

DESCRIPTION

HYDROREFINING PROCESS

Technical Field

[0001] The present invention relates to a hydrorefining method, and more specifically it relates to a hydrorefining method for oil to be treated that contains fat and oil components derived from animal or vegetable oils.

Background Art

[0002] Increasing interest is being focused on effective utilization of biomass energy as a strategy for preventing global warming. In particular, plant-derived biomass energy is "carbon neutral" because it allows effective utilization of the hydrocarbons converted from carbon dioxide by photosynthesis during the process of plant growth so that, considering natural life cycles, it does not contribute to increased carbon dioxide in the atmosphere.

[0003] Utilization of this type of biomass energy has also been extensively researched in the field of transportation fuels. For example, if fuels derived from animal or vegetable oils could be used as diesel fuels, the synergistic effect obtained with the high energy efficiency of a diesel engine would be expected to contribute substantially to carbon dioxide emission reduction. Known diesel fuels utilizing animal or vegetable oils include fatty acid methyl ester oils. Fatty acid methyl ester oils are produced by transesterification of the triglyceride structure as the general structure of animal or vegetable oils, with methanol using an alkali or the like. However, as described in Patent document 1 mentioned below, the process of producing fatty acid

methyl ester oils necessitates treatment of the glycerin by-product, or creates cost and energy requirements for purification of the product oil.

[Patent document 1] Japanese Unexamined Patent Publication No. 2005-154647

5 **Disclosure of the invention**

[Problems to Solved by the Invention]

[0004] The following problems are encountered in addition to those mentioned above when using animal or vegetable-derived fat and oil components or fuels produced using them as starting materials.
10 Specifically, since animal or vegetable-derived fat and oil components generally have oxygen atoms in the molecule, the oxygen can adversely affect the engine material and it is difficult to remove the oxygen to a very low concentration. Also, when an animal or vegetable-derived fat and oil component is used in combination with a petroleum
15 hydrocarbon fraction, current technology has not allowed sufficient reduction of both oxygen in the fat and oil component and sulfur in the petroleum hydrocarbon fraction.

[0005] It is therefore an object of the present invention to provide a hydrotreating method that can yield a hydrotreated oil with sufficiently
20 reduced oxygen and sulfur contents when using an oil to be treated that comprises an oxygen-containing hydrocarbon compound and a sulfur-containing hydrocarbon compound.

[Means for Solving the Problems]

[0006] In order to solve the problems described above, the invention
25 provides a hydrotreating method characterized in that by contacting an oil to be treated comprising an oxygen-containing hydrocarbon

compound and a sulfur-containing hydrocarbon compound with a catalyst comprising a porous inorganic oxide comprising two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium and at least one metal selected from among elements of Group 6A and Group 8 of the Periodic Table supported on the porous inorganic oxide, in the presence of hydrogen, under conditions with a hydrogen pressure of 2-13 MPa, a liquid space velocity of 0.1-3.0 h⁻¹, a hydrogen/oil ratio of 150-1500 NL/L and a reaction temperature of 180-380°C.

[0007] According to the hydrotreating method of the invention, it is possible to economically and very efficiently obtain a hydrotreated oil with reduced oxygen and sulfur contents, by contacting an oil to be treated comprising an oxygen-containing hydrocarbon compound and a sulfur-containing hydrocarbon compound with the catalyst specified above under the conditions specified above.

[0008] For the hydrotreating method of the invention, the oxygen content is preferably 0.1-15 % by mass and the sulfur content is preferably 1 ppm by mass-2 % by mass based on the total amount of the oil to be treated. If the oxygen and sulfur contents of the oil to be treated are within the aforementioned ranges, it will be possible to maintain stable deoxygenation activity for prolonged periods.

[0009] From the viewpoint of effective utilization of biomass energy, oxygen-containing hydrocarbon compounds in the hydrotreating method of the invention are preferably animal or vegetable-derived fat and oil components.

[0010] The proportion of compounds with a triglyceride structure

among the oxygen-containing hydrocarbon compounds is preferably at least 90 % by mol in order to reduce the level of energy required for processing of the starting material.

