

HYDRODESUFURIZATION CATALYST FOR HYDROCARBON OIL

BACKGROUND OF THE INVENTION

Field of the Invention

5 [0001]

The present invention relates to a hydrodesulfurization catalyst for a hydrocarbon oil, and more specifically, relates to a hydrodesulfurization catalyst having excellent activity which can reduce the sulfur content within a hydrocarbon oil such as a kerosene, gas oil or vacuum gas oil under comparatively mild conditions and over a long period of
10 time.

Description of Related Art

[0002]

Hydrocarbon oil fractions obtained by distilling and cracking crude oil generally
15 contain sulfur compounds, and when these oils are used as fuels, atmospheric pollutants such as sulfur oxides originating from these sulfur compounds are released into the atmosphere. However, recent increased awareness of environmental issues has meant that the restrictions on atmospheric pollution have become increasingly severe, and reductions in the sulfur content of fuel oils are deemed highly desirable.

20 [0003]

The technology for reducing the amount of sulfur compounds contained within this type of fuel oil typically involves using a catalyst having desulfurization activity to subject the hydrocarbon oil feedstock to a hydrodesulfurization treatment in a hydrodesulfuration unit, and all manner of hydrodesulfurization catalysts have been
25 proposed. For example, catalysts prepared by impregnation of a metal component having

hydrogenation activity such as molybdenum, tungsten, cobalt or nickel on an inorganic oxide carrier such as alumina are widely used as hydrodesulfurization catalysts, and in order to further improve the performance of such catalysts, investigations have been conducted into improving the carrier, examining the metal components, and improving
5 the method used for impregnating the metal components on the carrier (for example, see Japanese Unexamined Patent Application, First Publication No. 2000-342976).

[0004]

Conventional desulfurization levels (a product oil sulfur content of 0.2 to 0.05 mass %) can be achieved relatively easily using current desulfurization technology, but
10 performing desulfurization until an even lower sulfur content is obtained (a product oil sulfur content of 0.04 mass % or lower) becomes extremely difficult. This is because in the refractory sulfur compounds such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), the position of the alkyl substituent(s) is close to the sulfur atom, and therefore the alkyl substituent(s) cause steric hindrance when the
15 sulfur molecule attempts to contact the desulfurization active site of the catalyst, making desulfurization of these types of compounds extremely difficult.

[0005]

Under these circumstances, the development of hydrodesulfurization technology that enables removal of a refractory sulfur compounds within gas oil is becoming
20 increasingly important. Typically, in order to increase the proportion of the sulfur content removed from a gas oil, the operating conditions for the hydrodesulfurization such as the reaction temperature and the liquid hourly space velocity have needed to be made more severe. However, when the reaction temperature is increased, coke tends to be deposited on the catalyst, meaning the activity of the catalyst decreases rapidly,
25 whereas when the liquid hourly space velocity is lowered, although the desulfurization

performance improves, the efficiency of the refining process tends to reduce, meaning the capacity of the hydrodesulfurization unit must be increased. Moreover, these types of severe operating conditions tend to also have adverse effects on the properties of the product oil such as the product color and the storage stability. Accordingly, the best method for achieving desulfurization of a gas oil under relatively mild conditions, without requiring the severe operating conditions described above, is the development of a catalyst having markedly superior desulfurization activity.

[0006]

On the other hand, depending on the intended use of the kerosene or gas oil, a catalyst which has sufficient desulfurization activity to ensure a prescribed desulfurization rate, and is also able to be used over a long period, namely a catalyst with an extended life, may sometimes be required. Moreover, if the same catalyst could be used for performing desulfurization of kerosene, gas oil, and even vacuum gas oil, then managing the catalyst and the hydrodesulfurization unit can be performed more efficiently.

[0007]

The present invention has an object of providing a catalyst which has a prescribed desulfurization activity, has a long life, and is capable of hydrotreating a wide range of hydrocarbon oils from naphtha to vacuum gas oil under comparatively mild operating conditions.

SUMMARY OF THE INVENTION

[0008]

Under these circumstances and as a result of intensive research, the inventors of the present invention discovered, during investigations into complexing zeolites having a

variety of physical properties with an alumina-based carrier and then performing hydrodesulfurization reactions, that among a large variety of zeolites, by using an HY zeolite having specific physical properties, hydrodesulfurization reactions of a variety of different hydrocarbon oils including kerosene, gas oil and heavy gas oil proceeded more efficiently than when other zeolites were used. As a result of undertaking further research based on this discovery, the inventors discovered that by complexing an HY zeolite having specific physical properties with a carrier having an alumina base, and controlling the physical properties of the catalyst such as the mean pore diameter, they were able to achieve the object described above, thereby completing the present invention.

[0009]

In other words, a first aspect of the present invention is a hydrodesulfurization catalyst for a hydrocarbon oil, the catalyst prepared by impregnating cobalt, molybdenum and phosphorus on a complex oxide carrier containing 80 to 99 mass % of an alumina and 1 to 20 mass % of an HY zeolite, wherein based on the total mass of the catalyst, and calculated in terms of the oxide content, the catalyst contains 3 to 6 mass % of cobalt, 16 to 24 mass % of molybdenum and 0.8 to 4.5 mass % of phosphorus, the catalyst has a specific surface area measured by the nitrogen adsorption method of 210 to 280 m²/g, a pore volume measured by the mercury intrusion method of 0.3 to 0.6 ml/g, a mean pore diameter in a pore distribution measured by the mercury intrusion method of 75 to 95 Å, and a pore volume for pores within a range of ± 15 Å from the mean pore diameter that is at least 75% of the total pore volume, and the HY zeolite has:

(a) a SiO₂/Al₂O₃ (molar ratio) of 3 to 10,

(b) a crystal lattice constant of 2.435 to 2.465 nm,

(c) a molar ratio of Al within the zeolite framework relative to the total Al content of 0.2 to 0.9, and

(d) a crystallite diameter of 30 to 100 nm.

