

DESCRIPTION

Title of the Invention:

HYDROGENATION TREATMENT CATALYST FOR HYDROCARBON OIL, METHOD
FOR PRODUCING THE SAME, AND HYDROGENATION TREATMENT METHOD

Technical Field

[0001]

The present invention relates to a hydrogenation treatment catalyst for removing sulfur contents from a hydrocarbon oil in the presence of hydrogen, a method for producing the same, and a hydrogenation treatment method.

Background Art

[0002]

Hydrogenation treatment uses a catalyst to promote the reaction under high temperature and high pressure, but the economic efficiency of the process increases under low-temperature and low-pressure reaction conditions, and therefore the catalyst is desired to have high activity. Regarding the reduction temperature of molybdenum, the following knowledges are known.

[0003]

R. L. Cordero describes that the reduction temperature of molybdenum in a hydrogen stream of a catalyst supporting

molybdenum on alumina or silica greatly varies depending on the type and composition of the carrier species. However, a promoter of nickel or cobalt is not added, and it is difficult to say that the above could be a knowledge for a practicable catalyst. In addition, nothing relating to the relationship between the property and the desulfurization activity is not described, and therefore nothing relating to the optimum reduction temperature of the catalyst is not also described.

[0004]

J. Escobar et al. have clarified that an uncalcined catalyst containing nickel, molybdenum and phosphorus supported on an alumina carrier has two reduction peak temperatures, 384 to 403°C and 539 to 576°C, attributed to molybdenum in a hydrogen stream, and that the latter peak is larger than the former. However, though the knowledge relating to the reduction peak temperatures of the uncalcined catalyst is described, nothing is referred to relating to a calcined catalyst, and in addition, nothing is also described relating to the relationship between the reduction peak temperature or the reduction profile of molybdenum on a composite oxide and the desulfurization activity thereof.

[0005]

PTL 1 describes that a sulfide catalyst containing a base metal element selected from Groups 8 to 10 of the Periodic Table, such as nickel, cobalt, molybdenum, tungsten or the like, and

added with a noble metal element selected from Groups 8 to 10 of the Periodic Table, such as rhodium, palladium, platinum or the like, shows high hydrogenation treatment performance as utilizing spillover hydrogen. In addition, it describes that the behavior to receive reduction of the catalyst component to be the reaction active site has a close relationship to the catalytic activity of hydrogenation treatment, and the reduction peak temperature of the catalyst in a hydrogen stream is desirably 500°C or lower. However, as using a noble metal, the catalyst is more expensive than a base metal and is undesirable from the viewpoint of earth resources exhaustion.

As described above, some knowledge relating to the reduction temperature of molybdenum has been described, but no proposal is made relating to a catalyst that is inexpensive and excellent in desulfurization performance and can be readily regenerated.

[0006]

The current situation is that, not only for promoting energy saving and economic potential but also from the viewpoint of environmental load reduction, regeneration for reuse of used catalysts is increasing in refineries. In such a situation, there are known the following conventional knowledges relating to a method for producing an alumina carrier with a high performance of catalyst. PTL 2 discloses

a method for producing an alumina carrier from a boehmite sol using a pH regulator, as a method for producing a heat-resistant alumina carrier for catalyst combustion, referring to the effect of stably keeping a broad surface area even in use in a high-temperature atmosphere at 1000°C or higher. This knowledge is expected to be relatively unsuitable in industrial use since the boehmite to be used is sol and thin and since the pH regulation is somewhat complicated.

[0007]

PTL 3 discloses a method for producing an alumina catalyst carrier using an alumina hydrate having a pseudo-boehmite crystal structure. This says that, in a step of producing an alumina carrier, an alumina hydrate is plasticized with water added thereto, and the resultant plasticized product is kneaded to have an arbitrarily controlled pseudo-boehmite crystal size, and accordingly an alumina carrier having a desired pore size can be produced. In this production method, the crystal size is controlled by the reaction temperature and the reaction time of the plasticized product, and it is expected that in many cases, the product quality could not be stabilized since much technical skill is required for property control.

PTL 4 discloses a method for producing an alumina carrier using a pseudo-boehmite alumina powder, and it is considered that this method would be a method for producing an alumina

catalyst carrier having a high purity and a high activity by controlling the particle form of the alumina material. This production method includes a step of changing the aspect ratio of the particles by changing the mixing ratio of two different kinds of alumina material powders, and it is expected that the size control would greatly depend on the alumina materials and the mixing states thereof.

[0008]

PTL 5 describes a method for producing a hydrogenation treatment catalyst wherein a catalyst prepared by making a γ -alumina carrier loaded an active metal such as cobalt, nickel, molybdenum, tungsten or the like followed by calcining it is immersed in an organic additive of polyethylene glycol and then dried under the condition that the organic additive could remain in the catalyst. According to the catalyst production method, an effect of promoting hydrodesulfurization reaction can be expected by making the organic additive remain in the catalyst. On the other hand, however, the carbonaceous matter derived from the organic additive is extremely unstable and therefore may have some influence on the performance stability in use and, further in addition, the performance recovery of the regenerated product from the used catalyst is extremely poor, and in regeneration, the burned-off organic additive must be supplied.

[0009]

PTL 6 describes a production method for a porous alumina, in which water and at least one of a monobasic acid or a salt thereof are added to one or more of aluminum hydroxide and/or alumina and reacted for solation in a temperature range of 250°C or lower to give an aqueous alumina gel and/or an alumina gel, and the aqueous alumina gel and/or the alumina gel are dried and calcined. PTL 5 describes a method of adding an oxygen-containing organic material, an inorganic polybasic acid or the like as a pore size regulator to an alumina preparation liquid, in which the additive is used only in one step and nothing is referred to relating to OH group control on the surface of the carrier that has a significant influence on the catalyst performance. In addition, in this, the solation corresponding to an aging step is carried out in a closed vessel at a temperature higher than 100°C, and this treatment indispensably uses an autoclave (pressurized closed vessel) and therefore could not be said to be economical in industrial production.

PTL 7 describes a production method for an alumina hydrate fine powder, which includes a step of aging alumina hydrate fine particles added with a buffer and a deflocculant, which, however, does not refer to alumina crystallinity.

[0010]

PTL 8 describes a production method for a high-activity hydrodesulfurization catalyst, which includes a step of

forming shaped particles containing at least 90% by weight of boehmite and heating them to be converted into γ -alumina, saying that essentially the entire amount is converted into γ -alumina (where any other alumina than γ -alumina is less than 10% by mass). However, the crystallinity control factor is a calcination temperature alone.

PTL 9 discloses a production method for a catalyst using a phosphorus-silica-alumina carrier as an inorganic composite oxide carrier. In this, an aluminum salt solution containing a phosphate ion and a neutralizing agent are mixed to have a pH of 6.5 to 9.5 to give a phosphorus-containing alumina hydrate, and the hydrate is washed to give a slurry, and the resultant slurry is mixed with a silica sol, and shaped, dried and calcined to give a carrier. In the production method, the alumina crystallite size is not controlled, and nothing is referred to relating to the mixing state with any other element.

PTL 10 describes a granular carrier containing an oxide selected from alumina, silica, titania, zirconia and zeolite and having a diameter of 2 to 7 mm, and a catalyst using the carrier. This is characterized in that, when the cross section of the granular substance is observed with a transmission electron microscope at a magnifying power of 10,000, a shell-like concentrated layer is seen, and in addition, this is a granular carrier for hydrogenation treatment catalyst and the average pore diameter thereof is 150 to 300 Å and is

relatively large, and this therefore differs from the present invention in these points.

[0011]

PTL 11 discloses a catalyst for a fixed bed reactor, which contains a carrier with a base of alumina and with plural aggregates arranged in parallel, and an active metal in a total amount of 0.1 to 50% by weight. In this, an inorganic composite oxide carrier containing at least one additive element selected from the group consisting of phosphorus, boron, silicon and halogens is used, and the carrier partly contains aggregates in a stacked state of thin tabular substances and acicular state aggregates, and is characterized in that the acicular aggregates are uniformly dispersed simultaneously around the stacked state of thin tabular substances and between the stacked tabular substances. This significantly differs from the present invention in that it is a carrier of aggregates.

[0012]

PTL 12 discloses a production method for a catalyst carrier that contains a substantial amount of at least one metal oxide with an element of Group IVB of the Periodic Table and contains silica, and use of the catalyst carrier. The ratio by mass of the IVB Group metal oxide amount to the silica amount contained in the carrier falls between 5 and 70, and the carrier is characterized in that it contains silica and is additionally

mixed with titanium and zirconium. This differs from the present invention in point of the carrier composition.

[0013]

PTL 13 discloses a titanium-containing carrier, a method for producing it, a hydrogenation treatment catalyst for hydrocarbon oil, and a hydrogenation treatment method using the catalyst. The carrier contains a fireproof inorganic oxide and/or active carbon, titanium, and a basic oxide of an oxide of a rare earth metal, which is characterized in that titanium is homogeneously loaded by the fireproof inorganic oxide and/or active carbon. However, in this method, a titanium-containing aqueous solution is brought into contact with a fireproof inorganic oxide carrier according to an impregnation method, that is, this method includes a number of steps and is complicated, and is therefore expected to be relatively unsuitable for industrial use.

PTL 14 and PTL 15 describe a production method for a high-performance hydrogenation treatment catalyst using an inorganic composite oxide carrier prepared by mixing alumina and phosphorus, or phosphorus and titania. These have a significant characteristic feature in that, for the purpose of obtaining excellent desulfurization performance and denitrogenation performance, the catalyst is not calcined and contains an organic acid-derived carbon in an amount of 2% by mass based on the catalyst. However, though having high

performance, regeneration of the catalyst is expected to be difficult.

Citation List

Patent Literature

[0014]

PTL 1: JP-2002-210362A

PTL 2: JP-07-256100A

PTL 3: JP-07-155597A

PTL 4: WO97/12670

PTL 5: JP-08-332385A

PTL 6: WO2001/056951

PTL 7: JP-2014-133687A

PTL 8: WO2006/034073

PTL 9: JP-2000-135437A

PTL 10: JP-11-319554A

PTL 11: JP-2000-176288A

PTL 12: JP-2001-17860A

PTL 13: JP-2004-074148A

PTL 14: JP-2009-101362A

PTL 15: JP-2013-027847A

Non-Patent Literature

[0015]

NPL 1: R. L. Cordero et al., *Applied Catalysis*, 74, 125-136 (1991)

NPL 2: J. Escobar et al., Applied Catalysis B: Environmental, 88, 564-575 (2009)

Summary of Invention

Technical Problem

[0016]

An object of the present invention is to provide a hydrogenation treatment catalyst for hydrocarbon oil, which is excellent in desulfurization activity while maintaining industrially high productivity, and which can regenerate a high-performance catalyst, and a method for producing the hydrogenation treatment catalyst. The present invention is also to provide a hydrogenation treatment method for hydrocarbon oil, which can remove sulfur contents from hydrocarbon oil at a high removal rate.

Solution to Problem

[0017]

The hydrogenation treatment catalyst for hydrocarbon oil of the present invention is provided with the following:

(1) a carrier that contains alumina as the main component and is the following a or b:

a. the carrier is 100% γ -alumina,

b. the carrier contains aluminum in an amount of 80 to 98 parts by mass in terms of alumina relative to 100 parts by

mass of the carrier, and in the carrier, the crystallite diameter of the pseudo-boehmite of alumina to be the main component in the precursor is 15 or more and 40 or less Å as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof,

(2) a first metal component of at least one of molybdenum and tungsten, and a second metal component of at least one of cobalt and nickel are loaded on the carrier,

(3) the content of the first metal component is 15 to 27 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst, and the content of the second metal component is 2 to 7 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst,

(4) regarding the carrier of the above a, the specific surface area of the catalyst is 200 to 320 m²/g, and regarding the carrier of the above b, the specific surface area of the catalyst is 180 to 320 m²/g, and the mean pore diameter of the catalyst, as measured according to a mercury intrusion method, is 50 to 110 Å,

(5) the ignition loss is 5.0% by mass or less,

(6) the amount of carbon derived from an organic acid is 2.0 parts by mass or less on an elemental basis relative to 100 parts by mass of the catalyst, and

(7) the adsorption amount of nitrogen monoxide on the sulfurized catalyst is 8.0 ml/g or more.

[0018]

For example, the carrier contains 100 parts by mass of γ -alumina, and the crystallite diameter of the pseudo-boehmite of alumina precursor is 45 Å or less as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof.

[0019]

Methods of the present invention for producing the hydrogenation treatment catalyst for hydrocarbon oil of the present invention are as follows.

[0020]

When the carrier is the carrier a of the above-mentioned (1) (carrier of 100 parts by mass of γ -alumina), the method includes:

(A) a step of preparing a γ -alumina carrier, including:

a first aging stage of aging a slurry that contains an alumina obtained by mixing an aqueous solution of a basic aluminum salt and an aqueous solution of an acidic aluminum salt,

a stage of dehydrating the aged slurry and washing it, then a second aging stage of aging the slurry that contains the washed product,

thereafter, a stage of kneading and concentrating the slurry,

a stage of shaping the concentrated product prepared by

concentrating the slurry, and

then a stage of drying and calcining the shaped product,

(B) a step of preparing an impregnating liquid that contains a first metal component of at least one of molybdenum and tungsten, a second metal component of at least one of cobalt and nickel, and an organic acid, and making the first metal component and the second metal component loaded on the γ -alumina carrier, and

(C) a step of heat-treating the γ -alumina carrier on which the first metal component and the second metal component have been loaded, as obtained in the previous step (B), to produce a hydrogenation treatment catalyst.

[0021]

Specific methods of the present invention are recited below, which, however, do not restrict the scope of the present invention.

[0022]

In the second aging stage in the above-mentioned step (A), a first organic compound is added to the slurry. The first organic compound is added, for example, in an amount of 0.5 to 5.0 parts by mass relative to 100 parts by mass of alumina.

On and after the stage of kneading and concentrating the slurry in the step (A), the second organic compound is added before the stage of shaping the concentrated product. The second organic compound is added, for example, in an amount

of 0.5 to 5.0 parts by mass relative to 100 parts by mass of alumina.

The organic compound is, for example, at least one of organic acids and saccharides.

The aqueous solution of a basic aluminum salt in the step (A) contains a carboxylate.

In the first aging stage and the second aging stage included in the step (A), the alumina concentration is less than 20%, and in the stage of kneading and concentrating the slurry in the step (A), the alumina concentration is 20% or more.

The heat treatment temperature in the step (A) is a temperature of 100 to 600°C.

The above-mentioned techniques are for the case where the carrier is the carrier a of the above-mentioned (1) (carrier of 100 parts by mass of γ -alumina).

[0023]

Next, for the case where the carrier is b of the above-mentioned (1), more specific constitutions of the hydrogenation treatment catalyst for hydrocarbon oil of the present invention are recited below. In this case, the carrier contains aluminum in an amount of 80 to 98 parts by mass in terms of alumina relative to 100 parts by mass of the carrier, and in the carrier, the crystallite diameter of the pseudo-boehmite of alumina to be the main component in the

precursor is 15 or more and 40 or less Å as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof.

[0024]

The inorganic composite oxide carrier herein is such that the ratio of the absorbance of the spectral peak Sb in a wavenumber range of 3770 to 3774 cm^{-1} corresponding to the basic OH group therein to the absorbance of the spectral peak Sa in a wavenumber range of 3674 to 3678 cm^{-1} corresponding to the acidic OH group, as measured with a transmission Fourier transform IR spectrophotometer, the ratio of Sb/Sa is in a range of 0.20 to 0.45.

The inorganic composite oxide carrier corresponds to at least one of:

a. one containing phosphorus in an amount of 5.0 parts by mass or less in terms of phosphoric acid relative to 100 parts by mass of the inorganic composite oxide carrier,

b. one containing silicon in an amount of 3.0 parts by mass or less in terms of silica relative to 100 parts by mass of the inorganic composite oxide carrier,

c. one containing titanium in an amount of 18.0 parts by mass or less in terms of titania relative to 100 parts by mass of the inorganic composite oxide carrier, and

d. one containing zirconium in an amount of 9.0 parts by mass or less in terms of zirconia oxide relative to 100 parts

by mass of the inorganic composite oxide carrier.

The inorganic composite oxide carrier is such that, when the diffraction peak area showing the aluminum crystal structure attributed to the boehmite (020) plane measured in the XRD diffraction spectrum thereof is referred to as P1 and the diffraction peak area showing the crystal structure of the γ -alumina (440) plane is referred to as P2, the ratio of P2 to the total value of P1 and P2, $P2/(P1 + P2)$ is 0.9 or more. [0025]

The method for producing the hydrogenation treatment catalyst for hydrocarbon oil of the present invention (where the carrier corresponds to b of the above-mentioned (1)) includes:

(D) a step of preparing the inorganic composite oxide carrier,

(E) a step of preparing an impregnating liquid that contains a first metal component of at least one of molybdenum and tungsten, a second metal component of at least one of cobalt and nickel, and an organic acid, and making the first metal component and the second metal component loaded on the inorganic composite oxide carrier, and

(F) a step of heat-treating the inorganic composite oxide carrier on which the first metal component and the second metal component have been loaded, as obtained in the previous step (E), at a temperature of 100 to 600°C to produce a hydrogenation

treatment catalyst.

[0026]

A specific example of the step of preparing an inorganic composite oxide carrier in the above (1) includes:

(D-1) a slurry preparing step of mixing an aqueous solution of a basic metal salt and an aqueous solution of an acidic metal salt to prepare a composite metal hydrate slurry,

(D-2) a first aging step of aging the composite metal hydrate slurry,

(D-3) then a step of washing the composite metal hydrate slurry,

(D-4) thereafter, a second aging step of aging the composite metal hydrate slurry,

(D-5) subsequently, a kneading/concentrating step of kneading and concentrating the composite metal hydrate slurry,

(D-6) a step of shaping the concentrated product obtained by concentrating the composite metal hydrate slurry, and

(D-7) a step of drying and calcining the shaped product, wherein:

the first organic compound is added in the second aging step of the above (D-4).

Further specific examples of the step of preparing an inorganic composite oxide carrier in the above (D) are recited below.