[0011] The catalyst used in the hydrotreating method of the invention preferably has a pore volume of 0.30-0.85 ml/g, a mean pore diameter of 5-11 nm, and a proportion of pore volume due to pores with pore diameters of 3 nm and smaller of no greater than 35 % by volume of the total pore volume, based on the BET nitrogen adsorption method.

[0012] Also, the porous inorganic oxide composing the catalyst preferably contains the element phosphorus. By using a phosphorus-containing porous inorganic oxide it is possible to further improve the deoxygenation activity of the catalyst.

[Effect of the Invention]

[0013] According to the invention there is provided a hydrotreating method that can economically and very effectively yield a hydrotreated oil with sufficiently reduced oxygen and sulfur contents when using an oil to be treated that comprises an oxygen-containing hydrocarbon compound and a sulfur-containing hydrocarbon compound.

Best Mode for Carrying Out the Invention

[0014] Preferred embodiments of the invention will now be described in detail.

[0015] The oil to be treated that is used for the invention comprises an oxygen-containing hydrocarbon compound and a sulfur-containing hydrocarbon compound. As oxygen-containing hydrocarbon compounds there are preferred animal or vegetable oil-derived fat and oil components. Fat and oil components according to the invention

include naturally or artificially produced or manufactured animal or vegetable oils and animal or vegetable oil components and/or components produced or manufactured from these fats and oils and components added for the purpose of maintaining or enhancing the performance of such fat and oil products.

[0016] As examples of animal or vegetable-derived fat and oil components there may be mentioned beef tallow, rapeseed oil, soybean oil, palm oil and the like. The animal or vegetable-derived fat and oil components according to the invention may be from any fats and oils, and may even be waste oil from use of the fats and oils. From the standpoint of carbon neutrality, however, they are preferably vegetable fats and oils, and from the viewpoint of fatty acid alkyl chain carbon number and reactivity, rapeseed oil, soybean oil and palm oil are more preferred. The aforementioned fats and oils may be used alone or in combinations of two or more.

[0017] Animal or vegetable-derived fat and oil components generally have a fatty acid triglyceride structure, but they may also include other fat and oil components processed to fatty acids or esters such as fatty acid methyl esters. However, since production of fatty acids or fatty acid esters from vegetable fats and oils generates carbon dioxide, the vegetable fats and oils are preferably composed mainly of components with a triglyceride structure, from the viewpoint of reducing carbon dioxide emission. According to the invention, the proportion of compounds with a triglyceride structure among the oxygen-containing hydrocarbon compounds in the oil to be treated is preferably 90 % by mol or greater, more preferably 92 % by mol and even more preferably

95 % by mol or greater.

[0018] The oil to be treated may also contain as oxygen-containing hydrocarbon compounds, in addition to the animal or vegetable oil-derived fat and oil components mentioned above, also chemical compounds such as plastics or solvents, or synthetic oils obtained by Fischer-Tropsch reaction using synthetic gas comprising carbon monoxide and hydrogen as the starting material.

[0019] The oxygen content of the oil to be treated is preferably 0.1-15 % by mass, more preferably 1-15 % by mass, even more preferably 3-14 % by mass and most preferably 5-13 % by mass based on the total amount of the oil to be treated. If the oxygen content is less than 0.1 % by mass it will tend to be difficult to stably maintain the deoxygenation activity and desulfurization activity. On the other hand, an oxygen content exceeding 15 % by mass will create a need for equipment to treat the water by-product, and may lead to excessive interaction between the water and catalyst support, thus lowering activity and lowering the catalyst strength. The oxygen content may be measured by an ordinary elemental analyzer, and for example, a sample may be converted to carbon monoxide on platinum-carbon, or it may be converted to carbon dioxide and then measurement performed using a thermal conductivity detector.

[0020] The sulfur-containing hydrocarbon compound in the oil to be treated is not particularly restricted, and specifically there may be mentioned sulfides, disulfides, polysulfides, thiols, thiophenes, benzothiophenes, dibenzothiophenes and their derivatives. The sulfur-containing hydrocarbon compound in the oil to be treated may

be a single compound, or it may be a mixture of two or more. A sulfur-containing petroleum hydrocarbon fraction may also be blended with the oil to be treated.