[0010]

5 The hydrodesulfurization catalyst for a hydrocarbon oil according to the present invention has superior desulfurization activity, and therefore the sulfur content within a gas oil fraction can be reduced dramatically.

Further, the hydrodesulfurization catalyst for a hydrocarbon oil according to the present invention can be used under reaction conditions that are substantially the same as,
10 or even milder than, those used during conventional hydrotreatments, and therefore the catalyst can be used to replace conventional hydrodesulfurization catalysts without requiring significant improvements to conventional hydrodesulfurization unit.

Moreover, by using the hydrodesulfurization catalyst for a hydrocarbon oil according to the present invention, a gas oil base with a low sulfur content can be
15 supplied relatively easily.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

FIG. 1 is a diagram which illustrates, for catalysts A to D and catalyst X, the
20 relationship between the crystallite diameter (nm) of the zeolite contained within the catalyst, and the desulfurization reaction rate constant (K_s) .

EMBODIMENTS OF THE INVENTION

[0012]

The hydrodesulfurization catalyst for a hydrocarbon oil according to the present invention (hereafter also referred to as "the catalyst according to the present invention") is a catalyst prepared by impregnating cobalt, molybdenum and phosphorus on a complex oxide carrier containing alumina and an HY zeolite having specific physical properties,

5 wherein the specific surface area, the pore volume and the mean pore diameter of the catalyst satisfy specific ranges. By using an alumina carrier containing the HY zeolite having specific physical properties, and controlling the physical properties of the catalyst such as the specific surface area, the pore volume and the mean pore diameter so that they satisfy specific ranges, a long-life hydrodesulfurization catalyst can be obtained that

10 can perform a hydrotreatment with a satisfactory desulfurization rate even under comparatively mild desulfurization conditions.

[0013]

<HY Zeolite>

The HY zeolite used in the catalyst according to the present invention has the

15 following physical properties (a) to (d):

- (a) a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 3 to 10,
- (b) a crystal lattice constant of 2.435 to 2.465 nm,
- (c) a molar ratio of Al within the zeolite framework relative to the total Al content of 0.2 to 0.9, and
- (d) a crystallite diameter of 30 to 100 nm.

20

[0014]

(a) $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Molar Ratio)

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) can be measured by chemical composition analysis using an ICP analysis method.

The bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of the HY zeolite used in the catalyst according to the present invention, determined by chemical composition analysis, is within a range from 3 to 10, and preferably from 5 to 8. By ensuring that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) is at least 3, a satisfactory amount of active sites can be ensured, enabling
 5 the isomerization of alkyl groups of materials that are difficult to desulfurize, and the hydrogenation of benzene rings to proceed satisfactorily. Further, by ensuring that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) is not more than 10, cracking of the feedstock (hydrocarbon oil) is unlikely to occur, enabling any deterioration in the liquid yield to be suppressed.

The HY zeolite used in the present invention has basically the same crystal
 10 structure as a naturally occurring faujasite, and has the composition shown below in an oxide form.

[0015]

[Chemical Formula 1]

$(0.02 \text{ to } 1.0) \text{R}_2/\text{mO} \cdot \text{Al}_2\text{O}_3 \cdot (5 \text{ to } 11) \text{SiO}_2 \cdot (5 \text{ to } 8) \text{H}_2\text{O}$

15 wherein R represents Na, K and other alkali metal ions and alkaline earth metal ions, and m represents the atomic valence of R.

[0016]

(b) Crystal Lattice Constant

The crystal lattice constant (unit lattice dimension) of the HY zeolite can be
 20 measured using an X-ray diffraction apparatus (XRD). In this description, the "crystal lattice constant of the HY zeolite" refers to the size of a single unit that constitutes the HY zeolite.

The crystal lattice constant of the HY zeolite used in the present invention is within a range from 2.435 to 2.465 nm, and preferably from 2.440 to 2.460 nm. Provided
 25 the crystal lattice constant is at least 2.435 nm, the Al number (number of Al atoms) is

suitable for promoting the isomerization of alkyl groups of materials that are difficult to desulfurize, and the hydrogenation of benzene rings, whereas provided the crystal lattice constant is not more than 2.465 nm, cracking of the feedstock at the acid sites is suppressed, and coke deposition, which is one of the main causes of catalyst deactivation, can be inhibited.

[0017]

(c) Molar Ratio of Al within the Zeolite Framework relative to Total Al Content

The number of moles of aluminum atoms within the zeolite framework relative to the total number of moles of aluminum atoms in the zeolite can be calculated from the SiO₂/Al₂O₃ ratio determined by chemical composition analysis and the crystal lattice constant, using the following formulas (A) to (D). The formula (A) employs the formula disclosed by H.K. Beyer et al. in J. Chem. Soc., Faraday Trans., 1, (81), 2899 (1985).

[0018]

$$\text{Formula (A): } N_{\text{Al}} = (a_0 - 2.425) / 0.000868$$

In the formula (A), a_0 represents the crystal lattice constant (nm), N_{Al} represents the number of Al atoms per unit lattice, 2.425 is the crystal lattice constant when all the Al atoms within the unit lattice framework are removed outside the framework, and 0.000868 is a calculated value determined by experiment, and represents the gradient when a_0 and N_{Al} are correlated using a linear equation ($a_0 = 0.000868N_{\text{Al}} + 2.425$).

[0019]

$$\text{Formula (B): } [(\text{Si}/\text{Al}) \text{ calculation formula}] = (192 - N_{\text{Al}}) / N_{\text{Al}}$$

In the formula (B), 192 represents the number of atoms (Si+Al) per crystal lattice constant of the Y zeolite.

[0020]

$$\text{Formula (C): } [(\text{Si}/\text{Al}) \text{ chemical composition analysis value}] = [\text{SiO}_2/\text{Al}_2\text{O}_3 \text{ (molar$$

ratio)] / 2

Formula (D): [Al within zeolite framework] / [total Al] = [(Si/Al) chemical composition analysis value] / [(Si/Al) calculation formula]

[0021]

5 The molar ratio of the aluminum atoms within the zeolite framework relative to the total number of aluminum atoms within the HY zeolite used in the present invention (namely, [Al within zeolite framework] / [total Al]) is within a range from 0.2 to 0.9, and preferably from 0.4 to 0.7. Since the molar ratio of [Al within zeolite framework] / [total Al] is set in the above mentioned range, acid sites can be formed to suitably perform the isomerization and the hydrogenation, and thereby desirable desulfurization activity can be achieved.