The aqueous solution of a basic aluminum salt in the

slurry preparing step of the above (D-1) contains a carboxylate. The first organic compound is added in an amount of 0.5 to 4.0 parts by mass relative to 100 parts by mass of the inorganic composite oxide. In the kneading/concentrating step of the above (D-5), the second organic compound is added. The second organic compound is added in an amount of 0.5 to 4.0 parts by mass relative to 100 parts by mass of the inorganic composite oxide. The inorganic composite oxide concentration in the slurry in the second aging step of the above (D-4) is less than 20%, and the inorganic composite oxide concentration in the slurry in the kneading/concentrating step of the above (D-5) is 20% or more.

The organic compound is at least one selected from citric acid, malic acid, tartaric acid, gluconic acid, acetic acid, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and saccharides (monoses, polyoses, etc.).

The present invention is not limited to the specific examples mentioned in this section.

[0027]

The hydrogenation treatment method for hydrocarbon oil of the present invention includes hydrogenating hydrocarbon oil in the presence of the hydrogenation treatment catalyst of the present invention under the conditions of a hydrogen partial pressure of 3 to 8 MPa, a temperature of 260 to 420°C

and a liquid hourly space velocity of 0.3 to 5 hr⁻¹.

Advantageous Effects of Invention

[0028]

The hydrogenation treatment catalyst of the present invention uses a carrier of γ -alumina and can therefore obtain a high strength, a high stability and a large surface area and, in addition, the crystallinity thereof is easy to control, and high productivity thereof can be expected. In addition, the hydrogenation treatment catalyst of the present invention uses a carrier that contains γ -alumina as the main component and contains an inorganic composite oxide where the foreign element metal dispersibility has been improved, and can be therefore expected to provide a catalyst having a large surface area, a high strength and a high activity. With that, the catalyst has a suitable active metal composition, in which, therefore, the dispersibility of the active metals is high, and the adsorption amount of nitrogen monoxide (NO) that is an index of the number of active sites can be increased. Further, the OH group in the carrier surface is controlled, and from this point, high dispersibility of active metals can be attained. Furthermore, the ignition loss and the carbon content are optimized, and therefore catalyst regeneration is easy.

Using the hydrogenation treatment catalyst for

hydrocarbon oil of the present invention, a hydrogen desulfurization method for hydrocarbon oil can be carried out with a high desulfurization activity.

Brief Description of Drawings

[0029]

Fig. 1 shows results of transmission Fourier transform IR spectrophotometry of the carriers A and K of the first embodiment of the invention.

Fig. 2 shows graphs of examples of the results of analysis of the peak temperature of released water according to a temperature-programed-reduction method of the first embodiment of the invention.

Fig. 3 shows results of transmission Fourier transform IR spectrophotometry of the carriers of the second embodiment of the invention.

Fig. 4 shows graphs of examples of the results of analysis of the peak temperature of released water according to a temperature-programed-reduction method of the second embodiment of the invention.

Description of Embodiments

[0030]

<<First Embodiment>>

The first embodiment of the present invention is

described in detail hereinafter.

[Regarding hydrogenation treatment catalyst for hydrocarbon oil]

The hydrogenation treatment catalyst for hydrocarbon oil of the first embodiment of the present invention (hereinafter referred to as "the catalyst of the present invention" in the section of the first embodiment) contains a γ -alumina carrier (hereinafter this may also be referred to as an alumina carrier) and active metal components, and has predetermined properties. hereinafter the γ -alumina carrier, the active metal components and the properties of the catalyst are described in detail.

[0031]

< γ -Alumina carrier>

The γ -alumina carrier to constitute the hydrogenation treatment catalyst is an oxide of aluminum except impurities and the crystalline morphology thereof is grouped in a category of γ -alumina, and this is 100% γ -alumina. 100% γ -alumina means that this may contain impurities that may be contained therein unavoidably from the alumina carrier production process but does not contain any others, and for example, the γ -alumina content in the alumina carrier is 99% by mass (parts by mass) or more, preferably 99.5% by mass or more.

[0032]

Accordingly, the hydrogenation treatment catalyst of

the type can maintain not only high performance but also industrial high productivity.

For making the above-mentioned active metal components effectively loaded by the carrier in a high dispersion state and for sufficiently securing the catalytic activity, in general, a porous carrier is used, and a porous carrier having relatively small pores having a pore size of 500 Å or less is preferably used. For controlling the physical properties such as the mechanical strength, the heat resistance and the like of the carrier and the catalyst body, adequate binder components and additives may be added in forming the carrier or the catalyst body.

[0033]

The carrier of the catalyst of the present invention is such that the ratio of the absorbance of the spectral peak Sb in a wavenumber range of 3770 to 3774 cm^{-1} corresponding to the basic OH group therein to the absorbance of the spectral peak Sa in a wavenumber range of 3674 to 3678 cm^{-1} corresponding to the acidic OH group, as measured with a transmission Fourier transform IR spectrophotometer, the ratio of Sb/Sa is in a range of 0.15 to 0.40. The ratio of Sb/Sa is more preferably in a range of 0.20 to 0.40. It is known that the dispersibility of active metals varies depending on the characteristics of the surface of the alumina carrier, and when the ratio of Sb/Sa is in the above-mentioned range, high dispersibility of active

metals on the surface of the carrier of the present invention can be remarkably seen. As a result, the catalyst can have high desulfurization performance, and therefore, the ratio is preferably controlled to be in the above range. Fig. 1 shows examples of optical absorption spectra including a wavenumber range of 3674 to 3678 cm^{-1} corresponding to the acidic OH group and a wavenumber range of 3770 to 3774 cm^{-1} corresponding to the base OH group of carriers for the catalyst of the present invention (carriers A and K in Examples).

[0034]

In preparing the carrier of the catalyst of the present invention, a calcination step is carried out for preparing γ -alumina via a pseudo-boehmite crystalline state, which is characterized in that the crystallite diameter as obtained from the half-value width of the XRD diffraction spectral (020) peak of the pseudo-boehmite of the alumina precursor (before calcination) is 45 Å or less. It is important to control the crystallite size of the pseudo-boehmite for optimizing the pore structure of the alumina carrier and since the crystallite size may have some influence on the difficulty level in crystal dislocation in the subsequent calcination process. In the case where the crystallite size is more than 45 Å, the mean pore diameter is large and the specific surface area is small, and such is unfavorable since the catalyst performance may lower. In addition, since crystal dislocation could hardly

occur during calcination, a boehmite structure may remain in the crystal morphology of the alumina carrier, and such is also unfavorable as there may occur a risk of damaging the stability of catalyst performance.

[0035]

<Active metal component>

As active metal components, a first metal component of, for example, molybdenum and a second metal component of, for example, cobalt are loaded on the γ -alumina carrier.

The first metal component may be tungsten in place of molybdenum, and may be both molybdenum and tungsten. A preferred range of the content (supported amount) of the first metal component is 15 to 27% by mass in terms of oxide based on the catalyst (15 to 27 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst), and a more preferred range is 15 to 20% by mass.

[0036]

When the content of the first metal component is too excessively smaller than 15% by mass in terms of oxide, desulfurization activity necessary for reaction could not be secured, but when too excessively larger than 27% by mass, the metal components may readily aggregate to detract from dispersibility thereof.

The second metal component may be nickel in place of cobalt, or may be both cobalt and nickel. It is necessary that

the content (supported amount) of the second metal component is 2 to 7% by mass in terms of oxide based on the catalyst (2 to 7 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst). The second metal component acts as a promoter for the first metal component, and when the oxide-equivalent content thereof is smaller than 2% by mass, the first component and the second component that are the active metal components could hardly maintain a suitable structure, and when the oxide-equivalent content thereof is more than 7% by mass, the active metal components may readily aggregate to worsen the catalyst performance.

[0037]

In the case where the active metal components are loaded by the alumina carrier according to an impregnation method, an organic acid is generally contained in the impregnating liquid, and the organic acid is a supply source for carbon to be loaded by the alumina carrier. Examples of the organic acid for use for the active metal components include citric acid, malic acid, gluconic acid, tartaric acid, ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Citric acid, malic acid, tartaric acid and gluconic acid are more preferred. In the case where an organic additive such as, for example, saccharides (monoses, dioses, polyoses, etc.) and the like are used in addition to the organic acid, the content of the organic

acid-derived carbon as referred to in this description is the content of carbon derived from both the organic acid and the organic additive.

[0038]

<Properties of catalyst>

The catalyst of the present invention is needed to have a specific surface area (SA), as measured according to the BET (Brunauer-Emmett-Teller) method, falling within a range of 200 to 320 m²/g. When the specific surface area (SA) is smaller than 200 m²/g, such is unfavorable since the metal components may readily aggregate and since the desulfurization performance may lower. On the other hand, when larger than 320 m²/g, such is also unfavorable since the mean pore size and the pore volume may be small and the desulfurization activity tends to lower.

The mean pore size is needed to be 50 to 110 Å. The mean pore diameter is a value measured according to a mercury intrusion method (mercury contact angle: 130 degrees, surface tension: 480 dyn/cm), and means the pore diameter corresponding to 50% of the entire pore volume. The pore volume represents the volume of a pore having a pore diameter of 41 Å or more. When the mean pore size is smaller than 50 Å, the desulfurization performance may lower, but when the mean pore size is larger than 110 Å, the catalyst strength may lower.

[0039]

In the catalyst of the present invention, the ignition loss (Ig Loss) is 5.0% by mass or less. The ignition loss is calculated according to the measurement method described in the following section, in which the catalyst is heated at a high temperature. In order that the ignition loss of the catalyst can be 5.0% by mass or less, it is necessary that the γ -alumina carrier is, after sprayed with an impregnating liquid, calcined at a temperature of, for example, 300°C or higher.

When the ignition loss of the catalyst is made to be 5.0% by mass or less, the activity of the regenerated catalyst can be 80% or more, based on the desulfurization performance of the new and unused catalyst (fresh catalyst), 100%. When the ignition loss of the catalyst is large, there may be a risk of aggregation of the active metal components in the calcination step in catalyst regeneration.

[0040]

The carbon content in the catalyst is 2.0% by mass or less based on the catalyst and on an elemental basis. Under this situation, the activity in catalyst regeneration can be 80% or more, based on the desulfurization performance of the new and unused catalyst (fresh catalyst), 100%. When the carbon content is large, there is a risk of aggregation of active metal components in the calcination step in catalyst regeneration.

The peak temperature of released water from the catalyst

of the present invention within a range of up to 450°C (the temperature at which the water release spectrum peak appears), according to a temperature-programed-reduction method for catalyst, is 415°C or lower. A specific example of the temperature-programed-reduction method is described hereinafter. In general, sulfurization is carried out with hydrogen sulfide or the like in the presence of molybdenum in a hydrogen stream, and for the reaction, oxygen must remove from molybdenum oxide. The water release peak is to just detect the release of water with oxygen from the molybdenum oxide, and therefore it is considered that the sulfurization procedure and the molybdenum reduction temperature would have some correlation therebetween. Accordingly, by lowering the peak temperature of released water, it is considered that sulfurization with molybdenum could be promoted sufficiently.

[0041]

In the case where the reduction temperature is too high, that is, where the peak temperature of released water is too high, water may weakly interact with the alumina carrier and therefore there is a high probability that active metal aggregates may exist. As a result, the sulfurization step could not be sufficiently attained. Accordingly, it is necessary to lower the reduction temperature so as to reduce the interaction between water and the alumina carrier for attaining high dispersion of active metals.

Released water is formed mainly in the molybdenum reduction step, and the peak temperature thereof varies depending on the carrier composition, the active metal composition, etc. According to the present inventors' knowledge, it is necessary that, in order that the water release peak temperature (peak temperature of released water) could be 415°C or lower, at least one kind (one species) of molybdenum and tungsten is, as the active metal component thereon, needed to be present on the alumina carrier in an amount of 15 to 28% by mass in terms of oxide, and at least one kind (species) of cobalt and nickel is needed to be present thereon in an amount of 2 to 7% by mass in terms of oxide.

In the case where the amount of the active metal components is smaller than the range, such is unfavorable since the catalyst performance is poor; but in the case where the amount of the active metal components is larger than the range, such is also unfavorable since aggregates of active metals may form to worsen the dispersibility thereof.

[0042]

The catalyst of the present invention is such that the adsorption amount of nitrogen monoxide on the sulfurized catalyst is 8.0 ml/g or more. The adsorption amount is more preferably 8.3 ml/g or more. Based on the nitrogen monoxide molecule adsorption amount, the reaction active sites of the catalyst can be measured.

In the case where the amount of nitrogen monoxide adsorption is less than 8.0 ml/g, falling outside the present invention, such is unfavorable since the number of the reaction active sites of the catalyst is small and the catalyst performance improvement could not be attained.

The nitrogen monoxide adsorption amount on the catalyst after sulfurization varies depending on the physical properties and chemical properties of the carrier and on the active metal composition, etc. For nitrogen monoxide adsorption, sulfurization is necessary, and therefore, the reduction temperature of the active metals must be lowered down to a certain temperature or lower. According to the present inventors' knowledge, the following are important for controlling the carbon monoxide adsorption amount to be 8.0 ml/g or more.

a) The specific surface area (SA) of the alumina carrier is in a range of 180 to 320 m²/g.

b) The ratio of the absorbance of the spectral peak Sb in a wavenumber range of 3770 to 3774 cm⁻¹ corresponding to the basic OH group to the absorbance of the spectral peak Sa in a wavenumber range of 3674 to 3678 cm⁻¹ corresponding to the acidic OH group, as measured with a transmission Fourier transform IR spectrophotometer, the ratio of Sb/Sa is in a range of 0.15 to 0.40.

c) As active metal components, at least one of molybdenum

and tungsten is present on the alumina carrier in an amount of 15 to 28% by mass in terms of oxide, and at least one of cobalt and nickel is thereon in an amount of 2 to 7% by mass in terms of oxide.

d) The release peak temperature of water is 415°C or lower.

[0043]

[Production method for hydrogenation treatment catalyst for hydrocarbon oil]

Next, a production method for the hydrogenation treatment catalyst for hydrocarbon oil of the present invention is described.

The production method for the hydrogenation treatment catalyst for hydrocarbon oil of the present invention includes:

a first step of preparing a γ -alumina carrier,

a second step of preparing an impregnating liquid that contains a first metal component of at least one of molybdenum and tungsten and a second metal component of at least one of cobalt and nickel, and an organic acid, and making the first metal component and the second metal component loaded by the alumina carrier, and

a third step of heat-treating the alumina carrier on which the first metal component and the second metal component have been loaded, as obtained in the second step, at a

temperature of 100 to 600°C to produce a hydrogenation treatment catalyst.

The steps are described below.

[0044]

<First step>

<<1-1. Step of preparing alumina slurry>>

First, an aqueous solution of a basic aluminum salt and an aqueous solution of an acidic aluminum salt are mixed so as to have a pH of 6.5 to 9.5, preferably 6.5 to 8.5, more preferably 6.8 to 8.0, thereby preparing an inorganic oxide hydrate. In this stage, the aqueous solution of a basic aluminum salt preferably contains a carboxylate. After the inorganic oxide hydrate slurry is aged according to a desired method (first aging step), this is washed to remove by-product salts to thereby give a slurry that contains an alumina.

The carboxylate to be used here includes salts of polyacrylic acid, hydroxypropyl cellulose, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, maleic acid, gluconic acid, fumaric acid, phthalic acid, citric acid, etc. The carboxylate is preferably added in an amount of 0.5 to 5.0 parts by mass relative to 100 parts by mass of alumina.

<<1-2. Second aging step for alumina>>

At least one organic compound (first organic compound) is added to the hydrate slurry obtained in the previous step

1-1, and heated and aged in an aging tank equipped with a reflux unit, at 30°C or higher, preferably 80 to 100°C for about 1 to 20 hours, preferably 2 to 10 hours (second aging step). In the first aging stage and the second aging stage, the alumina concentration is preferably less than 20%.

<<1-3. Kneading/shaping and drying step>>

The aged product obtained in the previous step 1-2 is put into a steam-jacketed two-arm kneader and heated and concentrated therein so as to have an alumina concentration of 20% or more, and then at least one organic compound (second organic compound) is added thereto, and thereafter these are further heated and kneaded to give a shapeable kneaded product, and this is shaped through extrusion to be in a desired form. Regarding the timing of adding the second organic compound, the compound may be added during concentration of the aged product.

<<1-4. Heat-treating (drying, calcination) step>>

The shaped product obtained in the previous step 1-3 is then heated and dried at, for example, 70 to 150°C, preferably 90 to 130°C, and further calcined, for example, preferably at 400 to 800°C, more preferably 400 to 600°C, and for example, for 0.5 to 10 hours, preferably 2 to 5 hours to give an alumina carrier.

For the basic aluminum salt to be used herein, sodium aluminate, potassium aluminate and the like are preferred.

For the acidic aluminum salt, aluminum sulfate, aluminum chloride, aluminum nitrate and the like are preferably used.

When the two kinds of aluminum salt aqueous solutions are mixed, in general, they are kept heated at 40 to 90°C, preferably 50 to 70°C, and the aqueous mixed solution heated at a temperature $\pm 5^{\circ}\text{C}$ of the temperature of the solution, preferably $\pm 2^{\circ}\text{C}$, more preferably $\pm 1^{\circ}\text{C}$ is continuously added so as to have a pH of 6.5 to 9.5, preferably 6.5 to 8.5, more preferably 6.5 to 8.0, generally for 5 to 20 minutes, preferably 7 to 15 minutes for forming precipitates to thereby give a hydrate slurry.

[0045]

In the case where the time to be taken for adding the aqueous basic aluminum salt solution to the aqueous mixed solution is too long, unfavorable crystals of bayerite, gibbsite and the like may form in addition to pseudo-boehmite, and therefore the time is preferably 15 minutes or less, more preferably 13 minutes or less. Bayerite and gibbsite are unfavorable as causing specific surface area reduction in heat treatment.

The first organic compound and the second organic compound for use in the first step are preferably at least one selected from organic acids and saccharides. The organic acids include citric acid, malic acid, tartaric acid, gluconic acid, acetic acid, ethylenediaminetetraacetic acid (EDTA) and

diethylenetriaminepentaacetic acid (DTPA). The saccharides include monoses, dioses, polyoses, etc. The amount to be added is preferably within a range of 0.5 to 5.0 parts by mass relative to 100 parts by mass of alumina. In the case where the amount added is smaller than the range, the effect of adding the organic compound could hardly be obtained, but in the case where the amount is larger than the range, the pore structure would be too small owing to the too strong effect of the compound, and therefore such are unfavorable since not only the physical properties of the catalyst could not be in an optimum range but also the production efficiency worsens.