[0021] The petroleum hydrocarbon fraction used may be a fraction obtained by any common petroleum refining step. For example, there may be used a fraction corresponding to a prescribed boiling point range obtained from an atmospheric pressure distillation apparatus or vacuum distillation apparatus, or a fraction corresponding to a prescribed boiling point range obtained from a hydrodesulfurizer, hydrocracker, bottom oil direct desulfurizer or fluidized catalytic cracker. The fractions obtained from each of the aforementioned apparatuses may be used alone or in combinations of two or more.

[0022] The sulfur content of the oil to be treated is preferably 1 ppm by mass-1 % by mass, more preferably 15 ppm by mass-0.5 % by mass and even more preferably 30 ppm by mass-0.1 % by mass based on the total amount of the oil to be treated. A sulfur content of less than 1 ppm by mass will tend to make it difficult to maintain stable deoxygenation activity. On the other hand, a sulfur content exceeding 1 % by mass will tend to increase the sulfur content of the hydrorefined oil, risking adverse effects on engine exhaust gas purification devices when the use is as a fuel in diesel engines and the like. The sulfur content according to the invention is the mass content of sulfur as measured by the method described in JIS K 2541 "Sulfur Content Test Method" or ASTM-5453.

[0023] The sulfur-containing hydrocarbon compound may be mixed with the oil to be treated beforehand and introduced into the reactor of

a hydrotreating apparatus, or it may be supplied at an earlier stage of the reactor during introduction of the oil to be treated into the reactor.

[0024] The oil to be treated used for the invention preferably contains a fraction with a boiling point of 300°C or higher, and preferably it contains no heavy fractions with boiling points above 700°C. If the oil to be treated does not contain a fraction with a boiling point of 300°C or higher, it will tend to be difficult to obtain sufficient yield due to excessive decomposition. On the other hand, if the oil to be treated contains heavy fractions with boiling points above 700°C, deposition of carbon on the catalyst due to heavy components will be accelerated, tending to lower the activity. The boiling point according to the invention is the value measured by the method described in JIS K 2254 "Distillation Test Method" or ASTM-D86.

[0025] The hydrotreating method of the invention uses a catalyst comprising a porous inorganic oxide comprising two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium and at least one metal selected from among elements of Group 6A and Group 8 of the Periodic Table supported on the porous inorganic oxide.

[0026] The support of the catalyst used for the invention is a porous inorganic oxide comprising two or more elements selected from among aluminum, silicon, zirconium, boron, titanium and magnesium, as mentioned above. From the viewpoint of permitting further enhanced deoxygenation activity and desulfurization activity, the porous inorganic oxide is preferably two or more selected from among aluminum, silicon, zirconium, boron, titanium and magnesium, and it is

more preferably an inorganic oxide comprising aluminum and another element (a complex oxide of aluminum oxide and another oxide).

[0027] If the porous inorganic oxide contains aluminum as a constituent element, the aluminum content is preferably 1-97 % by mass, more preferably 10-97 % by mass and even more preferably 20-95 % by mass in terms of alumina based on the total amount of the porous inorganic oxide. If the aluminum content is less than 1 % by mass in terms of alumina, the properties such as support acidity will not be suitable and the deoxygenation activity and desulfurization activity exhibited will tend to be insufficient. On the other hand, an aluminum content of greater than 97 % by mass in terms of alumina will tend to result in inadequate catalyst surface area and reduced activity.

[0028] There are no particular restrictions on the method of introducing silicon, zirconium, boron, titanium and magnesium as support constituent elements other than aluminum onto the support, and a solution containing the elements may be used as starting materials. For example, silicic acid, water glass, silica sol and the like may be used for silicon, boric acid may be used for boron, phosphoric acid or a phosphoric acid alkali metal salt may be used for phosphorus, titanium sulfide and titanium tetrachloride and their alkoxide salts may be used for titanium, and zirconium sulfate and its alkoxide salts may be used for zirconium.