[0022]

(d) Crystallite Diameter

15 In the catalyst according to the present invention, the crystallite diameter of the HY zeolite that is used can be measured using an X-ray diffraction apparatus, and is defined by the procedure (1) to (4) described below.

(1) The diffraction peaks for the zeolite are calculated using an X-ray diffraction apparatus.

20 (2) The peaks corresponding with the (533) plane, the (642) plane and the (555) plane are used to calculate the full width at half maximum for each of the planes.

(3) For each of the (533) plane, the (642) plane and the (555) plane, the value for the full width at half maximum is inserted into the Scherrer formula (formula (E) below) to determine the size of each plane.

25 (4) The zeolite crystallite diameter is defined as the average value of the three plane sizes determined in (3).

[0023]

Formula (E): $D = K\lambda / \beta \cos\theta$

In formula (E), D represents the zeolite crystallite diameter (Å), K represents the Scherrer constant, λ represents the X-ray wavelength (nm), β represents the full width at half maximum (rad), and θ represents the diffraction angle (°).

[0024]

The crystallite diameter for the HY zeolite used in the present invention, determined using the above formula (E), is within a range from 30 to 100 nm, and preferably from 45 to 95 nm. By ensuring that the zeolite crystallite diameter satisfies this range, there is no loss in the function of the catalyst in promoting isomerization and hydrogenation, coke deposition, which is one of the main causes of reduced catalytic activity, can be inhibited, and any deterioration in the liquid yield caused by cracking reactions can be inhibited.

[0025]

<Complex Oxide Carrier>

In the catalyst according to the present invention, an inorganic oxide containing alumina as the main component and also containing the aforementioned HY zeolite is used as the carrier. Specifically, the catalyst according to the present invention is prepared by impregnating cobalt (Co), molybdenum (Mo) and phosphorus (P) on a complex oxide carrier containing, as essential components, 80 to 99 mass % of alumina and 1 to 20 mass % of the HY zeolite relative to the total mass of the carrier.

[0026]

The amount of the HY zeolite within the complex oxide carrier, relative to the total mass of the carrier, is preferably within a range from 2 to 10 mass %, and more preferably from 4 to 8 mass %. If the amount of the HY zeolite is either too small or too

large, then molding of the catalyst tends to become difficult. Further, if the amount is too small, then formation of the Bronsted acid sites or Lewis acid sites that function as the acid sites on the catalyst may be unsatisfactory, whereas if the amount is too large, there is a possibility that superior diffusion of the Mo may be inhibited.

5 [0027]

The alumina used in the carrier of the catalyst according to the present invention may be any of the various forms of alumina such as α -alumina, β -alumina, γ -alumina or δ -alumina, but a porous alumina having a high specific surface area is preferable, and γ -alumina is particularly suitable. The purity of the alumina is typically at least
10 approximately 98 mass %, and preferably 99 mass % or greater. Examples of impurities that may exist within the alumina include SO_4^{2-} , Cl^- , Fe_2O_3 and Na_2O , but the amounts of these impurities are preferably as small as possible. Specifically, the total amount of all impurities is typically not more than 2 mass %, and preferably 1 mass % or less. In terms of individual impurities, the amount of SO_4^{2-} is preferably less than 1.5 mass %, and the
15 amounts of Cl^- , Fe_2O_3 and Na_2O are preferably less than 0.1 mass %.

[0028]

There are no particular limitations on the specific surface area, the pore volume or the mean pore diameter of the alumina carrier containing the aforementioned HY zeolite (the complex oxide carrier), but in order to prepare a catalyst having a powerful
20 hydrodesulfurization activity relative to gas oils, the specific surface area is typically within a range from approximately 240 to 500 m^2/g , and preferably from approximately 300 to 450 m^2/g , the pore volume is typically within a range from approximately 0.55 to 0.9 ml/g , and preferably from approximately 0.65 to 0.8 ml/g , and the mean pore diameter is typically within a range from approximately 60 to 120 Å, and preferably from
25 approximately 65 to 90 Å.

[0029]

In the complex oxide carrier, by ensuring that the specific surface area is at least approximately 240 m²/g, the dispersibility of the active metals improves, and a catalyst having superior desulfurization activity is obtained. Further, if the pore diameter of the catalyst is too small, then diffusion of the sulfur compounds into the catalyst pores tends to be unsatisfactory, which can result in a deterioration in the desulfurization activity, but by ensuring that the specific surface area is not more than approximately 500 m²/g, the pore diameter of the carrier can be prevented from becoming very small, meaning the pore diameter of the catalyst also does not become too small.

[0030]

In the complex oxide carrier, if the amount of the solvent medium that penetrates into the pore volume is too small, then the solubility of the active metal compounds may decrease and the dispersibility of the active metals decrease, resulting in a low-activity catalyst. By ensuring that the pore volume is approximately 0.55 ml/g or greater, a satisfactory amount of the solvent is able to be introduced into the pore volume when the catalyst is prepared by a typical impregnation method. Further, a method may be used in which a large amount of an acid such as nitric acid is added to improve the solubility of the active metal compounds, but if the amount of added acid is too large, then the specific surface area of the carrier may sometimes decrease markedly, resulting in reduced desulfurization performance. By ensuring that the pore volume of the complex oxide carrier is not more than approximately 0.9 ml/g, a catalyst can be obtained which has a satisfactory specific surface area, and exhibits good dispersibility of the active metals and superior desulfurization activity.