[0046]

The OH group on the carrier surface is an important factor that has an influence on the supporting condition of active metals, such as the dispersibility of active metal species. Controlling the OH group may be carried out anytime in the carrier preparation process along with controlling the crystallinity of the carrier alumina precursor therein. However, it is extremely difficult to control the OH group while maintaining the physical properties of the carrier. To satisfy it, it is desirable that the OH group control is carried out in a different step after crystallinity control. Consequently, it is preferable that, after the crystallinity is controlled in the second aging step, an organic compound (second organic compound) is added in the

kneading/concentrating step to control the OH group state.

[0047]

<Second step>

An impregnating liquid that contains the above-mentioned first metal component, second metal component and carbon component is brought into contact with the alumina carrier.

As the raw material for the first metal component, for example, molybdenum trioxide, ammonium molybdate, ammonium metatungstate, ammonium paratungstate, tungsten trioxide and the like are preferably used. As the raw material for the second metal component, nickel nitrate, nickel carbonate, cobalt nitrate, cobalt carbonate and the like are preferably used.

In the case where phosphorus is made loaded by the alumina carrier, orthophosphoric acid (hereinafter this may be simply referred to as "phosphoric acid"), ammonium dihydrogenphosphate, diammonium hydrogenphosphate, trimetaphosphoric acid, pyrophosphoric acid, tripolyphosphoric acid and the like may be used.

[0048]

In the impregnating liquid, preferably, the metal components are dissolved using an organic acid at pH of 4 or less. When the pH is more than 4, the stability of the dissolved metal components may lower and the components tend to

precipitate out. Examples of the organic acid include citric acid, malic acid, tartaric acid, ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), and in particular, citric acid and malic acid are preferably used. The organic additive includes saccharides (monoses, dioses, polyoses, etc.). An organic additive, for example, glucose ($C_6H_{12}O_6$), fructose ($C_6H_{12}O_6$), maltose ($C_{12}H_{22}O_{11}$), lactose ($C_{12}H_{22}O_{11}$), sucrose ($C_{12}H_{22}O_{11}$) or the like may be added to the organic acid.

[0049]

<Third step>

The carrier on which the metal components have been loaded, as obtained by bringing the carrier into contact with the impregnating liquid in the second step, is heat-treated at 100 to 600°C, preferably 110 to 600°C, more preferably 400 to 600°C, for 0.5 to 1 hour, preferably 1 to 8 hours, and then the hydrogenation treatment catalyst of the present invention is produced. When the calcination temperature is excessively lower than 100°C, the processability may worsen owing to the residual water and, in addition, the metal components could not be uniformly loaded, and when the temperature is excessively higher than 600°C, the metals may aggregate and the dispersion maintaining effect for the metals could not be expected. Anyhow, such lower or higher temperatures are unfavorable.

One advantage in the first to third steps is described. In the second aging step for alumina in the first step, an organic compound (first organic compound) is added to the hydrate slurry and this is then heated and aged. According to this treatment, the crystallite diameter of the pseudo-boehmite of the alumina precursor can be controlled to be 45 Å or less, and therefore the mean pore diameter of the catalyst can be thereby reduced and the specific surface area thereof can be increased. In addition, crystal dislocation during calcination runs on readily and therefore a boehmite structure hardly remains in the crystal morphology of the alumina carrier and the catalyst performance can be stabilized.

[0050]

The hydrogenation treatment catalyst is desired to have well-balanced properties of high surface area and high strength. For preparing γ -alumina, the material is processed in a calcination step via a pseudo-boehmite crystal state, and by controlling the pseudo-boehmite crystal state, the catalyst performance improvement is expected. According to this embodiment of the present invention, the pseudo-boehmite crystal state can be controlled, therefore contributing toward producing a high-performance hydrogenation treatment catalyst.

[0051]

[Regarding hydrogenation treatment method for hydrocarbon oil]

Examples of the hydrocarbon oil that is to be desulfurized using the hydrogenation treatment catalyst of the present invention include straight kerosene or straight light gas oil obtained from an atmospheric crude oil distillation apparatus, reduced pressure light gas oil or reduced pressure heavy light oil obtained through treatment of straight heavy oil or residual oil as obtained from an atmospheric distillation apparatus in a reduced pressure distillation apparatus, hydrocracked kerosene or hydrocracked light gas oil obtained through hydrocracking desulfurized heavy oil, hydrocracked kerosene or hydrocracked light gas oil obtained through hydrocracking of reduced pressure heavy light oil or desulfurized heavy oil, thermal-cracked kerosene or thermal cracked light gas oil obtained from a thermal cracking apparatus such as a coker or the like, and the hydrocarbon oil is a fraction that contains a fraction having a boiling point of 180 to 390°C in an amount of 80% by volume or more. Regarding the hydrogenation treatment using the catalyst, the catalyst is filled in a fixed bed reactor, and in a hydrogen atmosphere, hydrocarbon oil is hydrogenated therein under high-temperature and high-pressure conditions.

[0052]

[Regarding measurement method]

As described hereinafter, the hydrogenation treatment catalysts in Examples and Comparative Examples given herein are numerically analyzed in point of the content of each constituent component, the specific surface area and the properties thereof, and the measurement methods for these are described below.

<Measurement method for content of carrier component (alumina) and metal components (molybdenum, cobalt, nickel, phosphorus)>

3 g of a sample to be analyzed was put into a zirconia bowl with a lid having a capacity of 30 ml, then heat-treated (200°C, 20 minutes) and calcined (700°C, 5 minutes), and thereafter 2 g of Na₂O₂ and 1 g of NaOH were added thereto and melted for 15 minutes. Further, 25 ml of H₂SO₄ and 200 ml of water were added and dissolved, and then this was diluted with pure water to be 500 ml, thereby preparing a sample. Using an ICP apparatus (manufactured by Shimadzu Corporation, ICPS-8100, analysis software ICP-8000), the resultant sample was analyzed to determine the content of each constituent component in terms of oxide (Al₂O₃, P₂O₅, MoO₃, NiO, CoO).

[0053]

<Method for identification of alumina crystal morphology and method for measurement of crystallite size>

A sample to be analyzed was compressed onto a laboratory non-reflecting plate to prepare an observation sample, and the

crystal morphology thereof was identified through X-ray diffractometry using an X-ray diffractometer (manufactured by Rigaku Corporation: RINT 2100). The crystallite size of the carrier alumina precursor was calculated according to a Scherrer method from the (020) plane attributed to boehmite, and the crystal structure of the calcined carrier was determined by comparing the diffraction peaks attributed to boehmite and γ -alumina. The alumina oxide carrier of the present invention is preferably γ -alumina, and specifically, the diffraction peak area indicating the crystal structure of the (020) plane and (120) plane of boehmite measured through X-ray diffractometry analysis is needed to be less than 1/10 relative to the diffraction peak area indicating the aluminum crystal structure attributed to the (440) plane of γ -alumina. Namely, when the diffraction peak area indicating the crystal structure of the (020) plane of boehmite measured through X-ray diffractometry is referred to as P1, the diffraction peak area indicating the crystal structure of the (120) plane is as P2, and the diffraction peak area indicating the aluminum crystal structure attributed to the (440) plane of γ -alumina is as P3, a larger one of the value $(P1/P3) \times 100$ (%) and the value $(P2/P3) \times 100$ (%) is less than 10%.

When the boehmite structure exists much in the carrier crystal, such is unfavorable since not only the carrier properties are difficult to control but also the catalyst

strength may lower.

[0054]

Here, the diffraction peak indicating the crystal structure of the (020) plane and the (120) plane of boehmite is detected at $2\theta = 14^\circ$ and $2\theta = 28^\circ$, and the diffraction peak indicating the aluminum crystal structure attributed to the (440) plane of γ -alumina is detected at $2\theta = 67^\circ$.

The calculation method for the diffraction peak area is as follows. The graph of X-ray diffraction analysis obtained using an X-ray diffractometer is fitted according to the least-square method and the baseline is corrected, and the height from the maximum peak value to the base line is measured (peak strength W), then the peak width (half-value width) at the half value of the resultant peak strength ($1/2W$) is determined, and the product of the half-value width and the peak strength is referred to as the diffraction peak area. From the resultant diffraction peak area data, "boehmite diffraction peak area/ γ -alumina diffraction peak area" is calculated.

[0055]

<Measurement method for OH group on carrier surface>

Using a transmission Fourier transform IR spectrophotometer (manufactured by JASCO Corporation: FT-IR/6100), the maximum peak wavenumber of acid OH group, the absorbance at the wavenumber, the maximum peak wavenumber of

basic OH group, and the absorbance at the wavenumber were determined.

(Measurement method)

20 mg of a sample was filled in a shaping vessel (inner diameter 20 mm ϕ) and compressed under pressure of 4 ton/cm² (39227 N/cm²) to be shaped into a thin disc. The shaped product was kept under a condition at a vacuum degree of 1.0×10^{-3} Pa or less and at 500°C for 2 hours, and then cooled down to room temperature, and the absorbance thereof was measured.

[0056]

Specifically, using a TGS detector, the sample was analyzed at a resolution of 4 cm⁻¹ and for an integration frequency of 200 times, and the baseline was corrected in a wavenumber range of 3000 to 4000 cm⁻¹. The absorbance was converted per the unit mass. The absorbance per unit mass (g⁻¹) = absorbance/mass of shaped product.

In every sample of Examples 1 to 13 given hereinafter, the wavenumber at the maximum peak position of the absorption spectrum corresponding to the acidic OH group therein is in a range of 3674 to 3678 cm⁻¹, and the wavenumber at the maximum peak position of the absorption spectrum caused by the basic OH group is in a range of 3770 to 3774 cm⁻¹.

[0057]

<Measurement method for specific surface area>

About 30 ml of a sample to be analyzed was weighed in

a porcelain crucible (B-2 type), heat-treated at a temperature of 300°C for 2 hours, then put in a desiccator, and cooled down to room temperature to prepare a sample for measurement. Next, 1 g of the sample was weighed, and the specific surface area (m²/g) thereof was measured according to the BET method using an automatic surface area measuring apparatus (manufactured by Yuasa Ionics Corporation, Multisorb 12 Model).

[0058]

<Measurement method for ignition loss>

A catalyst of a sample to be analyzed was calcined at 570°C for 2 hours, and from the mass reduction by calcination, the ignition loss of the sample was calculated.

<Method for measurement of peak temperature of released water according to temperature-programmed reduction method>

In a temperature-programmed reduction method, using a catalyst analyzer manufactured by Microtrac BEL Corporation (BEL CAT-A), 0.05 g of a catalyst that had been granulated in a size of 250 to 710 μm was pretreated in a helium gas stream at 120°C for 1 hour, then the ambient gas was changed to a hydrogen gas (99.99%), and the catalyst was heated from 50°C up to 900°C at a rate of 10°C/min. The water release spectrum in heating was measured using a quadrupolar mass analyzer manufactured by Pfeiffer Vacuum Corporation (m/z: 18.34), and on the resultant release spectrum, the water release peak temperature was read.

Fig. 2 shows graphs of examples of the results of analysis of the peak temperature of released water according to the temperature-programed-reduction method. The abscissa in Fig. 1 shows a temperature, and the ordinate shows a detected current of the quadrupolar mass analyzer.

[0059]

<Measurement method for nitrogen monoxide adsorption amount>

For measurement of the nitrogen monoxide adsorption amount, an automatic catalyst gas adsorption amount measuring apparatus (manufactured by Okura Riken Corporation) was used. A mixed gas of helium gas and nitrogen monoxide gas (nitrogen monoxide gas concentration, 10% by volume) was pulsewise applied to a sulfurized hydrogenation treatment catalyst, and the nitrogen monoxide molecule adsorption amount per gram of the hydrogenated catalyst was measured. Specifically, about 0.02 g of the catalyst ground to have a size of 60 meshes or less was weighed, this was filled in a quartz cell, the catalyst was heated up to 360°C, and a gas of hydrogen sulfide 5 vol%/hydrogen 95 vol% was applied thereto at a flow rate of 0.2 liter/min for sulfurization for 1 hour. Subsequently, this was kept at 340°C for 1 hour, and the physically-adsorbed hydrogen sulfide was discharged out of the system. Afterwards, nitrogen monoxide molecules were adsorbed using a mixed gas of helium gas and nitrogen monoxide gas at 50°C, and the nitrogen monoxide molecule adsorption amount was measured.

[0060]

[Examples]

Preparation examples for γ -alumina carrier, preparation examples for impregnating liquid, preparation examples for hydrogenation treatment catalyst that are examples of the present invention using alumina carrier and impregnating liquid, and preparation examples for hydrogenation treatment catalyst that are comparative examples using alumina carrier and impregnating liquid are described below.

First, carrier preparation examples are described.

[0061]

<Preparation of carrier A>

a) 9.09 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into steam-jacketed tank having a volume of 100 L (liter), and diluted with ion-exchanged water to be 40.00 kg. Next, 230.8 g of an aqueous sodium gluconate solution having a concentration of 26 % by mass was added to the solution and heated up to 60°C with stirring.

Separately, an aqueous solution of aluminum sulfate prepared by diluting 14.29 kg of an aqueous aluminum sulfate solution having a concentration of 7 % by mass in terms of Al_2O_3 with 25.71 kg of ion-exchanged water was heated up to 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the sodium aluminate/sodium gluconate mixed

solution having a concentration of 5 % by mass was stirred, an aqueous solution of aluminum sulfate was added thereto at a constant speed taking 10 minutes to prepare an alumina hydrate slurry having a concentration of 3.8% by mass as Al_2O_3 . At this time, the pH of the slurry was 7.2. Subsequently, the alumina hydrate slurry was, while stirred, aged at 60°C for 60 minutes.

b) Next, the aged alumina hydrate slurry was dewatered, and then washed with 1.5 L of an aqueous ammonia solution having a concentration of 0.3% by mass.

c) After washed, the cakey slurry was diluted with ion-exchanged water so as to have a concentration, in terms of Al_2O_3 , of 10% by mass and was thus made into a slurry, and then 0.60 kg of a solution of 10 mass% citric acid as the first organic compound was added thereto, and thereafter aqueous ammonia having a concentration of 15% by mass was added for pH control to 10.2, and this was aged at 95°C for 10 hours with stirring.

d) After aged, the slurry was dewatered and concentrated to have an alumina concentration of 20% or more while kneaded and heated with a steam-jacketed two-arm kneader, and thereafter 0.30 kg of a solution of 10 mass% malic acid was added, and then this was further heated, concentrated and kneaded to have a predetermined water content.

e) Subsequently, the resultant kneaded product was shaped into a column having a diameter of 1.6 mm, using a

screw-type extruder.

f) Next, this was dried at 110°C for 12 hours, and then calcined at 500°C for 3 hours to give a carrier A of γ -alumina for hydrogenation treatment catalyst.

[0062]

<Preparation of carrier B>

A carrier B was produced in the same manner as that for the carrier A, except that 0.60 kg of a 10 mass% solution of gluconic acid as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto.

<Preparation of carrier C>

A carrier C was produced in the same manner as that for the carrier A, except that 1.20 kg of a 10 mass% solution of gluconic acid as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto.

<Preparation of carrier D>

A carrier D was produced in the same manner as that for the carrier A, except that 0.60 kg of a 10 mass% solution of tartaric acid as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto.

<Preparation of carrier E>

A carrier E was produced in the same manner as that for

the carrier A, except that 0.60 kg of a 10 mass% solution of sucrose as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto.

<Preparation of carrier F>

A carrier F was produced in the same manner as that for the carrier A, except that 0.60 kg of a 10 mass% solution of malic acid as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto.

<Preparation of carrier G>

A carrier G was produced in the same manner as that for the carrier A, except that 1.50 kg of a 10 mass% solution of sucrose as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto.

[0063]

<Preparation of carrier H>

A carrier H was produced in the same manner as that for the carrier A, except that 0.60 kg of a 10 mass% solution of acetic acid as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto.

<Preparation of carrier I>

A carrier I was produced in the same manner as that for

the carrier A, except that 0.60 kg of a 10 mass% solution of gluconic acid as the first organic compound and 0.30 kg of a 10 mass% solution of citric acid as the second organic compound were added thereto.

<Preparation of carrier J>

A carrier J was produced in the same manner as that for the carrier A, except that 0.45 kg of a 10 mass% solution of gluconic acid as the first organic compound and 0.60 kg of a 10 mass% solution of citric acid as the second organic compound were added thereto.

<Preparation of carrier K>

A carrier K was produced in the same manner as that for the carrier A, to which, however, the first organic compound and the second organic compounds were not added at all.

<Preparation of carrier L>

A carrier L was produced in the same manner as that for the carrier A, except that 0.60 kg of a 10 mass% solution of citric acid as the first organic compound was added thereto but the second organic compound was not added at all.

<Preparation of carrier M>

A carrier M was produced in the same manner as that for the carrier A, except that 1.80 kg of a 10 mass% solution of sucrose as the first organic compound and 0.30 kg of a 10 mass% solution of malic acid as the second organic compound were added thereto. The other steps were the same as those for the carrier

A.

<Preparation of carrier N>

A carrier N was produced in the same manner as that for the carrier A, except that the calcination temperature in the electric furnace after drying at 110°C was 700°C, and the calcination was carried out for 3 hours.

<Preparation of carrier O>

A carrier O was produced in the same manner as that for the carrier A, except that the calcination temperature in the electric furnace after drying at 110°C was 350°C, and the calcination was carried out for 3 hours.

[0064]

<Preparation of carrier P>

A carrier P was produced in the same manner as that for the carrier A, except that the calcination temperature in the electric furnace after drying at 110°C was 430°C, and the calcination was carried out for 3 hours.

[0065]

<Preparation of impregnating liquid>

Next, preparation examples for impregnating liquids are described below.

<Preparation of impregnating liquid a>

255 g of molybdenum trioxide and 101 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 95°C for 5 hours using a suitable reflux

unit so as not to reduce the volume thereof, and then dissolved with 43 g of phosphoric acid and 121 g of citric acid added thereto, thereby preparing an impregnating liquid a.

[0066]

<Preparation of impregnating liquid b>

257 g of molybdenum trioxide and 135 g of nickel carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 95°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 44 g of phosphoric acid and 135 g of citric acid added thereto, thereby preparing an impregnating liquid b.

<Preparation of impregnating liquid c>

255 g of molybdenum trioxide, 78 g of cobalt carbonate and 27 g of nickel carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 95°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 43 g of phosphoric acid and 121 g of citric acid added thereto, thereby preparing an impregnating liquid c.