[0029] The porous inorganic oxide also preferably comprises phosphorus as a constituent element. The phosphorus content is preferably 0.1-10 % by mass, more preferably 0.5-7 % by mass and even more preferably 2-6 % by mass based on the total amount of the

porous inorganic oxide. If the phosphorus content is less than 0.1 % by mass, the deoxygenation activity and desulfurization activity exhibited will tend to be insufficient, while a content exceeding 10 % by mass will promote excessive decomposition, potentially lowering the hydrorefined oil yield.

[0030] The support constituent component starting materials other than aluminum oxide mentioned above are preferably added in a step prior to calcining of the support. For example, after first adding the starting materials to an aluminum aqueous solution, an aluminum hydroxide gel containing the constituent components may be prepared and the starting materials added to the prepared aluminum hydroxide gel. Alternatively, the starting materials may be added in a step of adding a commercially available aluminum oxide intermediate or boehmite powder to water or an acidic aqueous solution and kneading, but more preferably they are included at the stage of preparing the aluminum hydroxide gel. Although the mechanism by which the effects of the support constituent components other than aluminum oxide are exhibited is not completely understood, it is believed that complex oxides are formed with aluminum, and that this affects the activity by increasing the support surface area and causing interaction with the active metals.

[0031] The porous inorganic oxide used as the support supports one or more metals selected from among elements of Group 6A and Group 8 of the Periodic Table. Preferred among such metals are combinations of two or more metals selected from among cobalt, molybdenum, nickel and tungsten. As examples of preferred

combinations there may be mentioned cobalt-molybdenum, nickel-molybdenum, nickel-cobalt-molybdenum and nickel-tungsten. Preferred combinations among these are nickel-molybdenum, nickel-cobalt-molybdenum and nickel-tungsten. These metals are converted to sulfides for use in hydrotreating.

[0032] The content of active metals based on the catalyst mass, in terms of the range for the total loading amount of tungsten and molybdenum, is preferably 12-35 % by mass and more preferably 15-30 % by mass as oxides. If the total loading amount of tungsten and molybdenum is less than 12 % by mass, the number of active sites will be reduced and it may not be possible to obtain sufficient activity. On the other hand, if it is greater than 35 % by mass the metals will fail to effectively disperse, tending to prevent sufficient activity from being obtained. The range for the total loading amount of cobalt and nickel is preferably 1.0-15 % by mass and more preferably 1.5-12 % by mass as oxides. If the total loading amount of cobalt and nickel is less than 1.0 % by mass, a sufficient cocatalyst effect may not be achieved and the activity will tend to be reduced. On the other hand, if it is greater than 15 % by mass the metals will fail to effectively disperse, tending to prevent sufficient activity from being obtained.

[0033] There are no particular restrictions on the method of including the active metals in the catalyst, and any known method that is commonly applied for production of desulfurization catalysts may be used. For most cases, the preferred method is one in which the catalyst support is impregnated with a solution containing a salt of the active metal. Equilibrium adsorption methods, pore-filling methods and

incipient-wetness methods are also preferred. For example, pore-filling is a method in which the pore volume of the support is first measured and a metal salt solution of the same volume is used for impregnation. The impregnation method is not particularly restricted, and impregnation may be accomplished by an appropriate method for the metal loading amount and catalyst support properties.

[0034] According to the invention, there is no particular restriction on the number of types of hydrotreating catalysts used. For example, a single type of catalyst may be used alone, or a plurality of catalysts with different active metal species or support constituent components may be used. As examples of suitable combinations of multiple different catalysts there may be mentioned using a cobalt-molybdenum containing catalyst at a later stage of a nickel-molybdenum containing catalyst, a nickel-cobalt-molybdenum containing catalyst at a later stage of a nickel-molybdenum containing catalyst, a nickel-cobalt-molybdenum containing catalyst at a later stage of a nickel-tungsten containing catalyst, and a cobalt-molybdenum containing catalyst at a later stage of a nickel-cobalt-molybdenum containing catalyst. A nickel-molybdenum catalyst may also be combined before and/or after these combinations.

[0035] When using a combination of catalysts with different support components, for example, a catalyst with an aluminum oxide content in the range of 80-99 % by mass may be used after a catalyst with an aluminum oxide content of 30 % by mass or greater and less than 80 % by mass based on the total support mass.