[0031]

Furthermore, if the pore diameter of the catalyst is small, then there is a possibility that diffusion of the sulfur compounds into the catalyst pores may be inadequate, resulting in a reduction in the desulfurization activity. By ensuring that the pore diameter of the complex oxide carrier is at least approximately 60 Å, impregnating
 5 of the active metals yields a catalyst in which the pore diameter is satisfactorily large. On the other hand, if the specific surface area of the catalyst is too small, then there is a possibility that the dispersibility of the active metals may be decreased, resulting in a reduction in the desulfurization activity. By ensuring that the pore diameter of the complex oxide carrier is not more than approximately 120 Å, a catalyst having a
 10 satisfactory specific surface area can be obtained.

[0032]

Besides the alumina and the HY zeolite, the complex oxide carrier may also include other inorganic oxides such as boria, silica, silica-alumina, titania and zirconia, provided the physical properties of the carrier and the physical properties of the catalyst
 15 satisfy the prescribed ranges mentioned above.

[0033]

<Hydrodesulfurization Catalyst for Hydrocarbon Oil>

Examples of the Co compound impregnated on the complex oxide carrier include the carbonate salt, acetate salt, nitrate salt, sulfate salt and the oxide, and of these, the
 20 carbonate salt and acetate salt are preferred, and the carbonate salt is particularly desirable.

Examples of the Mo compound impregnated on the complex oxide carrier include molybdenum trioxide, phosphomolybdic acid, ammonium molybdate and molybdic acid, and of these, phosphomolybdic acid and molybdenum trioxide are preferred.

25 [0034]

In those cases where a compound such as phosphomolybdic acid which contains phosphorus (a phosphorus compound) is used as the Co compound or the Mo compound, the phosphorus derived from this phosphorus-containing compound may function as the phosphorus that is impregnated on the complex oxide carrier. Further, in those cases
5 where a phosphorus compound is not used as the Co compound or the Mo compound, or those cases where the phosphorus derived from such a phosphorus-containing compound alone is insufficient to satisfy the prescribed amount of phosphorus, another phosphorus source is used. Examples of this other phosphorus source include the various phosphoric acids, and specifically orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid,
10 triphosphoric acid, tetraphosphoric acid and polyphosphoric acid. Of these, orthophosphoric acid is particularly desirable.

[0035]

Of these active components, the Co content, relative to the total mass of the catalyst and calculated as the oxide, is within a range from 3 to 6 mass %, and preferably
15 from approximately 3.5 to 6 mass %. If the Co content is too small, then there is a possibility that the number of active sites attributable to Co may be inadequate, whereas if the Co content is too large, then not only can aggregation of the Co compound cause a decrease in the dispersibility of the active metals, but species of the inactive precursor Co_3O_4 (which exist as Co_9S_8 following catalyst presulfurization and during
20 hydrotreatment) and Co spinel species that have been incorporated within the carrier lattice tend to be generated, which can cause a decrease in the catalytic activity. By ensuring that the Co content satisfies the above range, a catalyst having superior desulfurization activity can be obtained which has a satisfactory number of active sites attributable to Co, exhibits good Co dispersibility, and contains a minimal amount of
25 inactive Co compounds.

[0036]

The Mo content, relative to the total mass of the catalyst and calculated as the oxide, is within a range from 16 to 24 mass %, and preferably from approximately 18 to 22 mass %. If the Mo content is too small, then there is a possibility that the amount of Mo may be insufficient to achieve the effects attributable to Mo. In contrast, if the Mo content is too large, then not only can aggregation of the Mo cause a decrease in the dispersibility of the active metals, but because the limit of the amount of active metals that can be dispersed efficiently is exceeded, and the specific surface area of the catalyst tends to decrease significantly, no further improvement can be expected in the catalytic activity. By ensuring that the Mo content satisfies the above range, a catalyst having superior desulfurization activity can be obtained which has a satisfactory effect attributable to Mo, exhibits good Mo dispersibility, and has a satisfactory catalyst surface area.

[0037]

Phosphorus is added as a component that improves the quality of the active sites in order to improve the desulfurization activity per unit weight of the active metals, and has a role of precisely creating the highly active Co-Mo-S phase (desulfurization active site). In other words, the phosphorus has the effect of improving the acid property of the catalyst, and when the catalyst displays a favorable value for the acid property, the dispersibility of the active components improves, the amount of acid sites on the carrier reaches an optimal value, and adsorption of sulfur compounds is promoted, thereby improving the sulfur compound hydrodesulfurization activity.

[0038]

The phosphorus content, relative to the total mass of the catalyst and calculated as the oxide, is within a range from 0.8 to 4.5 mass %, and preferably from approximately

1.0 to 4 mass %. If the phosphorus content is too small, then the aforementioned effects of adding the phosphorus are not realized satisfactorily, and there is a possibility that the sulfur content within the gas oil fraction may not be able to be removed efficiently. In contrast, if the phosphorus content is too large, then the aforementioned effects of the phosphorus become saturated, and the surface area and pore volume of the catalyst tend to decrease, resulting in a decrease in the desulfurization activity. By ensuring that the phosphorus content satisfies the above range, the aforementioned effects of the phosphorus can be satisfactorily realized, while suppressing any decrease in the surface area or pore volume of the catalyst.

[0039]

Within the above ranges for the amounts of the components Co, Mo and phosphorus, the optimal mass ratio between the active metals Co and Mo, reported as the value of $[\text{CoO}]/[\text{CoO}+\text{MoO}_3]$, is preferably within a range from approximately 0.12 to 0.24, and the optimal mass ratio between the active metal Mo and the phosphorus which functions as a component for improving the acid property of the catalyst, reported as the value of $[\text{P}_2\text{O}_5]/[\text{MoO}_3]$, is preferably within a range from approximately 0.05 to 0.25.

[0040]

If the mass ratio between Co and Mo as indicated by the value of $[\text{CoO}]/[\text{CoO}+\text{MoO}_3]$ is too small, then it is thought that the Co-Mo-S phase which is thought to represent a desulfurization active site may not be produced satisfactorily, meaning no improvement in the desulfurization activity. In contrast, if the above value is too large, then there is a possibility that wasted Co species which do not contribute to the catalytic activity (such as Co_9S_8 species and Co spinel species that have been incorporated within the carrier lattice) may be generated, resulting in a reduction in the catalytic activity. By ensuring that the mass ratio between the Co and the Mo, reported

as the above value, is within the range from approximately 0.12 to 0.24, the Co-Mo-S phase can be produced satisfactorily while suppressing any generation of inactive Co species, meaning a catalyst having superior desulfurization activity can be obtained.