<Preparation of impregnating liquid d>

201 g of molybdenum trioxide and 63 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 95°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 30 g of phosphoric acid and 75 g of citric acid added

thereto, thereby preparing an impregnating liquid d.

<Preparation of impregnating liquid e>

462 g of molybdenum trioxide and 162 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 95°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 99 g of phosphoric acid and 185 g of citric acid added thereto, thereby preparing an impregnating liquid e.

<Preparation of impregnating liquid f>

157 g of molybdenum trioxide and 40 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 95°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 39 g of phosphoric acid and 48 g of citric acid added thereto, thereby preparing an impregnating liquid f.

Hereinafter the present invention is described concretely with reference to Examples given below, but the present invention is not limited to these.

[0067]

<Example 1: Preparation of hydrogenation treatment catalyst>

1000 g of the carrier A was sprayed and impregnated with the impregnating liquid a, then dried at 200°C, and further calcined in an electric furnace at 450°C for 1 hour to produce a hydrogenation treatment catalyst (hereinafter this may be simply referred to as "catalyst", and the same shall apply to

the following Examples).

<Example 2 to Example 16: Preparation of hydrogenation treatment catalyst>

Catalysts of Example 2 to Example 16 were produced in the same manner as in Example 1, except that the kind (preparation example) of the carrier and the kind (preparation example) of the impregnating liquid prepared as previously described were combined as in Table 1 mentioned below.

[0068]

Next, comparative examples are described.

<Comparative Example 1 to Comparative Example 7: Preparation of hydrogenation treatment catalyst>

Catalysts of Comparative Example 1 to Comparative Example 7 were produced in the same manner as in Example 1, except that the kind (preparation example) of the carrier and the kind (preparation example) of the impregnating liquid prepared as previously described were combined as in Table 1 mentioned below.

<Comparative Example 8: Preparation of hydrogenation treatment catalyst>

The impregnating liquid a as in Example 1 was used, and 1000 g of the carrier A prepared in Example 1 was sprayed and impregnated with the impregnating liquid, and dried at 120°C, but thereafter this was not calcined to be a hydrogenation treatment catalyst.

The properties of the carriers prepared as above in Example 1 to Example 16 and Comparative Examples 1 to 8 are shown in Table 1A and Table 1B, and the properties of the catalysts are in Tables 2A and 2B. In Table 1A and Table 1B, the specific surface area means the specific surface area of the catalyst. In Tables 2A and 2B, the supported amount (% by mass) of each element is a value based on the catalyst as so described previously. Also the carbon amount is a value based on the catalyst.

[0069]

[Table 1A]

	Carrier Classification	Carrier Composition	First Organic Compound		Second Organic Compound		Carrier Properties					Catalyst Properties		Impregnating Liquid
			Kind	Added Amount	Kind	Added Amount	Specific Surface Area	Precursor Crystallite Diameter	IR peak ratio Sb/Sa	Carrier Alumina	γ /Boehmite Ratio	Specific Surface Area	Mean Pore Size	
	No.	mass%	Organic Substance	mass%	Organic Substance	mass%	m ² /g	Å		Crystal Morphology	%	m ² /g	Å	No.
Example 1	A	100	citric acid	2	malic acid	1	308	37	0.33	γ	98	242	78	a
Example 2	B	100	gluconic acid	2	malic acid	1	301	35	0.32	γ	100	234	83	a
Example 3	C	100	gluconic acid	4	malic acid	1	317	32	0.29	γ	96	251	75	a
Example 4	D	100	tartaric acid	2	malic acid	1	305	33	0.33	γ	95	240	79	a
Example 5	E	100	sucrose	2	malic acid	1	290	38	0.35	γ	100	217	90	a
Example 6	F	100	malic acid	2	malic acid	1	307	35	0.31	γ	99	236	77	a
Example 7	G	100	sucrose	5	malic acid	1	342	30	0.26	γ	93	259	72	a
Example 8	H	100	acetic acid	2	malic acid	1	301	33	0.34	γ	98	224	89	a
Example 9	I	100	gluconic acid	2	citric acid	1	307	34	0.31	γ	99	237	84	a
Example 10	J	100	gluconic acid	1.5	citric acid	2	322	42	0.25	γ	97	244	66	a
Example 11	A	100	citric acid	2	malic acid	1	308	37	0.33	γ	98	218	95	b
Example 12	A	100	citric acid	2	malic acid	1	308	37	0.33	γ	98	239	95	c
Example 13	A	100	citric acid	2	malic acid	1	308	37	0.33	γ	98	245	95	d
Example 14	P	100	citric acid	2	malic acid	1	315	37	0.32	γ	91	260	71	a
Example 15	P	100	citric acid	2	malic acid	1	315	37	0.32	γ	91	257	73	b
Example 16	P	100	citric acid	2	malic acid	1	315	37	0.32	γ	91	262	74	c

[0070]

[Table 1B]

	Carrier Classification	Carrier Composition	First Organic Compound		Second Organic Compound		Carrier Properties						Catalyst Properties	Impregnating Liquid
			Kind	Added Amount	Kind	Added Amount	Specific Surface Area	Precursor Crystallite Diameter	IR peak ratio Sb/Sa	Carrier Alumina	γ /Boehmite Ratio	Specific Surface Area		
	No.	mass%	Organic Substance	mass%	Organic Substance	mass%	m ² /g	Å		Crystal Morphology	%	m ² /g	Mean Pore Size	No.
Comparative Example 1	K	100	no	0	no	0	225	49	0.47	γ	100	176	119	a
Comparative Example 2	L	100	citric acid	2	no	0	248	44	0.42	γ	98	182	90	a
Comparative Example 3	M	100	sucrose	6	malic acid	1	349	27	0.22	γ	90	261	48	a
Comparative Example 4	N	100	citric acid	2	malic acid	1	211	37	0.43	γ	100	165	147	a
Comparative Example 5	O	100	citric acid	2	malic acid	1	363	37	0.30	γ^+ boehmite	87	278	62	a
Comparative Example 6	A	100	citric acid	2	malic acid	1	308	37	0.33	γ	98	179	47	e
Comparative Example 7	A	100	citric acid	2	malic acid	1	308	37	0.33	γ	98	249	126	f
Comparative Example 8	A	100	citric acid	2	malic acid	1	308	37	0.33	γ	98	272	71	a

[0071]

[Table 2A]

	Group VI Element of Periodic Table		Other Elements					H2-TPR Temperature	NO Adsorption Amount	Ig Loss	Carbon Amount
	Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount	Kind	Peak Temperature (450°C or lower)			
	Mo	mass%	Co	mass%	Ni	mass%	P	°C	ml/g	mass%	mass%
Example 1	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	400.2	9.3	1.4	0.3
Example 2	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	396.0	10.1	1.8	0.4
Example 3	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	401.8	9.8	1.2	0.9
Example 4	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	400.9	9.3	2.1	0.2
Example 5	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	410.0	9.2	1.8	0.9
Example 6	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	399.4	9.4	1.1	0.1
Example 7	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	413.5	9.9	1.9	0.7
Example 8	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	407.5	8.6	1.7	0.5
Example 9	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	395.5	9.2	1.1	0.5
Example 10	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	399.8	8.8	0.8	0.3
Example 11	MoO ₃	19	CoO	0	NiO	5.0	P ₂ O ₅	376.9	8.4	1.5	0.2
Example 12	MoO ₃	19	CoO	3.5	NiO	1.0	P ₂ O ₅	386.1	8.7	1.3	0.2
Example 13	MoO ₃	16	CoO	3	NiO	0.0	P ₂ O ₅	384.3	8.4	0.7	0.1
Example 14	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	399.8	9.5	1.6	0.1
Example 15	MoO ₃	19	CoO	0	NiO	5.0	P ₂ O ₅	379.2	8.2	1.4	0.2
Example 16	MoO ₃	19	CoO	3.5	NiO	1.0	P ₂ O ₅	381.5	8.7	1.5	0.2

[0072]

[Table 2B]

		Group VI Element of Periodic Table		Other Elements						H2-TPR Temperature		NO Adsorption Amount	Ig Loss	Carbon Amount
		Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount	Peak Temperature (450°C or lower)				
											Mo	mass%	Co	mass%
Comparative Example	1	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	2.0	419.4	8.2	2.4	0.6	
Comparative Example	2	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	2.0	392.4	7.1	3.2	1.4	
Comparative Example	3	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	2.0	422.8	6.1	1.7	1.1	
Comparative Example	4	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	2.0	421.7	7.8	1.1	0.5	
Comparative Example	5	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	2.0	420.3	8.8	2.6	1.8	
Comparative Example	6	MoO ₃	28.5	CoO	6	NiO	0	P ₂ O ₅	3.8	427.6	8.8	2.2	2.0	
Comparative Example	7	MoO ₃	13	CoO	2.0	NiO	0	P ₂ O ₅	2.0	372.1	7.6	0.5	0.2	
Comparative Example	8	MoO ₃	19	CoO	4.5	NiO	0.0	P ₂ O ₅	2.0	400.5	11.2	11.4	3.7	

<Evaluation of catalyst>

(Confirmation test for evaluation)

The catalysts of Example 1 to 16 and Comparative Examples 1 to 8 were evaluated in point of catalyst performance and catalyst regeneration performance.

(1) Confirmation test for evaluation of catalyst performance

Each catalyst was filled in a fixed bed reactor, and for activating it by releasing the oxygen atom contained in the catalyst, this was presulfurized. This treatment was carried out in the reactor where a liquid or vapor containing a sulfur compound was kept flowing therethrough under controlled conditions at a temperature of 200°C to 400°C and in a hydrogen pressure atmosphere at ordinary pressure to 100 MPa.

Next, straight light gas oil (density at 15°C, 0.8468 g/cm³; sulfur content, 1.13% by mass; nitrogen content, 0.083% by mass) was fed into the fixed bed flow reactor at a rate of 150 ml/hr for hydrodesulfurization treatment for hydrotreating. Regarding the reaction condition in this step, the hydrogen partial pressure was 4.5 MPa, the liquid hourly space velocity was 1.0 hr⁻¹, and the hydrogen oil ratio was 250 Nm³/kl. The reaction temperature was varied within a range of 300 to 385°C, and the refined oil was subjected to sulfur analysis at different temperatures falling within the range to determine the temperature at which the sulfur content in the refined oil reached 10 ppm.

[0073]

(2) Confirmation test for evaluation of catalyst regeneration performance

Catalysts were regenerated according to the following process. 100 g of the used catalyst that had been extracted after the reaction was put in a nitrogen atmosphere kept at 200°C to remove the adhering oil from the surface thereof. Subsequently, while the temperature thereof was kept at 400 to 450°C, the catalyst was calcined in an air atmosphere until the carbon amount could reach 1% by weight or less. After calcined, the catalyst was cooled and used again in the activity test.

The performance calculation method after regeneration is as follows. Regarding the test results in the activity test, the reaction speed constant was determined by Arrhenius plotting, and the regeneration rate from the fresh catalyst (unused catalyst) was calculated. Specifically, after sulfurization in a hydrogen sulfide flow, the catalyst was hydrodesulfurized under the condition described in the above (1). From the sulfur concentration change in the hydrocarbon oil before and after passing through the reactor, the reaction speed constant was determined based on the following equation (1). The ratio by percentage of the reaction speed constant (K_n) of the regenerated catalyst to the reaction speed constant (K_{n0}) of the unused catalyst ($(K_n/K_{n0}) \times 100$ [%]) is referred

to as the relative activity.

$$Kn = LHSV \times 1/(n-1) \times (1/S^{n-1} - 1/S_0^{n-1}) \quad \text{Equation (1)}$$

wherein:

Kn: reaction speed constant

n: what exponent (n) of the sulfur concentration in the crude oil is proportional to the desulfurization speed (1.5 for LGO)

S: sulfur concentration (%) in processed oil

S₀: sulfur concentration (%) in crude oil

LHSV: liquid hourly space velocity (hr⁻¹)

The results of the confirmation test are shown in Table 3.

[0074]

[Table 3]

		Evaluation	
		Catalyst Performance	Regeneration Performance
		HDS Activity	
		°C (10 ppm achieving temperature)	% (to fresh catalyst)
Example	1	352	95
Example	2	348	92
Example	3	349	94
Example	4	353	93
Example	5	356	90
Example	6	347	94
Example	7	346	93
Example	8	349	86
Example	9	352	95
Example	10	355	87
Example	11	357	94
Example	12	357	93
Example	13	360	96
Example	14	349	96
Example	15	354	92
Example	16	356	93
Comparative Example	1	365	92
Comparative Example	2	363	87
Comparative Example	3	373	93
Comparative Example	4	369	96
Comparative Example	5	365	78
Comparative Example	6	362	91
Comparative Example	7	379	97
Comparative Example	8	340	59

(Properties of catalyst and evaluation results of confirmation test)

In Example 1 to 16, the properties of the catalysts all have suitable values. As opposed to these, in Comparative Examples 1 and 4, the proportion of the OH group in the carrier is more than the upper limit of 0.40, and the catalyst surface area is lower than the lower limit of the suitable range 200 m²/g, and the mean pore size of the catalyst does not fall within a suitable range. Also in Comparative Example 2, the

proportion of the OH group in the carrier is more than the upper limit of 0.40, and though the mean pore size is in a suitable value range, the catalyst surface area is lower than the lower limit of the suitable range 200 m²/g.

In Comparative Example 1, in addition, the crystallite size of the carrier alumina precursor is more than the upper limit of the suitable range 45 Å. In Comparative Example 3, the catalyst surface area is large but the mean pore size is lower than the lower limit of the suitable range, and therefore the active metals were loaded unsuitably and the nitrogen monoxide adsorption amount is the lower limit of the suitable range. In Comparative Example 5, the crystal morphology of the carrier alumina unfavorably contains a different one than the γ -state. In Comparative Examples 6 and 7, the amount of the supported active metals is not within an optimum range. In Comparative Example 8, the ignition loss is remarkably more than the upper limit of the suitable range 5% by weight, and in addition, the contained carbon amount is more than the upper limit of the suitable range 2% by weight.

In Example 1 to Example 16, the temperature at which the sulfur content in the refined oil, which is an index of catalyst performance, reaches 10 ppm is not higher than 360°C, and the relative activity that is an index of catalyst regeneration performance is not less than 80%. As opposed to these, in Comparative Examples 5 and 8, the catalyst regeneration

performance is poor, in Comparative Examples 1 to 7, the catalyst performance is poor, and in Comparative Example 5, both catalyst performance and catalyst regeneration performance are poor.

<<Second Embodiment>>

[Regarding hydrogenation treatment catalyst for hydrocarbon oil]

The hydrogenation treatment catalyst for hydrocarbon oil of the second embodiment of the present invention (hereinafter referred to as "the catalyst of the present invention") contains a carrier of γ -alumina mixed with foreign element metals (hereinafter this may be referred to as an inorganic composite oxide carrier or simply as a carrier) and active metal components, and has predetermined properties. Hereinafter the inorganic composite oxide carrier, the active metal components and the properties of the catalyst are described in detail.

<Inorganic composite oxide carrier>

The inorganic composite oxide carrier to constitute the hydrogenation treatment catalyst includes various inorganic substances that are known as ones usable for catalysts of the type. The inorganic composite oxide carrier is an inorganic composite oxide mainly consisting of aluminum except impurities, in which the crystal morphology of alumina is in a state grouped in γ -alumina, and examples of the other

inorganic components constituting the carrier include various composite oxides with at least one selected from phosphorus, silica-titania, zirconia, boria, magnesia, etc. In other words, the composite oxide includes aluminum and at least one or more elements selected from phosphorus, silicon, titanium, zirconium, boron and magnesium.

[0075]

Specific examples of the composite oxide include, though not limited thereto, aluminum-silicon, zeolite, aluminum-titanium, aluminum-phosphorus, aluminum-boron, aluminum-magnesium, aluminum-zirconium, aluminum-titanium-phosphorus, etc. The properties and the morphologies of the inorganic composite oxide carrier can be adequately selected depending on various conditions such as the kind and the composition of the metal components to be loaded, and use of the catalyst.

In order that the active metal components could be effectively loaded on a carrier in a high dispersion state so as to sufficiently secure catalyst activity, in general, a porous carrier is used, and those having relatively small pores having a pore size of 500 Å or less are preferably used. For controlling the physical properties such as the mechanical strength, the heat resistance and the like of the carrier and the catalyst body, adequate binder and additives may be added in forming the carrier or the catalyst body.

[0076]

The carrier of the catalyst of the present invention is such that the ratio of the absorbance of the spectral peak Sb in a wavenumber range of 3770 to 3774 cm^{-1} corresponding to the basic OH group to the absorbance of the spectral peak Sa in a wavenumber range of 3674 to 3678 cm^{-1} corresponding to the acidic OH group therein, as measured with a transmission Fourier transform IR spectrophotometer, the ratio of Sb/Sa is in a range of 0.20 to 0.45. The ratio of Sb/Sa is more preferably within a range of 0.20 to 0.40. It is known that the dispersibility of active metals varies depending on the characteristics of the carrier surface, and when the ratio of Sb/Sa is in the above-mentioned range, high dispersibility of active metals on the carrier surface can be especially remarkably seen. As a result, the catalyst can have high desulfurization performance, and therefore, the ratio is preferably controlled to be in the above range. Fig. 1 shows examples of optical absorption spectra including a wavenumber range of 3674 to 3678 cm^{-1} corresponding to the acidic OH group and a wavenumber range of 3770 to 3774 cm^{-1} corresponding to the base OH group of carrier of the catalyst of the present invention. Fig. 1 shows the optical absorption spectra of the carriers of Examples given below, and (1) to (4) correspond to the carriers L, A2, F and A, respectively.

[0077]

In preparing the carrier of the catalyst of the present invention, the process for producing the main component alumina includes a calcination step for preparing γ -alumina via a pseudo-boehmite crystal state, and the alumina is characterized in that the crystallite diameter obtained from the half-value width of the XRD diffraction spectral (020) peak of the pseudo-boehmite of the alumina precursor (before calcination) is 15 to 40 Å. It is important to control the crystallite size of the pseudo-boehmite for optimizing the pore structure of the inorganic composite oxide carrier and since the crystallite size may have some influence on the difficulty level in crystal dislocation in the subsequent calcination process and on the dispersibility of foreign element metals. In the case where the crystallite size is more than 40 Å, the mean pore diameter is small and the specific surface area is large, and such is unfavorable since the catalyst performance may lower. In addition, since crystal dislocation could hardly occur during calcination, a boehmite structure may remain in the crystal morphology of the alumina carrier, and such is also unfavorable as there may occur a risk of damaging the stability of catalyst performance. Furthermore, such is unfavorable since the dispersibility of foreign element metals in the inorganic composite oxide carrier is low and since the effect of foreign element metals could not be sufficiently exhibited. In the case where the

crystallite size is smaller than 15 Å, such is also unfavorable because, though the specific surface area is large and the dispersibility of foreign element metals is high, but on the contrary, the mean pore size is small and therefore it becomes difficult to load the active metal component.