[0036] Further, a guard catalyst, a demetallizing catalyst or an inactive

filler may be used if necessary in addition to the hydrorefining catalyst, for the purpose of trapping the sludge portion flowing in with the oil to be treated, or supporting the hydrorefining catalyst in separated sections of the catalyst bed. These may be used either alone or in combinations.

[0037] The pore volume of the catalyst used for the invention according to the BET nitrogen adsorption method is preferably 0.30-0.85 ml/g and more preferably 0.45-0.80 ml/g. If the pore volume is not at least 0.30 ml/g, the dispersibility of the supported metal will be unsatisfactory and the active sites may be reduced in number. If the pore volume is greater than 0.85 ml/g, the catalyst strength may be insufficient and the catalyst may undergo degradation or fragmentation during use.

[0038] The mean pore diameter of the catalyst determined by the measuring method mentioned above is preferably 5-11 nm and more preferably 6-9 nm. If the mean pore diameter is less than 5 nm, the reaction substrate may not diffuse sufficiently in the pores, potentially lowering the reactivity. If the mean pore diameter is greater than 11 nm, the pore surface area may be reduced leading to insufficient activity.

[0039] In order to maintain effective catalyst pores and exhibit sufficient activity for the catalyst described above, the proportion of the pore volume of pores with pore diameters of 3 nm and smaller preferably constitutes no greater than 35 % by volume of the total pore volume.

[0040] According to the invention, any one of the aforementioned

catalysts may be used alone, or a combination of a plurality of catalysts with different active metal species or support constituent components may be used. As examples of suitable combinations of multiple different catalysts there may be mentioned using a cobalt-molybdenum containing catalyst at a later stage of a nickel-molybdenum containing catalyst, a nickel-cobalt-molybdenum containing catalyst at a later stage of a nickel-molybdenum containing catalyst, a nickel-cobalt-molybdenum containing catalyst at a later stage of a nickel-tungsten containing catalyst, and a cobalt-molybdenum containing catalyst at a later stage of a nickel-cobalt-molybdenum containing catalyst. A nickel-molybdenum catalyst may also be combined before and/or after these combinations.

[0041] Further, a guard catalyst, a demetallizing catalyst or an inactive filler may be used if necessary in addition to the catalyst (hydrorefining catalyst), for the purpose of trapping the scale portion flowing in with the oil to be treated, or supporting the hydrorefining catalyst in separated sections of the catalyst bed. These may be used either alone or in combinations.

[0042] The conditions for contacting the oil to be treated with the catalyst in the presence of hydrogen are a hydrogen pressure of 2-13 MPa, a liquid space velocity (LHSV) of $0.1-3.0 \text{ h}^{-1}$ and a hydrogen/oil ratio of 150-1500 NL/L, preferably a hydrogen pressure of 4.5-12 MPa, a liquid space velocity of $0.3-1.5 \text{ h}^{-1}$ and a hydrogen/oil ratio of 380-1200 NL/L, and more preferably a hydrogen pressure of 6-15 MPa, a space velocity of $0.3-1.5 \text{ h}^{-1}$ and a hydrogen/oil ratio of 350-1000 NL/L. These conditions are all factors affecting the reactivity,

and for example, if the hydrogen pressure and hydrogen/oil ratio are below the lower limits mentioned above, the reactivity may be reduced or the activity may rapidly decrease. On the other hand, if the hydrogen pressure and hydrogen/oil ratio are above the upper limits mentioned above, it may be necessary to make significant investment for a compressor or other equipment. Also, a lower liquid space velocity will tend to favor the reaction, but if it is below the lower limit mentioned above it will become necessary to provide a reactor with a very large internal volume and significant investment for equipment may be necessary, while if the liquid space velocity exceeds the upper limit mentioned above, the reaction may not proceed to a sufficient extent.

[0043] The type of reactor used may be a fixed bed system. Specifically, the system employed may be in a form with hydrogen in countercurrent or cocurrent flow with respect to the oil to be treated. Also, a plurality of reactors may be used in a form combining countercurrent and cocurrent. The most common form is a downflow, and a gas-liquid cocurrent flow system may be employed. The reactor may consist of a single one or a combination of two or more, or the interior of a single reactor may have a structure that is partitioned into multiple catalyst beds.