[0041]

5 If the mass ratio between phosphorus and Mo as indicated by the value of $[P_2O_5]/[MoO_3]$ is too small, then uniform blending of the Co and Mo becomes difficult, making it more difficult to obtain the Co-Mo-S desulfurization active sites, and resulting in a catalyst of lower activity. In contrast, if the above value is too large, then this may cause reductions in the surface area and pore volume of the catalyst, which not only
10 results in decrease of catalytic activity, but also causes an increase in the acidity, which can cause coke deposition, and increases the likelihood of a deactivation in the catalytic activity. By ensuring that the mass ratio between the phosphorus and the Mo, reported as the above value, is within the range from approximately 0.05 to 0.25, the Co-Mo-S phase can be produced satisfactorily while suppressing any reduction in the surface area or pore
15 volume of the catalyst and also suppressing coke deposition, meaning a catalyst having superior desulfurization activity can be obtained.

[0042]

The catalyst according to the present invention can be prepared by first complexing the aforementioned HY zeolite with the alumina, and then impregnating the
20 thus obtained complex oxide carrier with a solution prepared by dissolving the compounds of the various components mentioned above in a solvent such as water or an acid.

Examples of the method used for complexing the alumina and the HY zeolite include a coprecipitation method and a kneading method.

25 [0043]

The method used for impregnating the complex oxide carrier with the Co, Mo and phosphorus components is preferably a one-step impregnation method in which the carrier is impregnated simultaneously with all of these components. The reason for this preference is that a one-step impregnation method is considered more advantageous from the perspective of the catalyst properties such as the number of desulfurization active sites, the acid property and the pore properties, and also from an operational perspective. In other words, in a one-step impregnation method, because the Co and the Mo are uniformly blended together and incorporated within the carrier, the amount of the Co-Mo-S phase which represents the desulfurization active sites can be increased significantly. At this time, if the phosphorus component also exists in the impregnation solution, then the uniform blending of the Co and the Mo is accelerated. In contrast, in an impregnation method in which the Co and the Mo are impregnated via a two-step process, it is thought that the blending of the Co and Mo may sometimes not proceed satisfactorily, making formation of the Co-Mo-S phase of the desulfurization active sites more difficult. For example, the aforementioned inactive precursor Co_3O_4 , and Co spinel species that have been incorporated within the carrier lattice but do not contribute to the catalytic activity tend to be formed.

[0044]

One specific method of impregnating the Co and Mo on the carrier is described below.

First, a solution containing the Co, Mo and phosphorus compounds (when the Mo compound contains phosphorus, a phosphorus compound need not necessarily be added, but may still be added in an appropriate amount) is prepared. During preparation of the solution, heating (at approximately 30 to 100°C) or the addition of an acid may be used to accelerate the dissolution of the compounds. Examples of acids that may be added

include nitric acid, and organic acids such as citric acid, acetic acid, malic acid and tartaric acid.

Subsequently, the prepared solution is added gradually and impregnated uniformly into the complex oxide carrier. The impregnation time is typically within a range from approximately 1 minute to 5 hours and preferably from approximately 5 minutes to 3 hours, and the temperature is typically within a range from approximately 5 to 100°C and preferably from approximately 10 to 80°C. There are no particular limitations on the atmosphere, and the impregnation may be performed in the open atmosphere, within a nitrogen atmosphere, or under vacuum.

[0045]

Following impregnation of the compounds, the water content is partially removed (so that the LOI <Loss on ignition> is approximately 50% or less) at a temperature within a range from room temperature to approximately 80°C, under a stream of nitrogen or a stream of air, or in a vacuum, and the catalyst is then dried in a drying oven or under a stream of air at approximately 80 to 150°C for approximately 10 minutes to 10 hours. Subsequently, the catalyst is calcinated in a furnace under a stream of air at a temperature of approximately 300 to 700°C for a period of approximately 10 minutes to 10 hours.

[0046]

The state of the distribution of active metals within the catalyst according to the present invention is preferably uniform, with the active metals distributed evenly through the catalyst.

[0047]

For the catalyst according to the present invention prepared in the manner described above, in order to enhance the hydrogenation activity and desulfurization activity of the catalyst relative to kerosene, gas oil and heavy gas oil fractions and the

like, it is necessary to control the specific surface area, the pore volume and the mean pore diameter of the catalyst so as to satisfy the numerical ranges described below.

[0048]

The specific surface area (BET specific surface area) of the catalyst according to
5 the present invention, measured by the nitrogen adsorption method (BET <Brunauer-
Emmett-Teller specific surface area> method), is within a range from 210 to 280 m²/g,
and is preferably from approximately 220 to 250 m²/g. If the BET specific surface area
is too small, then the dispersibility of the active metals decreases and the desulfurization
activity decreases, whereas if the BET specific surface area is too large, then the pore
10 diameter becomes very small, meaning the pore diameter of the catalyst also decreases,
and therefore when the hydrotreatment is performed, diffusion of the sulfur compounds
into the catalyst pores tends to be inadequate, resulting in a reduction in the
desulfurization activity. By ensuring that the BET specific surface area of the catalyst
satisfies the above range, the dispersibility of the active metals is improved, and the pore
15 diameter can be formed with a satisfactory size, enabling a catalyst having superior
desulfurization activity to be obtained.

[0049]

The pore volume of the catalyst according to the present invention, measured by
the mercury intrusion method, is within a range from 0.3 to 0.6 ml/g, and is preferably
20 from approximately 0.35 to 0.5 ml/g. If the pore volume is too small, then when the
hydrotreatment is performed, diffusion of the sulfur compounds into the catalyst pores
tends to be inadequate, resulting in unsatisfactory desulfurization activity, whereas if the
pore volume is too large, then the specific surface area of the catalyst becomes very small,
causing a decrease in the dispersibility of the active metals and yielding a catalyst having
25 low desulfurization activity. By ensuring that the pore volume of the catalyst satisfies the

above range, the sulfur compounds can diffuse satisfactorily into the catalyst pores, and a catalyst having a satisfactory specific surface area and superior desulfurization activity can be obtained.