[0078]

In the case where a composite oxide of, for example, aluminum and phosphorus, silicon, titanium or zirconium is used as the inorganic composite oxide for the hydrogenation treatment catalyst for hydrocarbon oil of the present invention, the content of aluminum and others is described. The content of aluminum in the carrier is preferably 80% or more in terms of aluminum oxide (Al_2O_3) (80 parts by mass or more in terms of aluminum oxide (Al_2O_3) relative to 100 parts by mass of the carrier). When the content of aluminum in terms of oxide is less than 80% by mass, the catalyst tends to degrade rapidly.

[0079]

The content of phosphorus in the carrier is preferably 5.0% by mass or less in terms of phosphorus oxide (P_2O_5) (5.0 parts by mass in terms of phosphorus oxide (P_2O_5) relative to 100 parts by mass of the carrier). When the phosphorus content is excessively too large, the carrier pore size distribution may be broad and, in addition, the ratio of surface OH groups Sb/Sa may be lower than the predetermined range therefore

tending to lower desulfurization performance.

[0080]

The silicon content in the carrier is preferably 3.0% by mass or less in terms of silicon oxide (SiO_2) (3.0 parts by mass or less in terms of silicon oxide (SiO_2) relative to 100 parts by mass of the carrier). When the silicon content is excessively too large, silica may aggregate so that the carrier pore size distribution may be broad, therefore tending to lower desulfurization performance.

[0081]

The titanium content in the carrier is preferably 18.0% by mass or less in terms of titanium oxide (TiO_2) (18.0 parts by mass or less in terms of silicon oxide (TiO_2) relative to 100 parts by mass of the carrier). When the titanium content in terms of oxide is excessively too large, the carrier pore size may be insufficient and the pore size distribution may be broad, therefore tending to lower desulfurization performance.

[0082]

The zirconium content in the carrier is preferably 9.0% by mass or less in terms of zirconium oxide (ZrO_2) (9.0 parts by mass or less in terms of zirconium oxide (ZrO_2) relative to 100 parts by mass of the carrier). When the zirconium content is excessively too large, the carrier pore size distribution may be broad, and in addition, the ratio of the

surface OH groups Sb/Sa may be larger than the predetermined range, therefore tending to lower desulfurization performance.

[0083]

<Active metal components>

As active metal components, a first metal component of, for example, molybdenum and a second metal component of, for example, cobalt are loaded on the inorganic composite oxide carrier.

The first metal component may be tungsten in place of molybdenum, and may be both molybdenum and tungsten. It is necessary that the content (supported amount) of the first metal component is 15 to 27% by mass in terms of oxide based on the catalyst (15 to 27 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst).

[0084]

When the content of the first metal component is too excessively smaller than 15% by mass in terms of oxide, desulfurization activity necessary for reaction could not be secured, but when too excessively larger than 27% by mass, the metal components may readily aggregate to detract from dispersibility thereof.

The second metal component may be nickel in place of cobalt, or may be both cobalt and nickel. It is necessary that the content (supported amount) of the second metal component

is 2 to 7% by mass in terms of oxide based on the catalyst (2 to 7 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst). The second metal component acts as a promoter for the first metal component, and when the oxide-equivalent content thereof is smaller than 2% by mass, the first component and the second component that are the active metal components could hardly maintain a suitable structure, and when the oxide-equivalent content thereof is more than 7% by mass, the active metal components may readily aggregate to worsen the catalyst performance.

[0085]

In the case where the active metal components are loaded by the inorganic composite oxide carrier according to an impregnation method, an organic acid is generally contained in the impregnating liquid, and the organic acid is a supply source for carbon to be loaded by the alumina carrier. Examples of the organic acid for use for the active metal components include citric acid, malic acid, gluconic acid, tartaric acid, ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Citric acid, malic acid, tartaric acid and gluconic acid are more preferred. In the case where an organic additive such as, for example, saccharides (monoses, dioses, polyoses, etc.) and the like are used in addition to the organic acid, the content of the organic acid-derived carbon as referred to in this description is the

content of carbon derived from both the organic acid and the organic additive.

[0086]

<Properties of catalyst>

The catalyst of the present invention is needed to have a specific surface area (SA), as measured according to the BET (Brunauer-Emmett-Teller) method, falling within a range of 180 to 320 m²/g, preferably 190 m²/g or more, more preferably 200 m²/g or more. When the specific surface area (SA) is smaller than 180 m²/g, such is unfavorable since the metal components may readily aggregate and since the desulfurization performance may lower. On the other hand, when larger than 320 m²/g, such is also unfavorable since the mean pore size and the pore volume may be small and the desulfurization activity tends to lower.

The mean pore size is needed to be 50 to 110 Å. The mean pore diameter is a value measured according to a mercury intrusion method (mercury contact angle: 130 degrees, surface tension: 480 dyn/cm), and means the pore diameter corresponding to 50% of the entire pore volume. The pore volume represents the volume of a pore having a pore diameter of 41 Å or more. When the mean pore size is smaller than 50 Å, the desulfurization performance may lower, but when the mean pore size is larger than 110 Å, the catalyst strength may lower.

[0087]

Of the catalyst of the present invention, the ignition loss (Ig Loss) is 5.0% by mass or less. The ignition loss is calculated according to the measurement method described in the following section, in which the catalyst is heated at a high temperature. In order that the ignition loss of the catalyst can be 5.0% by mass or less, it is necessary that the inorganic composite oxide carrier is, after sprayed with an impregnating liquid, calcined at a temperature of, for example, 300°C or higher.

When the ignition loss of the catalyst is made to be 5.0% by mass or less, the activity of the regenerated catalyst can be 85% or more, based on the desulfurization performance of the new and unused catalyst (fresh catalyst), 100%. When the ignition loss of the catalyst is large, there may be a risk of aggregation of active metal components in the calcination step in catalyst regeneration.

When the content of carbon derived from an organic acid in the catalyst is 2.0% by mass or less based on the catalyst and on an elemental basis, the activity in catalyst regeneration can be 85% or more, based on the desulfurization performance of the new and unused catalyst (fresh catalyst), 100%. When the carbon content is large, there is a risk of aggregation of active metal components in the calcination step in catalyst regeneration.

[0088]

The peak temperature of released water from the catalyst of the present invention in a range of up to 450°C (the temperature at which the water release spectrum peak appears), according to a temperature-programed-reduction method for catalyst, is 415°C or lower. A specific example of the temperature-programed-reduction method is described hereinafter. In general, sulfurization is carried out with hydrogen sulfide or the like in the presence of molybdenum in a hydrogen stream, and for the reaction, oxygen must remove from molybdenum oxide. The water release peak is to just detect the release of water with oxygen from the molybdenum oxide, and therefore it is considered that the sulfurization procedure and the molybdenum reduction temperature would have some correlation therebetween. Accordingly, by lowering the peak temperature of released water, it is considered that sulfurization with molybdenum could be promoted sufficiently.

[0089]

In the case where the reduction temperature is too high, that is, where the peak temperature of released water is too high, water may weakly interact with the composite oxide carrier and therefore there is a high probability that active metal aggregates may exist. As a result, the sulfurization step could not be sufficiently attained. Accordingly, it is necessary to lower the reduction temperature so as to reduce the interaction between water and the inorganic composite

oxide carrier for attaining high dispersion of active metals.

[0090]

Released water is formed mainly in the molybdenum reduction step, and the peak temperature thereof varies depending on the carrier composition, the active metal composition, etc. According to the present inventors' knowledge, it is necessary that, in order that the water release peak temperature (peak temperature of released water) could be 415°C or lower, at least one kind (one species) of molybdenum and tungsten is, as the active metal component thereon, needed to be present on the inorganic composite oxide carrier in an amount of 15 to 27% by mass in terms of oxide, and at least one kind (species) of cobalt and nickel is needed to be present thereon in an amount of 2 to 7% by mass in terms of oxide.

In the case where the amount of the active metal components is smaller than the range, such is unfavorable since the catalyst performance is poor; but in the case where the amount of the active metal components is larger than the range, such is also unfavorable since aggregates of active metals may form to worsen the dispersibility thereof.

[0091]

The catalyst of the present invention is such that the adsorption amount of nitrogen monoxide on the sulfurized catalyst is 8.0 ml/g or more. The adsorption amount is more preferably 8.5 ml/g or more. Based on the nitrogen monoxide

molecule adsorption amount, the reaction active sites of the catalyst can be measured.

In the case where the nitrogen monoxide adsorption amount is less than 8.0 ml/g, falling outside the present invention, such is unfavorable since the number of the reaction active sites of the catalyst is small and the catalyst performance improvement could not be attained.

The nitrogen monoxide adsorption amount on the catalyst after sulfurization varies depending on the physical properties and chemical properties of the carrier and on the active metal composition, etc. For nitrogen monoxide adsorption, sulfurization is necessary, and therefore, the reduction temperature of the active metals must be lowered down to a certain temperature or lower.

[0092]

According to the present inventors' knowledge, the following are important for controlling the carbon monoxide adsorption amount to be 8.0 ml/g or more.

a) The specific surface area (SA) of the inorganic composite oxide carrier is in a range of 180 to 320 m²/g.

b) The inorganic composite oxide carrier contains aluminum in an amount of 80 to 98 parts by mass in terms of alumina relative to 100 parts by mass of the inorganic composite oxide carrier.

c) The crystallite diameter of the pseudo-boehmite of

alumina to be the main component in the carrier precursor is, as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof, 15 or more and 40 or less Å.

d) It is important that, as active metal components, at least one of molybdenum and tungsten is present on the inorganic composite oxide carrier in an amount of 15 to 27% by mass in terms of oxide, and at least one of cobalt and nickel is thereon in an amount of 2 to 7% by mass in terms of oxide.

In addition, d) it is desirable that the ratio of the absorbance of the spectral peak Sb in a wavenumber range of 3770 to 3774 cm^{-1} corresponding to the basic OH group to the absorbance of the spectral peak Sa in a wavenumber range of 3674 to 3678 cm^{-1} corresponding to the acidic OH group, as measured with a transmission Fourier transform IR spectrophotometer, the ratio of Sb/Sa is in a range of 0.20 to 0.45, and that the water release peak temperature is 415°C or lower.

[0093]

[Production method for hydrogenation treatment catalyst for hydrocarbon oil]

Next, a production method for the hydrogenation treatment catalyst for hydrocarbon oil of the present invention is described.

The production method for the hydrogenation treatment catalyst for hydrocarbon oil of the present invention

includes:

a first step of preparing an inorganic composite oxide carrier,

a second step of preparing an impregnating liquid that contains a first metal component of at least one of molybdenum and tungsten and a second metal component of at least one of cobalt and nickel, and an organic acid, and making the first metal component and the second metal component by the inorganic composite oxide carrier, and

a third step of heat-treating the alumina carrier on which the first metal component and the second metal component have been loaded, as obtained in the second step, at a temperature of 100 to 600°C to produce a hydrogenation treatment catalyst.

[0094]

The steps are described below.

<First step>

<<1-1. Step of preparing inorganic composite oxide slurry>>

First, an aqueous solution of a basic metal salt and an aqueous solution of an acidic metal salt are mixed so as to have a pH of 6.5 to 9.5, preferably 6.5 to 8.5, more preferably 6.8 to 8.0, thereby preparing an inorganic composite oxide hydrate. In this stage, the aqueous solution of a basic metal salt preferably contains a carboxylate. After the inorganic composite oxide hydrate slurry is aged according to a desired

method (first aging step), this is washed to remove by-product salts to thereby give a composite oxide slurry that contains an alumina as the main component.

The carboxylate to be used here includes salts of polyacrylic acid, hydroxypropyl cellulose, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, maleic acid, gluconic acid, fumaric acid, phthalic acid, citric acid, etc. The carboxylate is preferably added in an amount of 0.5 to 4.0 parts by mass relative to 100 parts by mass of alumina.

For obtaining an inorganic composite oxide hydrate containing any other element than aluminum, an aqueous acidic solution or an aqueous basic solution is previously mixed with a aqueous aluminum salt solution, and then these are mixed so as to have a pH falling within the above range depending on the pH of the metal salt to be used, thereby producing an inorganic composite oxide hydrate.

[0095]

The basic aluminum salt for use herein is preferably sodium aluminate, potassium aluminate, etc. The acidic aluminum salt for use herein is preferably aluminum sulfate, aluminum chloride, aluminum nitrate, etc. As the phosphate source, a phosphate compound that contains a phosphite ion and can produce a phosphate ion in water is usable, such as ammonium phosphate, potassium phosphate, sodium phosphate, phosphorus

acid, phosphorous acid, etc. Examples of the titanium mineral acid salt include titanium tetrachloride, titanium trichloride, titanium sulfate, titanyl sulfate, titanium nitrate, etc., and in particular, titanium sulfate and titanyl sulfate are preferably used as inexpensive.

[0096]

In mixing the above-mentioned two kinds of aqueous metal salt solutions, they are kept heated generally at 40 to 90°C, preferably 50 to 70°C, and the mixed aqueous solution heated at the temperature of the solution $\pm 5^{\circ}\text{C}$, preferably at $\pm 2^{\circ}\text{C}$, more preferably $\pm 1^{\circ}\text{C}$ is continuously added so as to have a pH of 6.5 to 9.5, preferably 6.5 to 8.5, more preferably 6.5 to 8.0, generally for 5 to 20 minutes, preferably 7 to 15 minutes thereby forming a precipitate to give a hydrate slurry.

In the case where the time to be taken for adding the aqueous basic metal salt solution to the aqueous mixed solution is too long, unfavorable crystals of bayerite, gibbsite and the like may form in addition to pseudo-boehmite, and therefore the time is preferably 15 minutes or less, more preferably 13 minutes or less. Bayerite and gibbsite are unfavorable as causing specific surface area reduction in heat treatment.

[0097]

<<1-2. Second aging step for inorganic composite oxide>>

At least one organic compound (first organic compound) is added to the hydrate slurry obtained in the previous step

1-1, and heated and aged in an aging tank equipped with a reflux unit, at 30°C or higher, preferably 80 to 100°C for about 1 to 20 hours, preferably 2 to 10 hours (second aging step). In the first aging stage and the second aging stage, the inorganic composite oxide concentration is preferably less than 20% (20% by weight).

<<1-3. Kneading/shaping and drying step>>

The aged product obtained in the previous step 1-2 is put into a steam-jacketed two-arm kneader and heated and kneaded to be a shapeable kneaded product, and this is shaped through extrusion to be in a desired form. In this step, at least one second organic additive may be added after the kneaded product is heated and concentrated to have an inorganic composite oxide concentration of 20% (20% by weight) or more, and then further heated and kneaded. Regarding the timing of adding the second organic compound, the compound may be added during concentration of the aged product.

[0098]

<<1-4. Heat-treating (drying, calcination) step>>

The shaped product obtained in the previous step 1-3 is then heated and dried at, for example, 70 to 150°C, preferably 90 to 130°C, and further calcined, for example, preferably at 400 to 800°C, more preferably 400 to 600°C, and for example, for 0.5 to 10 hours, preferably 2 to 5 hours to give an alumina carrier.

The first organic compound and the second organic compound for use in the first step are preferably at least one selected from organic acids and saccharides. The organic acids include citric acid, malic acid, tartaric acid, gluconic acid, acetic acid, ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). The saccharides include monoses, dioses, polyoses, etc. For both the first organic compound and the second organic compound, the amount thereof to be added is preferably in a range of 0.5 to 5.0 parts by mass relative to 100 parts by mass of the inorganic composite oxide. In the case where the amount added is smaller than the range, the effect of adding the organic compound could hardly be obtained, but in the case where the amount is larger than the range, the pore structure would be too small owing to the too strong effect of the compound, and therefore such are unfavorable since not only the physical properties of the catalyst could not be in an optimum range but also the production efficiency worsens.

[0099]

The OH group on the carrier surface is an important factor that has an influence on the loading condition of active metals, such as the dispersibility of active metal species. Controlling the OH group may be carried out anytime in the carrier preparation process along with controlling the inorganic composite oxide carrier composition and the

crystallinity of the carrier alumina precursor therein. However, it is extremely difficult to control the OH group while maintaining the physical properties of the carrier. To satisfy it, it is desirable to adequately define the inorganic composite oxide carrier composition. In addition to it, it may also be possible, though a little, to carry out the OH group control in a separate step after crystallinity control. Consequently, it is preferable that, after the crystallinity is controlled in the second aging step, an organic compound (second organic compound) is added in the kneading/concentrating step to control the OH group state.

[0100]

<Second step>

An impregnating liquid that contains the above-mentioned first metal component, second metal component and carbon component is brought into contact with the inorganic composite oxide carrier.

As the raw material for the first metal component, for example, molybdenum trioxide, ammonium molybdate, ammonium metatungstate, ammonium paratungstate, tungsten trioxide and the like are preferably used. As the raw material for the second metal component, nickel nitrate, nickel carbonate, cobalt nitrate, cobalt carbonate and the like are preferably used.

In the case where phosphorus is made loaded by the

composite oxide carrier, orthophosphoric acid (hereinafter this may be simply referred to as "phosphoric acid"), ammonium dihydrogenphosphate, diammonium hydrogenphosphate, trimetaphosphoric acid, pyrophosphoric acid, tripolyphosphoric acid and the like may be used.

In the impregnating liquid, preferably, the metal components are dissolved using an organic acid at pH of 4 or less. When the pH is more than 4, the stability of the dissolved metal components may lower and the components tend to precipitate out. Examples of the organic acid include citric acid, malic acid, tartaric acid, ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), and in particular, citric acid and malic acid are preferably used. The organic additive includes saccharides (monoses, dioses, polyoses, etc.). An organic additive, for example, glucose ($C_6H_{12}O_6$), fructose ($C_6H_{12}O_6$), maltose ($C_{12}H_{22}O_{11}$), lactose ($C_{12}H_{22}O_{11}$), sucrose ($C_{12}H_{22}O_{11}$) or the like may be added to the organic acid.

