst according to claim 1.

[Claim 5] A method for hydrorefining hydrocarbon oils according to claim 4, wherein said hydrocarbon oil is selected from the group consisting of straight-run gas oil, vacuum gas oil, light cycle oil, hydrocracked gas oil, and thermal-cracked gas oil.

[Claim 6] A method for hydrorefining hydrocarbon oils according to claim 4, wherein the oil produced from the hydrotreating of a hydrocarbon oil has a sulfur content of 10 ppm by mass or less and a nitrogen content of 3 ppm by mass or less.

[Claim 7] A method for hydrorefining hydrocarbon oils according to claim 4, wherein the reaction pressure is from 1 to 12 MPa, the liquid-space velocity is from 0.1 to 4.0 h^{-1}, the hydrogen/oil ratio is from 80 to 500 NL/L and the reaction temperature is from 250 to 400°C.

[Claim 8] A process of producing an uncalcined hydrodesulfurization catalyst for hydrocarbon oil, comprising:

(1) a first step of mixing a basic aluminum salt aqueous solution and a mixed aqueous solution of a titanium mineral acid salt and an acidic aluminum salt

in the presence of silicate ion so that the pH is from 6.5 to 9.5 to produce a hydrate;

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

(3) a third step of contacting the support with an impregnating solution containing at least one type of metal component selected from VIB and VIII groups of the periodic table (provided that molybdenum is indispensably contained) and a chelating agent;

(4) a fourth step of drying the support with the metal supported thereon, produced by contacting the support with the impregnating solution to produce an uncalcined hydrodesulfurization catalyst Y; and

(5) a fifth step of pre-sulfurizing the uncalcined hydrodesulfurization catalyst Y, the total area (titania diffraction area) 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 in the support, measured by X-ray diffraction analysis being 1/4 or less of the diffraction peak area (alumina diffraction peak area) indicating the aluminum crystal structure assigned to γ-alumina (400) planes, the molybdenum being formed into molybdenum disulfide crystal and disposed in layers on the support by the

pre-sulfurization, and the molybdenum disulfide crystal layers having an average length between 3.5 nm and 7 nm in the plane direction and an average number of laminated layers between 1.0 and 1.9, the impregnating solution having a peak intensity in the range of 940 to 950 cm^{-1} 2.5 times or more of the peak intensity in the range of 890 to 910 cm^{-1} in the Raman spectrum.

[Claim 9] A process of producing an uncalcined hydrodesulfurization catalyst according to claim 8, wherein the pre-sulfurization of the fifth step is carried out by contacting the uncalcined hydrodesulfurization catalyst Y with a mix oil of a hydrocarbon oil and a sulfating agent or hydrogen sulfide at a temperature of 200 to 400°C.

[Claim 10] A process of producing an uncalcined hydrodesulfurization catalyst according to claim 8, wherein said impregnating solution further contains a phosphoric compound.

[Claim 11] A process of producing an uncalcined hydrodesulfurization catalyst according to claim 8, wherein said chelating agent is citric or malic acid.

[Claim 12] The process according to claim 8, wherein the drying in step (4) is performed at a temperature of 200°C. or lower for 0.5 to 3 hours.