[0050]

5 For the catalyst according to the present invention, the mean pore diameter in a pore distribution measured by the mercury intrusion method is within a range from 75 to 95 Å, and preferably from approximately 80 to 90 Å. If the mean pore diameter is too small, then diffusion of the reactants into the pores becomes more difficult, and therefore the desulfurization reaction does not proceed efficiently, whereas if the mean pore
10 diameter is too large, then although diffusion into the pores is favorable, the total surface area inside the pores decreases, resulting in a reduction in the effective specific surface area of the catalyst, and a reduction in the catalytic activity. By ensuring that the mean pore diameter of the catalyst satisfies the above range, the effective specific surface area of the catalyst is satisfactorily large, and the reactants are able to diffuse easily into the
15 pores, meaning a catalyst can be obtained that enables the desulfurization reaction to proceed with good efficiency.

[0051]

Further, in order to increase the effective number of pores that satisfy the pore conditions described above, the proportion of pores within the catalyst pore distribution
20 that have a pore diameter within a range of ± 15 Å from the mean pore diameter is typically at least 75%, and preferably approximately 80% or more, of the total pore volume.

Moreover, the pore distribution is preferably monomodal. A catalyst for which the pore distribution is sharp has fewer pores that do not contribute to the catalytic
25 activity, and therefore enables a higher level of desulfurization activity to be obtained.

[0052]

There are no particular limitations on the shape of the catalyst according to the present invention, and the types of shapes typically used for these types of catalysts may be employed, including cylindrical shapes, trilobe shapes and quadlobe shapes. The size
5 of the catalyst according to the present invention typically includes a diameter of 1 to 2 mm and a length of approximately 2 to 5 mm.

[0053]

The mechanical strength of the catalyst according to the present invention in terms of the side crush strength (SCS) is preferably at least approximately 21 lbs/mm. If
10 the SCS value is less than this value, then there is a possibility that the catalyst packed inside the reactor of hydrodesulfurization unit may be crushed, generating a differential pressure inside the reactor and making continuous operation of the hydrotreatment impossible. The compacted bulk density (CBD) of the catalyst according to the present invention is preferably within a range from approximately 0.6 to 1.2.

15 [0054]

<Hydrotreatment Method using the Hydrodesulfurization Catalyst>

The catalyst according to the present invention can be used for hydrotreating hydrocarbon oils in a similar manner to other desulfurization catalysts. The catalyst according to the present invention exhibits an extremely high level of desulfurization
20 activity, and can substantially reduce the sulfur content within a hydrocarbon oil, and particularly a gas oil fraction, not only under similar reaction conditions to those employed in conventional hydrotreatments, but even under milder conditions than are conventionally used.

[0055]

For example, by bringing the catalyst according to the present invention and a hydrocarbon oil containing sulfur compounds (such as a gas oil fraction) into contact and performing a desulfurization under conditions including a hydrogen partial pressure of approximately 3 to 8 MPa, a temperature of approximately 300 to 420°C, and a liquid
5 hourly space velocity of approximately 0.3 to 5 h⁻¹, the amount of sulfur compounds within the hydrocarbon oil can be reduced, including those sulfur compounds that are difficult to desulfurize.

[0056]

The sulfur content of the product oil obtained by performing a hydrotreatment
10 using the catalyst according to the present invention is typically not more than 500 ppm, and more specifically within a range from approximately 20 to 300 ppm. Although dependent on the properties of the feedstock, by using the catalyst according to the present invention, a product oil having a similar sulfur content to conventional product oils can be produced for a long period under milder hydrotreatment conditions than those
15 conventionally employed.

[0057]

The treatment target oil (feedstock) for hydrotreatment using the catalyst according to the present invention may be any oil containing hydrocarbons, and examples of suitable oils include kerosene and gas oil fractions such as straight-run kerosene,
20 straight-run gas oil, catalytically cracked gas oil, thermally cracked gas oil, hydrotreated gas oil, desulfurized gas oil and vacuum gas oil (VGO). Examples of representative properties of these types of feedstocks include a boiling point range of 150 to 450°C, and a sulfur content of not more than 5 mass %.

[0058]

In order to enable the hydrotreatment method using the catalyst according to the present invention to be conducted on a commercial scale, a catalyst layer composed of a fixed bed, moving bed or fluidized bed of the catalyst according to the present invention is formed inside a reactor of hydrodesulfurization unit, and the feedstock is then

5 introduced into the reactor of hydrodesulfurization unit and subjected to a hydrogenation reaction under the conditions described above. In the most general examples, a fixed-bed catalyst layer is formed inside the reactor of hydrodesulfurization unit, and either the feedstock is introduced from the upper section of the reactor of hydrodesulfurization unit and passed through the fixed bed from top to bottom, with the product flowing from the
10 lower section of the reactor of hydrodesulfurization unit, or alternatively, the feedstock is introduced from the lower section of the reactor of hydrodesulfurization unit and passed through the fixed bed from bottom to top, with the product flowing from the upper section of the reactor of hydrodesulfurization unit.

[0059]

15 The hydrotreatment method may be a single stage hydrotreatment method which is performed with the catalyst according to the present invention packed into a single reactor of hydrodesulfurization unit, or a multistage continuous hydrotreatment method which is performed with the catalyst packed into a series of reactor of hydrodesulfurization unit.

20 [0060]

The catalyst according to the present invention is activated by a pre-sulfurization treatment inside the reactor of hydrodesulfurization unit prior to use (namely, prior to performing the hydrotreatment). This pre-sulfurization treatment is performed at a temperature of approximately 200 to 400°C, and preferably approximately 250 to 350°C,
25 in a hydrogen atmosphere at normal pressure or with a higher hydrogen partial pressure,

using a petroleum distillate containing sulfur compounds, a petroleum distillate to which a sulfurizing agent such as dimethyl disulfide or carbon disulfide has been added, or hydrogen sulfide.