[0101]

<Third step>

The carrier on which the metal components have been loaded, as obtained by bringing the carrier into contact with the impregnating liquid in the second step, is heat-treated at 100 to 600°C, preferably 110 to 600°C, more preferably 400 to 600°C, for 0.5 to 10 hour, preferably 1 to 8 hours, and then

the hydrogenation treatment catalyst of the present invention is produced. When the calcination temperature is excessively lower than 100°C, the processability may worsen owing to the residual water and, in addition, the metal components could not be uniformly loaded, and when the temperature is excessively higher than 600°C, the metals may aggregate and the dispersion maintaining effect for the metals could not be expected. Anyhow, such lower or higher temperatures are unfavorable.

[0102]

One advantage in the first to third steps is described. In the second aging step for the inorganic composite oxide in the first step, an organic compound (first organic compound) is added to the hydrate slurry and this is then heated and aged. According to this treatment, the crystallite diameter of the pseudo-boehmite of a precursor of alumina, which is the main ingredient in the inorganic composite oxide, can be controlled to be 40 Å or less, and therefore the specific surface area can be increased while adequately regulating the pore structure of the carrier. Further, crystal dislocation during calcination runs on readily and therefore a boehmite structure hardly remains in the crystal morphology and the catalyst performance can be thereby stabilized. In addition, the dispersibility of foreign element metals in the composite oxide carrier can be increased, therefore contributing toward

sufficiently exhibiting the foreign element metals addition effect.

[0103]

[Regarding hydrogenation treatment method for hydrocarbon oil]

Examples of the hydrocarbon oil that is to be desulfurized using the hydrogenation treatment catalyst of the present invention include straight kerosene or straight light gas oil obtained from an atmospheric crude oil distillation apparatus, reduced pressure light gas oil or reduced pressure heavy light oil obtained through treatment of straight heavy oil or residual oil as obtained from an atmospheric distillation apparatus in a reduced pressure distillation apparatus, hydrocracked kerosene or hydrocracked light gas oil obtained through hydrocracking desulfurized heavy oil, hydrocracked kerosene or hydrocracked light gas oil obtained through hydrocracking of reduced pressure heavy light oil or desulfurized heavy oil, thermal-cracked kerosene or thermal cracked light gas oil obtained from a thermal cracking apparatus such as a coker or the like, and the hydrocarbon oil is a fraction that contains a fraction having a boiling point of 180 to 390°C in an amount of 80% by volume or more. Regarding the hydrogenation treatment using the catalyst, the catalyst is filled in a fixed bed reactor, and in a hydrogen atmosphere, hydrocarbon oil is hydrogenated therein under

high-temperature and high-pressure conditions. As one example of the treatment condition, the hydrogen pressure is 3 to 8 MPa, the temperature is 260 to 420°C, and the liquid (hydrocarbon oil of a liquid to be treated) hourly space velocity is 0.3 to 5 hr⁻¹.

[0104]

[Regarding measurement method]

As described hereinafter, the hydrogenation treatment catalysts in Examples and Comparative Examples given herein are numerically analyzed in point of the content of each constituent component, the specific surface area and the properties thereof, and the measurement methods for these are described below.

<Measurement method for content of carrier components (alumina, phosphorus, silica, titania, zirconia) and metal components (molybdenum, cobalt, nickel, phosphorus)>

3 g of a sample to be analyzed was put into a zirconia bowl with a lid having a capacity of 30 ml, then heat-treated (200°C, 20 minutes) and calcined (700°C, 5 minutes), and thereafter 2 g of Na₂O₂ and 1 g of NaOH were added thereto and melted for 15 minutes. Further, 25 ml of H₂SO₄ and 200 ml of water were added and dissolved, and then this was diluted with pure water to be 500 ml, thereby preparing a sample. Using an ICP apparatus (manufactured by Shimadzu Corporation, ICPS-8100, analysis software ICP-8000), the resultant sample

was analyzed to determine the content of each constituent component in terms of oxide (Al_2O_3 , P_2O_5 , SiO_2 , TiO_2 , ZrO_2 , MoO_3 , NiO , CoO).

[0105]

<Method for identification of alumina crystal morphology and method for measurement of crystallite size>

A sample to be analyzed was compressed onto a laboratory non-reflecting plate to prepare an observation sample, and the crystal morphology thereof was identified through X-ray diffractometry using an X-ray diffractometer (manufactured by Rigaku Corporation: RINT 2100). The crystallite size of the carrier alumina precursor was calculated according to a Scherrer method from the (020) plane attributed to boehmite, and the crystal structure of the calcined carrier was determined by comparing the diffraction peaks attributed to boehmite and γ -alumina. A major part of the inorganic composite oxide carrier of the present invention is preferably γ -alumina. Specifically, when the diffraction peak area indicating the crystal structure of the (020) plane of boehmite measured through X-ray diffractometry is referred to as P1, the diffraction peak area indicating the aluminum crystal structure of the (440) plane is as P2, the ratio of P2 to the total of P1 and P2, $P2/(P1 + P2)$ is needed to be 0.9 or more. It may also be said that P2 is 9 times or more of P1 ($9 \leq (P2/P1)$). When the boehmite structure exists much in the carrier crystal,

such is unfavorable since not only the carrier properties are difficult to control but also the catalyst strength may lower.

[0106]

Here, the diffraction peak indicating the crystal structure of the (020) plane and the (120) plane of boehmite is detected at $2\theta = 14^\circ$ and $2\theta = 28^\circ$, and the diffraction peak indicating the aluminum crystal structure attributed to the (440) plane of γ -alumina is detected at $2\theta = 67^\circ$.

The calculation method for the diffraction peak area is as follows. The graph of X-ray diffraction analysis obtained using an X-ray diffractometer is fitted according to the least-square method and the baseline is corrected, and the height from the maximum peak value to the baseline is measured (peak strength W), then the peak width (half-value width) at the half value of the resultant peak strength ($1/2W$) is determined, and the product of the half-value width and the peak strength is referred to as the diffraction peak area. From the resultant diffraction peak area data, "boehmite diffraction peak area/ γ -alumina diffraction peak area" is calculated.

[0107]

<Measurement method for OH group on carrier surface>

Using a transmission Fourier transform IR spectrophotometer (manufactured by JASCO Corporation: FT-IR/6100), the maximum peak wavenumber of acid OH group, the

absorbance at the wavenumber, the maximum peak wavenumber of basic OH group, and the absorbance at the wavenumber were determined.

(Measurement method)

20 mg of a sample was filled in a shaping vessel (inner diameter 20 mm ϕ) and compressed under pressure of 4 ton/cm² (39227 N/cm²) to be shaped into a thin disc. The shaped product was kept under a condition at a vacuum degree of 1.0×10^{-3} Pa or less and at 500°C for 2 hours, and then cooled down to room temperature, and the absorbance thereof was measured.

Specifically, using a TGS detector, the sample was analyzed at a resolution of 4 cm⁻¹ and for an integration frequency of 200 times, and the baseline was corrected in a wavenumber range of 3000 to 4000 cm⁻¹. The absorbance was converted per the unit mass. The absorbance per unit mass (g⁻¹) = absorbance/mass of shaped product.

Of every sample in Examples 1 to 19 given hereinafter, the wavenumber at the maximum peak position of the absorption spectrum corresponding to the acidic OH group in a range of 3674 to 3678 cm⁻¹, and the wavenumber at the maximum peak position of the absorption spectrum caused by the basic OH group in a range of 3770 to 3774 cm⁻¹.

[0108]

<Measurement method for specific surface area>

About 30 ml of a sample to be analyzed was weighed in

a porcelain crucible (B-2 type), heat-treated at a temperature of 300°C for 2 hours, then put in a desiccator, and cooled down to room temperature to prepare a sample for measurement. Next, 1 g of the sample was weighed, and the specific surface area (m²/g) thereof was measured according to the BET method using an automatic surface area measuring apparatus (manufactured by Yuasa Ionics Corporation, Multisorb 12 Model).

<Measurement method for ignition loss>

A catalyst of a sample to be analyzed was calcined at 570°C for 2 hours, and from the mass reduction by calcination, the ignition loss of the sample was calculated.

[0109]

<Method for measurement of peak temperature of released water according to temperature-programmed reduction method>

In a temperature-programmed reduction method, using a catalyst analyzer manufactured by Microtrac BEL Corporation (BEL CAT-A), 0.05 g of a catalyst that had been granulated in a size of 250 to 710 μm was pretreated in a helium gas stream at 120°C for 1 hour, then the ambient gas was changed to a hydrogen gas (99.99%), and the catalyst was heated from 50°C up to 900°C at a rate of 10°C/min. The water release spectrum in heating was measured using a quadrupolar mass analyzer manufactured by Pfeiffer Vacuum Corporation (m/z : 18.34), and on the resultant release spectrum, the water release peak temperature was read.

Fig. 2 shows graphs of examples of the results of analysis of the peak temperature of released water according to the temperature-programed-reduction method. The abscissa shows a temperature, and the ordinate shows a detected current of the quadrupolar mass analyzer. The solid line corresponds to Example 3 to be mentioned below, and the dotted line corresponds to Comparative Example 5 mentioned below.

<Measurement method for nitrogen monoxide adsorption amount>

For measurement of the nitrogen monoxide adsorption amount, an automatic catalyst gas adsorption amount measuring apparatus (manufactured by Okura Riken Corporation) was used. A mixed gas of helium gas and nitrogen monoxide gas (nitrogen monoxide gas concentration, 10% by volume) was pulsewise applied to a sulfurized hydrogenation treatment catalyst, and the nitrogen monoxide molecule adsorption amount per gram of the hydrogenated catalyst was measured. Specifically, about 0.02 g of the catalyst ground to have a size of 60 meshes or less was weighed, this was filled in a quartz cell, the catalyst was heated up to 360°C, and a gas of hydrogen sulfide 5 vol%/hydrogen 95 vol% was applied thereto at a flow rate of 0.2 liter/min for sulfurization for 1 hour. Subsequently, this was kept at 340°C for 1 hour, and the physically-adsorbed hydrogen sulfide was discharged out of the system. Afterwards, nitrogen monoxide molecules were adsorbed using a mixed gas of helium gas and nitrogen monoxide gas at 50°C, and the nitrogen

monoxide molecule adsorption amount was measured.

[0110]

[Examples]

Preparation examples for inorganic composite oxide carrier, preparation examples for impregnating liquid, preparation examples for hydrogenation treatment catalyst that are examples of the present invention using inorganic composite oxide carrier and impregnating liquid, and preparation examples for hydrogenation treatment catalyst that are comparative examples using inorganic composite oxide carrier and impregnating liquid are described below.

First, carrier preparation examples are described.

[0111]

<Preparation of carrier A>

a) 7.23 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 39.8 kg of ion-exchanged water, and then 4.5 kg of a sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 was added thereto with stirring, and this was heated up to 60°C with stirring to prepare a basic aluminum salt mixed aqueous solution. In addition, 11.37 kg of an aqueous aluminum sulfate solution having a concentration of 7% by mass in terms of Al_2O_3 was diluted with 20.46 kg of ion-exchanged water to prepare an aqueous aluminum sulfate

solution and this was kept heated at 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous aluminum sulfate solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry A containing phosphorus and alumina. Subsequently, this hydrate slurry was aged at 60°C for 60 minutes with stirring.

b) Next, the aged alumina hydrate slurry was dewatered, and then washed with 120 L of an aqueous ammonia solution having a concentration of 0.3% by mass.

c) After washed, the cakey slurry was diluted with ion-exchanged water so as to have a concentration, in terms of Al_2O_3 , of 10% by mass and was thus made into a slurry, and then 0.50 kg of a solution of 10 mass% citric acid as the first organic compound was added thereto, and thereafter aqueous ammonia having a concentration of 15% by mass was added for pH control to 10.3, and this was aged at 95°C for 10 hours with stirring.

d) After aged, the slurry was dewatered and concentrated and kneaded to have a predetermined water content while heated with a steam-jacketed two-arm kneader.

e) Subsequently, the resultant kneaded product was shaped into a column having a diameter of 1.6 mm, using a screw-type extruder.

f) Next, this was dried at 110°C for 12 hours, and then calcined at 500°C for 3 hours to give a carrier A for hydrogenation treatment catalyst.

[0112]

<Preparation of carrier B>

a) 7.39 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 41.0 kg of ion-exchanged water, and then 2.5 kg of a sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 was added thereto with stirring, and this was heated up to 60°C with stirring to prepare a basic aluminum salt mixed aqueous solution. In addition, 11.61 kg of an aqueous aluminum sulfate solution having a concentration of 7% by mass in terms of Al_2O_3 was diluted with 20.89 kg of ion-exchanged water to prepare an aqueous aluminum sulfate solution and this was kept heated at 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous aluminum sulfate solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry B containing phosphorus and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier B.

[0113]

<Preparation of carrier C>

a) 7.23 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 42.0 kg of ion-exchanged water. Next, 91.8 g of an aqueous solution of sodium gluconate having a concentration of 26% by mass was added to the solution, and then heated up to 60°C with stirring to prepare a basic aluminum salt mixed aqueous solution. An aqueous aluminum sulfate solution prepared by diluting 11.37 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 20.46 kg of ion-exchanged water was mixed with an aqueous titanium sulfate solution prepared by diluting 0.34 kg of titanium sulfate having a concentration of 33% by mass in terms of TiO_2 with 2.25 kg of ion-exchanged water, and heated at 60°C to prepare an acidic mixed aqueous solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the acidic mixed aqueous solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry C containing titania and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier C.

[0114]

<Preparation of carrier D>

a) 6.82 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 41.2 kg of ion-exchanged water. Next, 86.5 g of an aqueous solution of sodium gluconate having a concentration of 26% by mass was added to the solution, and then heated up to 60°C with stirring to prepare a basic aluminum salt mixed aqueous solution. An aqueous aluminum sulfate solution prepared by diluting 10.71 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 19.29 kg of ion-exchanged water was mixed with an aqueous titanium sulfate solution prepared by diluting 0.76 kg of titanium sulfate having a concentration of 33% by mass in terms of TiO_2 with 5.00 kg of ion-exchanged water, and heated at 60°C to prepare an acidic mixed aqueous solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the acidic mixed aqueous solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry D containing titania and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier D.

[0115]

<Preparation of carrier E>

a) 6.14 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 40.0 kg of ion-exchanged water, and then 1.5 kg of a sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 was added thereto with stirring, and this was heated up to 60°C with stirring to prepare an aqueous basic aluminum salt mixed solution. An aqueous aluminum sulfate solution prepared by diluting 9.64 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 17.36 kg of ion-exchanged water was mixed with an aqueous titanium sulfate solution prepared by diluting 1.33 kg of titanium sulfate having a concentration of 33% by mass in terms of TiO_2 with 8.75 kg of ion-exchanged water, and heated at 60°C to prepare an acidic mixed aqueous solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the acidic mixed aqueous solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry E containing phosphorus, titania and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier E.

[0116]

<Preparation of carrier F>

a) 7.35 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 41.4 kg of ion-exchanged water, and then 0.75 kg of a sodium silicate solution having a concentration of 5% by mass in terms of SiO_2 and 1.5 kg of a sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 were added thereto with stirring, and this was heated up to 60°C with stirring to prepare an aqueous basic aluminum salt mixed solution. An aqueous aluminum sulfate solution prepared by diluting 11.55 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 20.79 kg of ion-exchanged water was heated at 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous aluminum sulfate solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry F containing phosphorus, silica and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier F.

[0117]

<Preparation of carrier G>

a) 7.35 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was

put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 42.2 kg of ion-exchanged water. Then, 93.3 g of an aqueous sodium gluconate solution having a concentration of 26% by mass and 1.50 kg of a sodium silicate solution having a concentration of 5% by mass in terms of SiO_2 were added thereto with stirring, and this was heated up to 60°C with stirring to prepare an aqueous basic aluminum salt mixed solution. An aqueous aluminum sulfate solution prepared by diluting 11.55 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 20.79 kg of ion-exchanged water was heated at 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous aluminum sulfate solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry G containing silica and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier G.

[0118]

<Preparation of carrier H>

a) 6.67 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 39.3 kg of ion-exchanged water, and then, 3.0

kg of an aqueous sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 was added thereto with stirring, and this was heated up to 60°C with stirring to prepare an aqueous basic aluminum salt mixed solution. An aqueous aluminum sulfate solution prepared by diluting 10.48 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 18.86 kg of ion-exchanged water, and an aqueous titanium sulfate solution prepared by diluting 0.76 kg of titanium sulfate having a concentration of 33% by mass in terms of TiO_2 with 5.00 kg of ion-exchanged water were mixed and heated at 60°C to prepare an aqueous acidic mixed solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous acidic mixed solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry H containing phosphorus, titania and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier H.

[0119]

<Preparation of carrier I>

a) 7.20 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 44.5 kg of ion-exchanged water. Then, 91.3

g of an aqueous sodium gluconate solution having a concentration of 26% by mass was added to the solution, and heated at 60°C with stirring to prepare an aqueous basic aluminum salt solution. An aqueous aluminum sulfate solution prepared by diluting 11.31 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 20.36 kg of ion-exchanged water, and an aqueous zirconium sulfate solution prepared by diluting 0.69 kg of zirconium sulfate having a concentration of 18% by mass in terms of ZrO_2 with 2.50 kg of ion-exchanged water were mixed and heated at 60°C to prepare an aqueous acidic mixed solution.

Next, while the basic aluminum salt aqueous solution was stirred in a tank, the aqueous acidic mixed solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry I containing zirconia and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier I.

[0120]

<Preparation of carrier J>

a) 6.89 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 42.6 kg of ion-exchanged water, and then, 1.0 kg of an aqueous sodium phosphate solution having a

concentration of 2.5% by mass in terms of P_2O_5 was added to the solution with stirring, and heated at 60°C with stirring to prepare an aqueous basic aluminum salt solution. An aqueous aluminum sulfate solution prepared by diluting 10.83 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 19.50 kg of ion-exchanged water, an aqueous titanium sulfate solution prepared by diluting 0.38 kg of titanium sulfate having a concentration of 33% by mass in terms of TiO_2 with ion-exchanged water to be 2.5 kg, and an aqueous zirconium sulfate solution prepared by diluting zirconium sulfate having a concentration of 18% by mass in term of ZrO_2 with ion-exchanged water to be 1.50 kg were mixed and heated at 60°C to prepare an aqueous acidic mixed solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous acidic mixed solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry J containing phosphorus, titania, zirconia and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier J.