[0044] The hydrorefined oil which has been hydrorefined in the reactor is then subjected to a gas-liquid separation or rectification step for fractionation into hydrorefined oil comprising prescribed fractions. For example, it is fractionated into a gas oil fraction and residual fraction. If necessary it may be further fractionated into the gas,

naphtha fraction and kerosene fraction. A portion of the produced light hydrocarbon fraction may be reformed with a steam reformer to produce hydrogen. Since the hydrogen produced in such a manner is carbon neutral because the starting material used for the steam reforming consists of biomass-derived hydrocarbons, the environmental burden is reduced. Reaction of the oxygen and sulfur portions contained in the oil to be treated may be accompanied by generation of carbon monoxide, carbon dioxide, hydrogen sulfide and the like, and a gas-liquid separation apparatus or other by-product gas removal apparatus may be installed between a plurality of reactors or in the product recovery step.

[0045] Hydrogen gas is usually introduced through the inlet port of the first reactor adjoining the oil to be treated either before or after passing through the heating furnace, but hydrogen gas may also be introduced separately between catalyst beds or between multiple reactors, in order to control the temperature in the reactor while maintaining hydrogen pressure throughout the entire reactor. Hydrogen introduced in this manner is generally referred to as "quench hydrogen". The proportion of quench hydrogen with respect to hydrogen gas introduced adjoining the oil to be treated is preferably 10-60 % by volume and more preferably 15-50 % by volume. If the proportion of quench hydrogen is less than 10 % by volume the reaction may not proceed sufficiently at the reaction site in the subsequent steps, and if the proportion of quench hydrogen is greater than 60 % by volume, the reaction may not proceed sufficiently near the reactor inlet port.

[0046] When a hydrorefined oil produced according to the invention is used as a gas oil fraction stock, the hydrorefined oil contains at least a fraction with a boiling point of 260-300°C, preferably with a sulfur content of no greater than 15 ppm by mass and an oxygen content of no greater than 0.5 % by mass, and more preferably a sulfur content of no greater than 12 ppm by mass and an oxygen content of no greater than 0.3 % by mass. If the sulfur and oxygen contents are above the aforementioned upper limits, this may adversely affect the filter or catalyst used in diesel engine exhaust gas treatment devices, as well as the other engine materials.

[0047] The hydrorefined oil produced according to the invention is particularly suitable for use as a diesel gas oil or heavy oil stock. The hydrorefined oil may be used alone as a diesel gas oil or heavy oil stock, but it may instead be used as a diesel gas oil or heavy oil stock blended with other components of stocks or the like. As other stocks there may be used blends of the gas oil and/or kerosene fractions obtained from general petroleum refining steps and the residual fraction obtained from the hydrorefining method of the invention. Also, a synthetic gas oil or a synthetic kerosene oil may be mixed therewith, which are obtained by a Fischer-Tropsch reaction or the like using so-called "synthetic gas" composed of hydrogen and carbon monoxide as the starting material. These synthetic gas oils or synthetic kerosene oils are characterized by containing virtually no aromatic components, being composed mainly of saturated hydrocarbons, and having high cetane numbers. The process for production of a synthetic gas may be any publicly known process and is not particularly restricted.

[0048] The residual fraction obtained by the hydrorefining method of the invention has a sulfur content of no greater than 0.1 % by mass and an oxygen content of no greater than 1 % by mass, and may therefore be used as a low-sulfur heavy oil stock . The residual fraction is also suitable as a feedstock oil for catalytic cracking. By supplying a low-sulfur residual fraction to the catalytic cracker in this manner, it is possible to produce a low-sulfur gasoline stock or other fuel oil stock. The residual fraction may also be used as a feedstock oil for hydrocracking. By supplying such a residual fraction to a hydrocracker, it is possible to achieve improved cracking activity and properties of each fraction of the product oil with higher quality.

[Examples]

[0049] The present invention will now be explained in greater detail based on examples and comparative examples, with the understanding that these examples are in no way limitative on the invention.