5

EXAMPLES

[0061]

Embodiments of the present invention and their effects are described below in further detail using a series of examples and comparative examples, but the present invention is in no way limited by these examples.

10

First, the analysis methods used for measuring the physical properties and determining the chemical composition of the catalysts in the examples and comparative examples are described below.

[0062]

<Specific Surface Area>

15

The specific surface area was measured by the BET method using nitrogen adsorption. A surface area measuring device (Belsorp 28) manufactured by Bel Japan, Inc. was used as the nitrogen adsorption device.

[0063]

<Pore Volume, Mean pore diameter, and Pore Distribution>

20

(Device used)

The pore volume, the mean pore diameter, and the pore distribution were measured using the mercury intrusion method. A porosimeter (Micromeritics Auto-Pore 9200, manufactured by Shimadzu Corporation) was used as the mercury intrusion device.

[0064]

25

(Measurement principles)

The mercury intrusion method is based on the law of the capillary phenomenon. In the case of mercury and circular cylindrical pores, this law is represented by formula (F) shown below. In formula (F), D represents the pore diameter, P represents the applied pressure, γ represents the surface tension, and θ represents the contact angle. The volume of mercury entering the pores is measured as a function of the applied pressure P. The surface tension of mercury within the pores of the catalyst was 484 dyne/cm, and the contact angle was 130 degrees.

$$\text{Formula (F): } D = -\frac{4\gamma \cos\theta}{P}$$

[0065]

The pore volume is the total volume of mercury that entered the pores per gram of the catalyst. The mean pore diameter is the average value of D calculated as a function of P.

The pore distribution is the distribution of D calculated as a function of P.

[0066]

(Measurement procedure)

(1) The power to a vacuum heat deaerator was turned on, and it was confirmed that the atmosphere had reached a temperature of 400°C and a vacuum degree of not more than 5×10^{-2} Torr.

(2) The empty sample burette was placed in the vacuum heat deaerator.

(3) Once the vacuum degree was not more than 5×10^{-2} Torr, the cock of the sample burette was closed, and the sample burette was removed from the vacuum heat deaerator and cooled, and the weight was measured.

(4) The sample (catalyst) was placed in the sample burette.

(5) The sample burette containing the sample was placed in the vacuum heat deaerator, the vacuum degree was reduced to not more than 5×10^{-2} Torr, and the sample was held in this state for at least one hour.

(6) The sample burette containing the sample was removed from the vacuum heat deaerator and cooled, and the weight was then measured to determine the sample weight.

(7) The sample was placed in the cell of the Auto-Pore 9200.

(8) Measurement was performed using the Auto-Pore 9200.

[0067]

<Analysis of Chemical Composition>

10 (Device used and analysis method)

Analysis of the metals within the catalyst was performed using inductively coupled plasma emission analysis (ICPS-2000, manufactured by Shimadzu Corporation).

Quantitative determination of the amount of each metal was conducted using the absolute calibration curve method.

15 [0068]

(Measurement procedure)

(1) In a uniseal were placed 0.05 g of the catalyst, 1 ml of hydrochloric acid (50% by volume), one drop of hydrofluoric acid and 1 cc of pure water, and the mixture was heated and dissolved.

20 (2) Following dissolution, the solution was transferred to a propylene measuring flask (50 ml), and pure water was added to bring the volume up to 50 ml.

(3) The resulting solution was measured using the ICPS-2000.

[0069]

[Production Example 1] Preparation of Zeolite

A zeolite 1 used in the following example was prepared using the method described below.

An autoclave vessel was charged with 230 g of a 21.7 mass % aqueous solution of sodium hydroxide, and 29 g of sodium aluminate containing 17.0 mass % of Na_2O and 22.0 mass % of Al_2O_3 was then added to the autoclave under constant stirring. The solution obtained following addition of the sodium aluminate was added, with constant stirring, to 232 g of a sodium silicate solution No. 3 having an SiO_2 concentration of 24 mass %, and following thorough stirring of the resulting mixture, the mixture was aged by heating at 95°C for 12 hours. Following completion of this aging, the temperature was cooled to 70°C or lower, and the synthesized product was removed, filtered, washed and dried, completing preparation of Na-Y seed crystals. The composition of the thus obtained seed composition, reported as molar ratios of oxides, was $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 16$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 15$, $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 330$.

[0070]

Next, an autoclave vessel was charged with 220 g of a sodium silicate solution having an SiO_2 concentration of 29 mass %, 31.7 g of sodium aluminate containing 33.0 mass % of Na_2O and 36.5 mass % of Al_2O_3 , 6 g of sodium hydroxide and 747.0 g of pure water, and following thorough stirring, 8.0 g (dry mass) of the above seed crystals were added, the resulting mixture was stirred thoroughly once again, and the mixture was then aged by heating at 95°C for 12 hours. Following completion of this aging, the temperature was cooled to 70°C or lower, and the synthesized product was removed, filtered, washed and dried, yielding the Na-Y zeolite 1.

Subsequently, the Na-Y zeolite 1 was placed in a 5 mass % aqueous solution of ammonium nitrate, and following stirring for 20 minutes under constant conditions at 60°C , the mixture was filtered to complete an ion exchange treatment. This ion exchange

treatment was repeated twice, and the product was then dried at 120°C for 12 hours to obtain an NH₃-type Y zeolite 1.

The thus obtained NH₃-type Y zeolite 1 was calcinated at 600°C for 4 hours under a stream of air, thus obtaining an H-type Y zeolite 1 (hereafter simply referred to as the "zeolite 1"). The amount of the aforementioned seed Al₂O₃ relative to the total amount of Al₂O₃ within the reaction mixture was 0.098 mol%.

[0071]

Zeolite 2 to zeolite 5 were prepared using the same method as that described for the zeolite 1.