[0121]

<Preparation of carrier B2>

In preparing a carrier in the same manner as that for the carrier B, 0.13 kg of a solution of 10 mass% citric acid

was added as the first organic compound. The other process is the same as that for the carrier B to produce a carrier B2.

<Preparation of carrier B3>

In preparing a carrier in the same manner as that for the carrier B, 0.50 kg of a solution of 10 mass% gluconic acid was added as the first organic compound. The other process is the same as that for the carrier B to produce a carrier B3.

<Preparation of carrier B4>

In preparing a carrier in the same manner as that for the carrier B, 0.25 kg of a solution of 10 mass% malic acid was added as the first organic compound. The other process is the same as that for the carrier B to produce a carrier B4.

<Preparation of carrier B5>

In preparing a carrier in the same manner as that for the carrier B, 1.00 kg of a solution of 10 mass% sucrose was added as the first organic compound. The other process is the same as that for the carrier B to produce a carrier B5.

<Preparation of carrier B6>

In preparing a carrier in the same manner as that for the carrier B, 0.50 kg of a solution of 10 mass% acetic acid was added as the first organic compound. The other process is the same as that for the carrier B to produce a carrier B6.

[0122]

<Preparation of carrier C2>

a) In preparing a carrier in the same manner as that for

the carrier C, 0.50 kg of a solution of 10 mass% gluconic acid was added as the first organic compound, and then an aqueous ammonia having a concentration of 15% by mass was added thereto for pH control to be 10.3, and with stirring this was aged at 95°C for 10 hours.

d) After aged, the slurry was dewatered, and concentrated while kneaded and warmed in a steam-jacketed two-arm kneader to have an alumina concentration of 20% or more, then 0.25 kg of a 10 mass% citric acid was added thereto as the second organic compound, and further this was heated, concentrated and kneaded up to a predetermined water content. The other process is the same as that for the carrier C to produce a carrier C2. [0123]

<Preparation of carrier A2>

In preparing a carrier in the same manner as that for the carrier A, the first compound and the second compound were not added at all to produce a carrier A2.

<Preparation of carrier A3>

In preparing a carrier in the same manner as that for the carrier A, 1.25 kg of a 10 mass% citric acid was added as the first organic compound. The other process is the same as that for the carrier A to produce a carrier A3.

<Preparation of carrier C3>

In preparing a carrier in the same manner as that for the carrier C, the calcination temperature in the electric

furnace after dried at 110°C was 700°C, and calcination was carried out for 3 hours to produce a carrier C3.

[0124]

<Preparation of carrier K>

a) 5.83 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 38.8 kg of ion-exchanged water, and then, 3.0 kg of an aqueous sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 was added thereto with stirring, and heated at 60°C with stirring to prepare an aqueous basic aluminum salt solution. An aqueous aluminum sulfate solution prepared by diluting 9.17 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 9.17 kg of ion-exchanged water, and an aqueous titanium sulfate solution prepared by diluting 1.52 kg of titanium sulfate having a concentration of 33% by mass in terms of TiO_2 with ion-exchanged water to be 10.00 kg were mixed and heated at 60°C to prepare an aqueous acidic mixed solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous acidic mixed solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry K containing phosphorus, titania, zirconia and alumina. Subsequently,

this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier K.

[0125]

<Preparation of carrier L>

a) 7.05 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 41.0 kg of ion-exchanged water, and then, 2.75 kg of an aqueous sodium silicate solution having a concentration of 5% by mass in terms of SiO_2 and 1.5 kg of a sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 were added thereto with stirring, and heated at 60°C with stirring to prepare an aqueous basic aluminum salt mixed solution. An aqueous aluminum sulfate solution prepared by diluting 11.07 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 19.93 kg of ion-exchanged water was heated at 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous aluminum sulfate solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry L containing phosphorus, silica and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier L.

[0126]

<Preparation of carrier M>

a) 6.97 kg of an aqueous solution of sodium aluminate having a concentration of 22 % by mass in terms of Al_2O_3 was put into a steam-jacketed tank having a volume of 100 L (liter), and diluted with 37.7 kg of ion-exchanged water, and then, 8.0 kg of an aqueous sodium phosphate solution having a concentration of 2.5% by mass in terms of P_2O_5 was added thereto with stirring, and heated at 60°C with stirring to prepare an aqueous basic aluminum salt mixed solution. An aqueous aluminum sulfate solution prepared by diluting 10.95 kg of an aqueous solution of aluminum sulfate having a concentration of 7% by mass in terms of Al_2O_3 with 19.71 kg of ion-exchanged water was heated at 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the basic aluminum salt mixed aqueous solution was stirred in a tank, the aqueous aluminum sulfate solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare a hydrate slurry M containing phosphorus and alumina. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier M.

[0127]

<Preparation of carrier N>

a) 7.58 kg of an aqueous solution of sodium aluminate

having a concentration of 22 % by mass in terms of Al_2O_3 was put into steam-jacketed tank having a volume of 100 L (liter), and diluted with ion-exchanged water to be 42.42 kg. Then, 192.3 g of an aqueous sodium gluconate solution having a concentration of 26% by mass was added to the solution and heated up to 60°C with stirring to prepare an aqueous basic aluminium salt solution. Separately, an aqueous aluminum solution prepared by diluting 11.90 kg of an aqueous aluminum sulfate solution having a concentration of 7% by mass in terms of Al_2O_3 was heated at 60°C to prepare an aqueous aluminum sulfate solution.

Next, while the basic aluminum salt aqueous solution was stirred in a tank, the aqueous aluminum sulfate solution was added thereto using a roller pump at a constant speed taking 10 minutes to prepare an alumina hydrate slurry N. Subsequently, this was processed in the same manner as that for the carrier A in Example 1 to produce a carrier N.

[0128]

<Preparation of carrier H2>

A carrier H2 was produced in the same manner as that for the carrier H, except that the calcination temperature in the electric furnace after drying at 110°C was 350°C, and the calcination was carried out for 3 hours.

[0129]

<Preparation of impregnating liquid>

Next, preparation examples for impregnating liquids are described below.

<Preparation of impregnating liquid a>

292 g of molybdenum trioxide and 116 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 90°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 45 g of phosphoric acid and 118 g of citric acid added thereto, thereby preparing an impregnating liquid a.

<Preparation of impregnating liquid b>

292 g of molybdenum trioxide and 125 g of nickel carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 90°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 56 g of phosphoric acid and 106 g of citric acid added thereto, thereby preparing an impregnating liquid b.

<Preparation of impregnating liquid c>

253 g of molybdenum trioxide, 73 g of cobalt carbonate and 32 g of nickel carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 90°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 32 g of phosphoric acid and 1021 g of citric acid added thereto, thereby preparing an impregnating liquid c.

<Preparation of impregnating liquid d>

219 g of molybdenum trioxide and 86 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 90°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 31 g of phosphoric acid and 88 g of citric acid added thereto, thereby preparing an impregnating liquid d.

<Preparation of impregnating liquid e>

435 g of molybdenum trioxide and 158 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 90°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 84 g of phosphoric acid and 161 g of citric acid added thereto, thereby preparing an impregnating liquid e.

<Preparation of impregnating liquid f>

156 g of molybdenum trioxide and 40 g of cobalt carbonate were suspended in 700 ml of ion-exchanged water, and the suspension was heated at 95°C for 5 hours using a suitable reflux unit so as not to reduce the volume thereof, and then dissolved with 39 g of phosphoric acid and 41 g of citric acid added thereto, thereby preparing an impregnating liquid f.

[0130]

Hereinafter the present invention is described concretely with reference to Examples given below, but the present invention is not limited to these.

<Example 1: Preparation of hydrogenation treatment catalyst>

1000 g of the carrier A was sprayed and impregnated with the impregnating liquid a, then dried at 200°C, and further calcined in an electric furnace at 450°C for 1 hour to produce a hydrogenation treatment catalyst (hereinafter this may be simply referred to as "catalyst", and the same shall apply to the following Examples).

<Example 2 to Example 19: Preparation of hydrogenation treatment catalyst>

Catalysts of Example 2 to Example 19 were produced in the same manner as in Example 1, except that the kind (preparation example) of the carrier and the kind (preparation example) of the impregnating liquid prepared as previously described were combined as in Table 1 mentioned below.

[0131]

Next, comparative examples are described.

<Comparative Example 1 to Comparative Example 10: Preparation of hydrogenation treatment catalyst>

Catalysts of Comparative Example 1 to Comparative Example 7 were produced in the same manner as in Example 1, except that the kind (preparation example) of the carrier and the kind (preparation example) of the impregnating liquid prepared as previously described were combined as in Table 1 mentioned below.

<Comparative Example 11: Preparation of hydrogenation treatment catalyst>

The impregnating liquid a as in Example 1 was used, and 1000 g of the carrier B prepared in Example 2 was sprayed and impregnated with the impregnating liquid, and dried at 120°C, but thereafter this was not calcined to be a hydrogenation treatment catalyst.

The properties of the carriers prepared as above in Example 1 to 19 and Comparative Examples 1 to 11 are shown in Tables 4A and 4B, and the properties of the catalysts are in Tables 5A and 5B. In Tables 4A and 4B, the specific surface area means the specific surface area of the catalyst. In Tables 5A and 5B, the supported amount (% by mass) of each element is a value based on the catalyst as so described previously. Also the carbon amount is a value based on the catalyst.

[0132]

[Table 4A]

	Carrier Species	Carrier Composition					First Organic Compound		Second Organic Compound		Carrier Properties						Catalyst Properties	
		Al ₂ O ₃	P ₂ O ₅	SiO ₂	TiO ₂	ZrO ₂	Kind	Added Amount	Kind	Added Amount	Specific Surface Area	Precursor Crystallite Diameter	IR peak ratio Sb/Sa	Carrier Alumina Morphology	γ/Boehmite Ratio	Specific Surface Area	Mean Pore Size	
	No.	mass%	mass%	mass%	mass%	mass%	organic substance	mass%	organic substance	mass%	m ² /g	Å	-	Crystal Morphology	%	m ² /g	Å	
Example 1	A	95.5	4.5	0.0	0.0	0.0	citric acid	2	-	-	307	26	0.22	γ	96	226	96	
Example 2	B	97.5	2.5	0.0	0.0	0.0	citric acid	2	-	-	301	29	0.24	γ	98	223	84	
Example 3	C	95.5	0.0	0.0	4.5	0.0	citric acid	2	-	-	295	34	0.32	γ	97	220	78	
Example 4	D	90.0	0.0	0.0	10.0	0.0	citric acid	2	-	-	280	29	0.29	γ	97	204	80	
Example 5	E	81.0	1.5	0.0	17.5	0.0	citric acid	2	-	-	265	17	0.28	γ	91	197	63	
Example 6	F	97.0	1.5	1.5	0.0	0.0	citric acid	2	-	-	281	40	0.22	γ	97	206	68	
Example 7	G	97.0	0.0	3.0	0.0	0.0	citric acid	2	-	-	315	38	0.45	γ	95	231	70	
Example 8	H	87.0	3.0	0.0	10.0	0.0	citric acid	2	-	-	280	33	0.38	γ	98	208	75	
Example 9	I	95.0	0.0	0.0	0.0	5.0	citric acid	2	-	-	271	20	0.44	γ	93	199	69	
Example 10	J	91.0	1.0	0.0	5.0	3.0	citric acid	2	-	-	279	19	0.39	γ	92	202	72	
Example 11	B2	97.5	2.5	0.0	0.0	0.0	citric acid	0.5	-	-	256	31	0.24	γ	100	191	82	
Example 12	B3	97.5	2.5	0.0	0.0	0.0	gluconic acid	2	-	-	270	28	0.22	γ	99	198	79	
Example 13	B4	97.5	2.5	0.0	0.0	0.0	malic acid	1	-	-	269	30	0.22	γ	99	195	78	
Example 14	B5	97.5	2.5	0.0	0.0	0.0	sucrose	4	-	-	273	22	0.25	γ	95	200	65	
Example 15	B6	97.5	2.5	0.0	0.0	0.0	acetic acid	2	-	-	267	27	0.27	γ	97	193	79	
Example 16	C2	95.5	0.0	0.0	4.5	0.0	gluconic acid	2	citric acid	1	303	29	0.35	γ	99	222	69	
Example 17	C	95.5	0.0	0.0	4.5	0.0	citric acid	2	-	-	299	34	0.32	γ	99	217	77	
Example 18	C	95.5	0.0	0.0	4.5	0.0	citric acid	2	-	-	299	34	0.32	γ	99	223	86	
Example 19	C	95.5	0.0	0.0	4.5	0.0	citric acid	2	-	-	299	34	0.32	γ	99	240	97	

[0133]

[Table 4B]

	Carrier Species	Carrier Composition					First Organic Compound		Second Organic Compound		Carrier Properties					Catalyst Properties	
		Al ₂ O ₃	P ₂ O ₅	SiO ₂	TiO ₂	ZrO ₂	Kind	Added Amount	Kind	Added Amount	Specific Surface Area	Precursor Crystallite Diameter	IR peak ratio Sb/Sa	Carrier Alumina	γ /Boehmite Ratio	Specific Surface Area	Mean Pore Size
	No.	mass%	mass%	mass%	mass%	mass%	organic substance	mass%	organic substance	mass%	m ² /g	Å	-	Crystal Morphology	%	m ² /g	Å
Comparative Example	1	A2	95.5	4.5	0.0	0.0	-	0	-	-	290	43	0.18	γ	100	209	111
Comparative Example	2	A3	95.5	4.5	0.0	0.0	citric acid	5	-	-	330	12	0.20	γ	97.0	241	47
Comparative Example	3	C3	95.5	0.0	0.0	4.5	citric acid	2	-	-	211	32	0.41	γ	98	164	90
Comparative Example	4	K	77.0	3.0	0.0	20.0	citric acid		-	-	260	14	0.46	γ	91	190	69
Comparative Example	5	L	93.0	1.5	5.5	0.0	citric acid	2	-	-	331	18	0.53	γ	94	242	70
Comparative Example	6	M	92.0	8.0	0.0	0.0	citric acid	2	-	-	248	30	0.13	γ	94	184	119
Comparative Example	7	N	100.0	0.0	0.0	0.0	citric acid	2	-	-	245	44	0.42	γ	98	181	83
Comparative Example	8	H2	90.0	0.0	0.0	10.0	citric acid	2	-	-	339	23	0.25	γ +boehmite	74	238	62
Comparative Example	9	B	97.5	2.5	0.0	0.0	citric acid	2	-	-	266	29	0.24	γ	98	170	72
Comparative Example	10	B	97.5	2.5	0.0	0.0	citric acid	2	-	-	266	29	0.24	γ	98	221	73
Comparative Example	11	B	97.5	2.5	0.0	0.0	citric acid	2	-	-	266	29	0.24	γ	98	249	66

[0134]

[Table 5A]

Hydrogenation treatment Catalyst															
Impregnating Liquid		Group VI Element of Periodic Table		Other Elements						H2-TPR Temperature	NO Adsorption Amount	lg Loss	Carbon Amount		
				Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount					Kind	Supported Amount
		Calcination	Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount	Peak Temperature (450°C or lower)				
No.		yes or no	Mo	mass%	Co	mass%	Ni	mass%	P	mass%	°C	ml/g	mass%	mass%	
Example 1	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	398.9	9.2	1.8	0.3	
Example 2	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	386.9	9.4	1.1	0.5	
Example 3	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	410.4	9.3	1.0	0.4	
Example 4	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	408.2	10.5	1.7	0.1	
Example 5	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	389.1	10.9	1.0	0.3	
Example 6	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	413.0	9.6	0.5	0.2	
Example 7	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	413.0	9.3	1.8	0.2	
Example 8	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	406.2	11.0	1.1	0.1	
Example 9	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	409.9	8.3	1.6	0.2	
Example 10	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	409.4	8.6	0.8	1.0	
Example 11	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	411.3	8.9	0.7	0.1	
Example 12	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	409.9	9.2	2.0	1.3	
Example 13	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	410.4	9.1	0.6	0.8	
Example 14	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	410.7	9.4	1.8	0.4	
Example 15	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	411.0	9.0	2.3	0.7	
Example 16	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.0	406.0	10.2	2.1	0.5	
Example 17	b	yes	MoO ₃	21	CoO	0	NiO	4.5	P ₂ O ₅	2.5	371.5	8.4	1.3	0.6	
Example 18	c	yes	MoO ₃	19	CoO	3.3	NiO	1.2	P ₂ O ₅	1.5	389.2	8.7	0.8	0.3	
Example 19	d	yes	MoO ₃	17	CoO	4	NiO	0.0	P ₂ O ₅	1.5	378.8	8.4	1.9	0.1	

[0135]

[Table 5B]

	Impregnating Liquid	Hydrogenation treatment Catalyst												
		Calcination	Group VI Element of Periodic Table		Other Elements					H ₂ -TPR Temperature		NO Adsorption Amount	lg Loss	Carbon Amount
			Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount	Kind	Supported Amount	Peak Temperature (450°C or lower)			
	No.	yes or no	Mo	mass%	Co	mass%	Ni	mass%	P	mass%		ml/g	mass%	mass%
Comparative Example 1	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	411.1	8.5	1.4	0.6
Comparative Example 2	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	414.8	7.2	2.1	0.5
Comparative Example 3	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	410.9	7.0	1.2	0.1
Comparative Example 4	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	390.8	7.9	0.9	0.8
Comparative Example 5	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	432.2	8.6	1.5	0.5
Comparative Example 6	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	423.5	7.1	2.1	0.8
Comparative Example 7	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	392.4	8.8	1.8	0.5
Comparative Example 8	a	yes	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	427.7	9.5	2.1	1.3
Comparative Example 9	e	yes	MoO ₃	27.5	CoO	6.0	NiO	0.0	P ₂ O ₅	3.3	431.0	8.1	3.2	1.0
Comparative Example 10	f	yes	MoO ₃	13	CoO	2.0	NiO	0.0	P ₂ O ₅	2.0	377.7	6.4	0.6	0.4
Comparative Example 11	a	no	MoO ₃	21	CoO	5	NiO	0.0	P ₂ O ₅	2.2	405.9	12.3	14.8	3.5

<Evaluation of catalyst>

(Confirmation test for evaluation)

The catalysts of Example 1 to 19 and Comparative Examples 1 to 11 were evaluated in point of catalyst performance and catalyst regeneration performance.