[0050] (Catalyst preparation)

<Catalyst A>

After adding 18.0 g of water glass No.3 to 3000 g of a 5 % by mass sodium aluminate aqueous solution, the mixture was placed in a vessel that had been heated to 65°C. Separately, a solution was prepared by adding 6.0 g of phosphoric acid (85% concentration) to 3000 g of a 2.5 % by mass aluminum sulfate aqueous solution in a different vessel heated to 65°C, and the sodium aluminate-containing aqueous solution was added as droplet thereto. The end point was defined as the time at which the pH of the mixture reached 7.0, and the obtained slurry product was filtered through a filter to obtain a cake-like slurry.

[0051] The cake-like slurry was transferred to a vessel equipped with a reflux condenser, and then 150 ml of distilled water and 10 g of a 27% ammonia aqueous solution were added and the mixture was heated and stirred at 75°C for 20 hours. The slurry was then placed in a kneader and heated to above 80°C, and kneading was performed while removing the moisture to obtain a clay-like kneaded blend. The obtained kneaded blend was extruded using an extruder into the cylindrical form with a diameter of 1.5 mm, dried at 110°C for 1 hour and then calcined at 550°C to obtain a molded support.

[0052] After placing 50 g of the molded support into a round-bottomed flask, an impregnating solution containing 17.3 g of molybdenum trioxide, 13.2 g of nickel(II) nitrate hexahydrate, 3.9 g of phosphoric acid (85% concentration) and 4.0 g of malic acid was poured into the flask while deairing with a rotary evaporator. The impregnated sample was dried at 120°C for 1 hour and then calcined at 550°C to obtain catalyst A. The properties of the prepared catalyst A are shown in Table 1.

[0053] <Catalyst B>

3000 g of a 5 % by mass concentration sodium aluminate aqueous solution was placed in a vessel that had been heated to 65°C. Separately, 3000 g of a 2.5 % by mass aluminum sulfate aqueous solution was prepared in a different vessel heated to 65°C, and the sodium aluminate-containing aqueous solution was added as droplet thereto. The end point was defined as the time at which the pH of the mixture reached 7.0, and the obtained slurry product was filtered through a filter to obtain a cake-like slurry.

[0054] The cake-like slurry was transferred to a vessel equipped with a reflux condenser, and then 150 ml of distilled water and 10 g of a 27% ammonia aqueous solution were added and the mixture was heated and stirred at 75°C for 10 hours. The slurry was then placed in a kneader and heated to above 80°C, and kneading was performed while removing the moisture to obtain a clay-like kneaded blend. The obtained kneaded blend was extruded using an extruder into the cylindrical form with a diameter of 1.5 mm, dried at 110°C for 1 hour and then calcined at 550°C to obtain a molded support.

[0055] After placing 50 g of the molded support into a round-bottomed flask, an impregnating solution containing 17.3 g of molybdenum trioxide, 13.2 g of nickel(II) nitrate hexahydrate, 3.9 g of phosphoric acid (85% concentration) and 4.0 g of malic acid was poured into the flask while deairing with a rotary evaporator. The impregnated sample was dried at 120°C for 1 hour and then fired at 550°C to obtain catalyst B. The properties of the prepared catalyst B are shown in Table 1.

[0056] [Table 1]

	Catalyst A	Catalyst B
Al ₂ O ₃ content (% by mass, based on support mass)	91.2	100
SiO ₂ content (% by mass, based on support mass)	4.8	-
P ₂ O ₅ content (% by mass, based on support mass)	4.0	-
MoO ₃ content (% by mass, based on catalyst mass)	24.0	24.0
NiO content (% by mass, based on catalyst mass)	2.6	2.5
P ₂ O ₅ content (% by mass, based on catalyst mass)	4.0	4.0
Pore volume (ml/g)	0.75	0.47
Mean pore diameter (nm)	7.0	5.2
Proportion of total pore volume due to pores with pore diameters of 3 nm and smaller (% by volume)	22	39

[0057] (Example 1)

A first reaction tube (inner diameter: 20 mm) packed with catalyst A (50 ml) and a second reaction tube (inner diameter: 20 mm) packed with the same catalyst A (50 ml) were installed in series in a fixed bed circulating reactor. Next, straight-run gas oil including dimethyl disulfide added (sulfur content: 3 % by mass) was used for presulfurizing of the catalyst for 4 hours under conditions with a catalyst layer mean temperature of 300°C, a hydrogen partial pressure of 6 MPa, a liquid space velocity of 1 h⁻¹ and a hydrogen/oil ratio of 200 NL/L.