(1) Confirmation test for evaluation of catalyst performance

Each catalyst was filled in a fixed bed reactor, and for activating it by releasing the oxygen atom contained in the catalyst, this was presulfurized. This treatment was carried out in the reactor where a liquid or vapor containing a sulfur compound was kept flowing therethrough under controlled conditions at a temperature of 200°C to 400°C and in a hydrogen pressure atmosphere at ordinary pressure to 100 MPa.

Next, straight light gas oil (density at 15°C, 0.8468 g/cm³; sulfur content, 1.13% by mass; nitrogen content, 0.083% by mass) was fed into the fixed bed flow reactor at a rate of 150 ml/hr for hydrodesulfurization for hydrorefining. Regarding the reaction condition in this step, the hydrogen partial pressure was 4.5 MPa, the liquid hourly space velocity was 1.0 hr⁻¹, and the hydrogen oil ratio was 250 Nm³/kl. The reaction temperature was varied within a range of 300 to 385°C, and the refined oil was subjected to sulfur analysis at different temperatures in the range to determine the temperature at which the sulfur content in the refined oil reached 10 ppm.

[0136]

(2) Confirmation test for evaluation of catalyst regeneration performance

Catalysts were regenerated according to the following process. 100 g of the used catalyst that had been extracted after the reaction was put in a nitrogen atmosphere kept at 200°C to remove the adhering oil from the surface thereof. Subsequently, while the temperature thereof was kept at 400 to 450°C, the catalyst was calcined in an air atmosphere until the carbon amount could reach 1% by weight or less. After calcined, the catalyst was cooled and used again in the activity test.

The performance calculation method after regeneration is as follows. Regarding the test results in the activity test, the reaction speed constant was determined by Arrhenius plotting, and the regeneration rate from the fresh catalyst (unused catalyst) was calculated. Specifically, after sulfurization in a hydrogen sulfide flow, the catalyst was hydrodesulfurized under the condition described in the above (1). From the sulfur concentration change in the hydrocarbon oil before and after passing through the reactor, the reaction speed constant was determined based on the following equation (1). The ratio by percentage of the reaction speed constant (K_n) of the regenerated catalyst to the reaction speed constant (K_{n0}) of the unused catalyst ($(K_n/K_{n0}) \times 100$ [%]) is referred

to as the relative activity.

$$K_n = LHSV \times 1/(n-1) \times (1/S^{n-1} - 1/S_0^{n-1}) \quad \text{Equation (1)}$$

wherein:

K_n : reaction speed constant

n : what exponent (n) of the sulfur concentration in the crude oil is proportional to the desulfurization speed (1.5 for LGO)

S : sulfur concentration (%) in processed oil

S_0 : sulfur concentration (%) in crude oil

LHSV: liquid hourly space velocity (hr^{-1})

The results of the confirmation test are shown in Tables 6A and 6B. In consideration of easiness in understanding the data, Tables 6A and 6B are arranged in parallel to each other in Table 6.

[0137]

[Table 6]

(Table 6A)

		Evaluation	
		Catalyst Performance	Regeneration Performance
		HDS Activity	
		°C (10 ppm achieving temperature)	% (to fresh catalyst)
Example	1	342	91
Example	2	347	94
Example	3	346	91
Example	4	342	94
Example	5	339	86
Example	6	353	97
Example	7	354	97
Example	8	340	95
Example	9	355	90
Example	10	350	94
Example	11	351	95
Example	12	348	92
Example	13	350	93
Example	14	349	90
Example	15	348	90
Example	16	345	94
Example	17	344	86
Example	18	352	89
Example	19	355	96

(Table 6B)

		Evaluation	
		Catalyst Performance	Regeneration Performance
		HDS Activity	
		°C (10 ppm achieving temperature)	% (to fresh catalyst)
Comparative Example	1	357	88
Comparative Example	2	370	83
Comparative Example	3	372	96
Comparative Example	4	363	93
Comparative Example	5	368	89
Comparative Example	6	375	90
Comparative Example	7	363	94
Comparative Example	8	358	83
Comparative Example	9	368	82
Comparative Example	10	380	97
Comparative Example	11	332	63

(Properties of catalyst and evaluation results of confirmation test)

In Example 1 to 19, the parameters of the composition of the carrier, the added amount of the organic compound, the composition of the active metal, the processing condition and others are defined each within a suitable range, and consequently, the properties of the catalysts all have suitable values.

As opposed to these, in Comparative Example 1, the organic compound was not added, and in Comparative Example 2, the organic compound was added excessively. In Comparative Example 3, the carrier calcination temperature was too high, in Comparative Examples 4 to 6, and the inorganic composition range was unsuitable, in Comparative Example 7, any other inorganic substance than aluminum was not added. In Comparative Example 8, the carrier calcination temperature was too low, in Comparative Example 9, the active metals were excessive, and in Comparative Example 10, the active metals were insufficient. In Comparative Example 11, the carrier impregnated with the impregnating liquid was not calcined.

[0138]

Consequently, the crystallite diameter of the alumina precursor is more than the upper limit of a suitable value, 40 Å in Comparative Examples 1 and 7, and is lower than the lower limit, 15 Å in Comparative Examples 2 and 4. The proportion of the OH group is lower than the lower limit, 0.20 in Comparative Examples 1 and 6, and is higher than the higher

limit, 0.45 in Comparative Examples 4 and 5. Regarding the crystal dislocation of alumina, the crystal morphology of the carrier alumina contains much boehmite in Comparative Example 8 and therefore the γ -alumina proportion therein is small, since the carrier calcination temperature was lower than the lower limit of the preferred carrier calcination temperature, 400°C. The surface area of the catalyst is lower than the lower limit of a suitable value, 180 m²/g in Comparative Examples 3 and 8. The mean pore size is lower than the lower limit of a suitable value, 50 Å in Comparative Example 2, and is larger than the upper limit of a suitable value, 110 Å.

[0139]

The released water peak temperature is higher than the upper limit of a suitable range, 415°C in Comparative Examples 5, 6, 8 and 9; and the nitrogen monoxide adsorption amount is lower than the lower limit of a suitable range, 8.0 ml/g in Comparative Examples 2, 3, 4, 6 and 10. The ignition loss is greatly higher than the upper limit of a suitable value, 5.0% by mass in Comparative Example 11, and in Comparative Example 11, the contained carbon amount is also higher than the upper limit of a suitable range, 2.0% by mass.

As a result, in Example 1 to Example 19, the temperature at which the sulfur content in the refined oil, which is an index of catalyst performance, reaches 10 ppm is not higher than 355°C, and the relative activity that is an index of

catalyst regeneration performance is not less than 85%. As opposed to these, in Comparative Examples 1 to 10, the catalyst performance is poor, and in Comparative Example 11, the catalyst regeneration performance is poor. In addition, Comparative Examples 2, 8 and 9, not only catalyst performance but also catalyst regeneration performance is poor.

Industrial Applicability

[0140]

The hydrodesulfurization catalyst of the present invention can catalyze hydrodesulfurization in a high degree and is extremely useful for industrial use.

CLAIMS

[Claim 1]

A hydrogenation treatment catalyst for hydrocarbon oil comprising:

(1) a carrier that contains alumina as the main component and is the following a or b:

a. the carrier is 100% γ -alumina,

b. the carrier contains aluminum in an amount of 80 to 98 parts by mass in terms of alumina relative to 100 parts by mass of the carrier, and in the carrier, the crystallite diameter of the pseudo-boehmite of alumina to be the main component in the precursor is 15 or more and 40 or less Å as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof,

(2) a first metal component of at least one of molybdenum and tungsten, and a second metal component of at least one of cobalt and nickel are loaded on the carrier,

(3) the content of the first metal component is 15 to 27 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst, and the content of the second metal component is 2 to 7 parts by mass in terms of oxide relative to 100 parts by mass of the catalyst,

(4) regarding the carrier of the above a, the specific surface area of the catalyst is 200 to 320 m²/g, and regarding

the carrier of the above b, the specific surface area of the catalyst is 180 to 320 m²/g, and the mean pore diameter of the catalyst, as measured according to a mercury intrusion method, is 50 to 110 Å,

(5) the ignition loss is 5.0% by mass or less,

(6) the amount of carbon derived from an organic acid is 2.0 parts by mass or less on an elemental basis relative to 100 parts by mass of the catalyst, and

(7) the adsorption amount of nitrogen monoxide on the sulfurized catalyst is 8.0 ml/g or more.

[Claim 2]

The hydrogenation treatment catalyst for hydrocarbon oil according to claim 1, wherein the peak temperature of released water from the catalyst within a range of up to 450°C (the temperature at which the water release spectrum peak appears), according to a temperature-programed-reduction method for catalyst, is 415°C or lower.

[Claim 3]

The hydrogenation treatment catalyst for hydrocarbon oil according to claim 1, wherein:

the carrier is 100% γ-alumina, and

the carrier is such that the ratio of the absorbance of the spectral peak Sb in a wavenumber range of 3770 to 3774 cm⁻¹ corresponding to the basic OH group therein to the absorbance of the spectral peak Sa in a wavenumber range of 3674 to 3678

cm⁻¹ corresponding to the acidic OH group, as measured with a transmission Fourier transform IR spectrophotometer, the ratio of Sb/Sa is in a range of 0.15 to 0.40.

[Claim 4]

The hydrogenation treatment catalyst for hydrocarbon oil according to claim 1, wherein:

the carrier is 100% γ -alumina, and

the carrier is such that, when the diffraction peak area indicating the crystal structure of the (020) plane of boehmite measured through X-ray diffractometry is referred to as P1, the diffraction peak area indicating the crystal structure of the (120) plane is as P2, and the diffraction peak area indicating the aluminum crystal structure attributed to the (440) plane of γ -alumina is as P3;

a larger one of the value $(P1/P3) \times 100$ (%) and the value $(P2/P3) \times 100$ (%) is less than 10%.

[Claim 5]

The hydrogenation treatment catalyst for hydrocarbon oil according to claim 1, wherein:

the carrier is 100% γ -alumina, and

the carrier is such that the crystallite diameter of the pseudo-boehmite of the alumina precursor is 45 Å or less as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof.

[Claim 6]

A method for producing a hydrogenation treatment catalyst for hydrocarbon oil stated in claim 1 wherein the carrier is 100% γ -alumina, the method comprising:

(A) a step of preparing a γ -alumina carrier, which comprises:

a first aging stage of aging a slurry that contains an alumina obtained by mixing an aqueous solution of a basic aluminum salt and an aqueous solution of an acidic aluminum salt,

a stage of dewatering the aged slurry and washing it,
then a second aging stage of aging the slurry that contains the washed product,

thereafter, a stage of kneading and concentrating the slurry,

a stage of shaping the concentrated product prepared by concentrating the slurry, and

then a stage of drying and calcining the shaped product,

(B) a step of preparing an impregnating liquid that contains a first metal component of at least one of molybdenum and tungsten, a second metal component of at least one of cobalt and nickel, and an organic acid, and making the first metal component and the second metal component loaded on the γ -alumina carrier, and

(C) a step of heat-treating the γ -alumina carrier on which the first metal component and the second metal component

have been loaded, as obtained in the previous step (B), to produce a hydrogenation treatment catalyst.

[Claim 7]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 6, wherein in the second aging stage in the step (A), the first organic compound is added to the slurry.

[Claim 8]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 7, wherein the first organic compound is added in an amount of 0.5 to 5.0 parts by mass relative to 100 parts by mass of alumina.

[Claim 9]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 6, wherein on and after the stage of kneading and concentrating the slurry in the step (A), the second organic compound is added before the stage of shaping the concentrated product.

[Claim 10]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 9, wherein the second organic compound is added in an amount of 0.5 to 5.0 parts by mass relative to 100 parts by mass of alumina.

[Claim 11]

The method for producing a hydrogenation treatment

catalyst for hydrocarbon oil according to claim 7, wherein the first organic compound is at least one of organic acids and saccharides.

[Claim 12]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 9, wherein the second organic compound is at least one of organic acids and saccharides.

[Claim 13]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 6, wherein the aqueous solution of a basic aluminum salt in the step (A) contains a carboxylate.

[Claim 14]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 6, wherein in the first aging stage and the second aging stage included in the step (A), the alumina concentration is less than 20%, and

in the stage of kneading and concentrating the slurry in the step (A), the alumina concentration is 20% or more.

[Claim 15]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 6, wherein the heat treatment temperature in the step (C) is a temperature of 100 to 600°C.

[Claim 16]

The hydrogenation treatment catalyst for hydrocarbon oil according to claim 1, wherein:

the carrier contains aluminum in an amount of 80 to 98 parts by mass in terms of alumina relative to 100 parts by mass of the carrier, and in the carrier, the crystallite diameter of the pseudo-boehmite of alumina to be the main component in the precursor is 15 or more and 40 or less Å as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof, and

the carrier is such that the ratio of the absorbance of the spectral peak Sb in a wavenumber range of 3770 to 3774 cm^{-1} corresponding to the basic OH group therein to the absorbance of the spectral peak Sa in a wavenumber range of 3674 to 3678 cm^{-1} corresponding to the acidic OH group, as measured with a transmission Fourier transform IR spectrophotometer, the ratio of Sb/Sa is in a range of 0.20 to 0.45.

[Claim 17]

The hydrogenation treatment catalyst for hydrocarbon oil according to claim 1, wherein:

the carrier contains aluminum in an amount of 80 to 98 parts by mass in terms of alumina relative to 100 parts by mass of the carrier, and in the carrier, the crystallite diameter of the pseudo-boehmite of alumina to be the main component in the precursor is 15 or more and 40 or less Å as obtained from

the half-value width of the XRD diffraction spectral (020) peak thereof,

and the carrier corresponds to at least one of:

c. one containing phosphorus in an amount of 5.0 parts by mass or less in terms of phosphoric acid relative to 100 parts by mass of the carrier,

d. one containing silicon in an amount of 3.0 parts by mass or less in terms of silica relative to 100 parts by mass of the carrier,

e. one containing titanium in an amount of 18.0 parts by mass or less in terms of titania relative to 100 parts by mass of the carrier, and

f. one containing zirconium in an amount of 9.0 parts by mass or less in terms of zirconia oxide relative to 100 parts by mass of the carrier.

[Claim 18]

The hydrogenation treatment catalyst for hydrocarbon oil according to claim 1, wherein:

the carrier contains aluminum in an amount of 80 to 98 parts by mass of alumina relative to 100 parts by mass of the carrier, and in the carrier, the crystallite diameter of the pseudo-boehmite of alumina to be the main component in the precursor is 15 or more and 40 or less Å as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof, and

the carrier is such that, when the diffraction peak area showing the aluminum crystal structure attributed to the boehmite (020) plane measured in the XRD diffraction spectrum thereof is referred to as P1 and the diffraction peak area showing the crystal structure of the γ -alumina (440) plane is referred to as P2, the ratio of P2 to the total value of P1 and P2, $P2/(P1 + P2)$ is 0.9 or more.

[Claim 19]

A method for producing a hydrogenation treatment catalyst for hydrocarbon oil stated in claim 1 wherein the carrier contains aluminum in an amount of 80 to 98 parts by mass in terms of alumina relative to 100 parts by mass of the carrier, and in the carrier, the crystallite diameter of the pseudo-boehmite of alumina to be the main component in the precursor is 15 or more and 40 or less Å as obtained from the half-value width of the XRD diffraction spectral (020) peak thereof, the method comprising:

(D) a step of preparing the carrier,

(E) a step of preparing an impregnating liquid that contains a first metal component of at least one of molybdenum and tungsten, a second metal component of at least one of cobalt and nickel, and an organic acid, and making the first metal component and the second metal component loaded on the inorganic composite oxide carrier, and

(F) a step of heat-treating the carrier on which the first

metal component and the second metal component have been loaded, as obtained in the previous step (E), at a temperature of 100 to 600°C to produce a hydrogenation treatment catalyst.

[Claim 20]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 19, wherein the step (D) for preparing the carrier comprises:

(D-1) a slurry preparing step of mixing an aqueous solution of a basic metal salt and an aqueous solution of an acidic metal salt to prepare a composite metal hydrate slurry,

(D-2) a first aging step of aging the composite metal hydrate slurry,

(D-3) then a step of washing the composite metal hydrate slurry,

(D-4) thereafter, a second aging step of aging the composite metal hydrate slurry,

(D-5) subsequently, a kneading/concentrating step of kneading and concentrating the composite metal hydrate slurry,

(D-6) a step of shaping the concentrated product obtained by concentrating the composite metal hydrate slurry, and

(D-7) a step of drying and calcining the shaped product, and wherein:

the first organic compound is added in the second aging step of the above (D-4).

[Claim 21]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 20, wherein the aqueous solution of a basic aluminum salt in the slurry preparing step of the above (D-1) contains a carboxylate.

[Claim 22]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 20, wherein the first organic compound is added in an amount of 0.5 to 4.0 parts by mass relative to 100 parts by mass of the inorganic composite oxide.

[Claim 23]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 20, wherein in the kneading/concentrating step of the above (D-5), the second organic compound is added.

[Claim 24]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 23, wherein the second organic compound is added in an amount of 0.5 to 4.0 parts by mass relative to 100 parts by mass of the inorganic composite oxide.

[Claim 25]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 20, wherein the inorganic composite oxide concentration in the slurry in

the second aging step of the above (D-4) is less than 20%, and the inorganic composite oxide concentration in the slurry in the kneading/concentrating step of the above (D-5) is 20% or more.

[Claim 26]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 19, wherein the first organic compound is at least one selected from citric acid, malic acid, tartaric acid, gluconic acid, acetic acid, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and saccharides (monoses, polyoses, etc.).

[Claim 27]

The method for producing a hydrogenation treatment catalyst for hydrocarbon oil according to claim 23, wherein the second organic compound is at least one selected from citric acid, malic acid, tartaric acid, gluconic acid, acetic acid, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and saccharides (monoses, polyoses, etc.).

[Claim 28]

A hydrogenation treatment method for hydrocarbon oil, which comprises hydrogenating a hydrocarbon oil in the presence of a hydrogenation treatment catalyst stated in claim 1 under the conditions of a hydrogen partial pressure of 3 to

8 MPa, a temperature of 260 to 420°C and a liquid hourly space velocity of 0.3 to 5 hr⁻¹.