[0058] After the presulfurizing, dimethyl sulfide was added to palm oil to prepare an oil to be treated with a sulfur content of 51 ppm by mass, and it was hydrotreated. The 15°C density of the oil to be treated was 0.916 g/ml, and the oxygen content was 11.4 % by mass. The

conditions for hydrorefining were a reaction temperature of 280°C in the first and second reaction tube, a pressure of 10 MPa and a liquid space velocity of 0.6 h⁻¹. The volume ratio (quench hydrogen proportion) of hydrogen gas introduced between the first reaction tube and second reaction tube was 20 % by volume of the total hydrogen introduced, and the hydrogen/oil ratio determined by the total hydrogen introduced was 500 NL/L. The results are shown in Table 2.

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[0059] (Comparative Example 1)

Hydrorefining was carried out in the same manner as Example 1, except that catalyst B was used instead of catalyst A. The results are shown in Table 2.

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[0060] (Comparative Example 2)

Hydrorefining was carried out in the same manner as Example 1, except that the reaction temperature for the hydrorefining in the first and second reaction tube was 160°C. The results are shown in Table 2.

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[0061] Hydrorefining was carried out in the same manner as Example 1, except that the reaction temperature for the hydrorefining in the first and second reaction tube was 410°C. The results are shown in Table 2.

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[0062] [Table 2]

		Example 1	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Catalyst		Catalyst A	Catalyst B	Catalyst A	Catalyst A
Oxygen content (% by mass, based on total hydrorefined oil)		<0.2	0.8	1.6	<0.2
Sulfur content (ppm by mass, based on total hydrorefined oil)		<1	<1	8	6
Yield (% by mass, based on feedstock oil)	C1-C4 (fraction with b.p. $\leq 80^{\circ}\text{C}$)	2.2	1.9	1.7	3.0
	Naphtha (fraction with b.p. $80-135^{\circ}\text{C}$)	0.0	0.0	0.0	7.5
	Kerosene (fraction with b.p. $135-250^{\circ}\text{C}$)	0.0	0.0	0.0	9.0
	Gas oil (fraction with b.p. $250-350^{\circ}\text{C}$)	82.6	80.2	79.2	65.3

CLAIMS:

1. A hydrotreating method characterized by contacting an oil to be treated comprising an oxygen-containing hydrocarbon compound and a sulfur-containing hydrocarbon compound with a catalyst comprising a porous inorganic oxide comprising two or more elements selected from among aluminum, silicon, zirconium, boron, titanium, and magnesium and further containing the element phosphorus, and two or more metals selected from among cobalt, molybdenum, nickel and tungsten supported on the porous inorganic oxide in the presence of hydrogen and under conditions with a hydrogen pressure of 2-13 MPa, a liquid space velocity of 0.1-3.0 h⁻¹, a hydrogen/oil ratio of 150-1500 NL/L and a reaction temperature of 180-380°C;

wherein the hydrogen gas comprises a first hydrogen gas introduced adjoining the oil to be treated and a second hydrogen gas introduced as a quench hydrogen;

wherein the proportion of the second hydrogen gas with respect to the first hydrogen gas is 10-60% by volume; and

a pore volume of the catalyst is 0.30-0.85 ml/g, a mean pore diameter is 5-11 nm, and a proportion of the pore volume due to pores with pore diameters of 3 nm and smaller is no greater than 35% by volume of a total pore volume.

2. The hydrotreating method of claim 1, wherein the oxygen content is 0.1-15% by mass and the sulfur content is 1 ppm by mass-1% by mass based on the total amount of the oil to be treated.

3. The hydrotreating method according to claim 1 or 2, wherein the oxygen-containing hydrocarbon compounds are animal or vegetable-derived fat and oil components.

4. The hydrotreating method according to anyone of claims 1 to 3, wherein a proportion of compounds with a triglyceride structure among the oxygen-containing hydrocarbon compounds is 90% by mol or greater.