For the zeolites 1 to 5, the SiO₂/Al₂O₃ molar ratio, the crystal lattice constant, the molar ratio of Al within the zeolite framework relative to the total Al content ([Al within the zeolite framework] / [total Al]), and the crystallite diameter are shown in Table 1.

The SiO₂/Al₂O₃ molar ratio was measured by chemical composition analysis using an ICP analysis method. The crystal lattice constant was measured using an X-ray diffraction apparatus (XRD) in accordance with ASTM D3906. The molar ratio of Al within the zeolite framework relative to the total Al content was calculated from the chemical composition analysis values and the XRD measurement values. Details regarding these measurements are as described above.

[0072]

[Table 1]

	SiO ₂ /Al ₂ O ₃ (molar ratio)	Crystal lattice constant (nm)	[Al within the zeolite framework] / [total Al]	Crystallite diameter (nm)
Zeolite 1	5.6	2.442	0.32	93
Zeolite 2	5.8	2.452	0.56	90
Zeolite 3	6.0	2.439	0.28	50
Zeolite 4	6.0	2.439	0.28	35
Zeolite 5	5.8	2.441	0.31	118

[0073]

5 [Example 1]

First, 2.0 g of the zeolite 1 and 109.4 g of alumina hydrate were kneaded together, and following extrusion molding, the product was calcinated at 600°C for 2 hours to obtain a columnar molded product having a diameter of 1/16 inch composed of a zeolite-alumina complex carrier (zeolite/alumina mass ratio = 7/93, pore volume = 0.63 ml/g, specific surface area = 336 m²/g, mean pore diameter = 69 Å).

In a separate preparation, 5.51 g of cobalt carbonate, 19.02 g of phosphomolybdic acid and 2.46 g of orthophosphoric acid (85% aqueous solution) were dissolved in 40.0 g of ion-exchanged water to prepare an impregnation solution.

In a round-bottom flask was placed 50.0 g of the above zeolite-alumina complex carrier, the entire volume of the above impregnation solution was then added to the flask using a pipette, and impregnation was allowed to occur at approximately 25°C for one hour. Subsequently, the product was blow-dried under a stream of nitrogen, and a muffle furnace was then used to dry the product at 120°C for approximately one hour, and then the product was calcinated at 500°C for 4 hours, thus obtaining a catalyst A.

The catalyst A had a specific surface area of $227 \text{ m}^2/\text{g}$, a pore volume of 0.40 ml/g , and a mean pore diameter of $80 \text{ \AA}$.

[0074]

[Example 2]

5 First, 2.0 g of the zeolite 2 and 109.4 g of alumina hydrate were kneaded together, and following extrusion molding, the product was calcinated at 600°C for 2 hours to obtain a columnar molded product having a diameter of $1/16$ inch composed of a zeolite-alumina complex carrier (zeolite/alumina mass ratio = $7/93$, pore volume = 0.61 ml/g , specific surface area = $342 \text{ m}^2/\text{g}$, mean pore diameter = $68 \text{ \AA}$).

10 In a separate preparation, 5.51 g of cobalt carbonate, 19.02 g of phosphomolybdic acid and 2.46 g of orthophosphoric acid (85% aqueous solution) were dissolved in 40.0 g of ion-exchanged water to prepare an impregnation solution.

In a round-bottom flask was placed 50.0 g of the above zeolite-alumina complex carrier, the entire volume of the above impregnation solution was then added to the flask
15 using a pipette, and impregnation was allowed to occur at approximately 25°C for one hour. Subsequently, the product was blow-dried under a stream of nitrogen, and a muffle furnace was then used to dry the product at 120°C for approximately one hour, and then the product was calcinated at 500°C for 4 hours, thus obtaining a catalyst B.

The catalyst B had a specific surface area of $223 \text{ m}^2/\text{g}$, a pore volume of 0.43
20 ml/g , and a mean pore diameter of $81 \text{ \AA}$.

[0075]

[Example 3]

First, 2.0 g of the zeolite 3 and 109.4 g of alumina hydrate were kneaded together, and following extrusion molding, the product was calcinated at 600°C for 2 hours to
25 obtain a columnar molded product having a diameter of $1/16$ inch composed of a zeolite-

alumina complex carrier (zeolite/alumina mass ratio = 7/93, pore volume = 0.63 ml/g, specific surface area = 333 m²/g, mean pore diameter = 69 Å).

In a separate preparation, 5.51 g of cobalt carbonate, 19.02 g of phosphomolybdic acid and 2.46 g of orthophosphoric acid (85% aqueous solution) were dissolved in 40.0 g of ion-exchanged water to prepare an impregnation solution.

In a round-bottom flask was placed 50.0 g of the above zeolite-alumina complex carrier, the entire volume of the above impregnation solution was then added to the flask using a pipette, and impregnation was allowed to occur at approximately 25°C for one hour. Subsequently, the product was blow-dried under a stream of nitrogen, and a muffle furnace was then used to dry the product at 120°C for approximately one hour, and then the product was calcinated at 500°C for 4 hours, thus obtaining a catalyst C.

The catalyst C had a specific surface area of 220 m²/g, a pore volume of 0.38 ml/g, and a mean pore diameter of 83 Å.

[0076]

[Example 4]

First, 2.0 g of the zeolite 4 and 109.4 g of alumina hydrate were kneaded together, and following extrusion molding, the product was calcinated at 600°C for 2 hours to obtain a columnar molded product having a diameter of 1/16 inch composed of a zeolite-alumina complex carrier (zeolite/alumina mass ratio = 7/93, pore volume = 0.64 ml/g, specific surface area = 330 m²/g, mean pore diameter = 70 Å).

In a separate preparation, 5.51 g of cobalt carbonate, 19.02 g of phosphomolybdic acid and 2.46 g of orthophosphoric acid (85% aqueous solution) were dissolved in 40.0 g of ion-exchanged water to prepare an impregnation solution.

In a round-bottom flask was placed 50.0 g of the above zeolite-alumina complex carrier, the entire volume of the above impregnation solution was then added to the flask

using a pipette, and impregnation was allowed to occur at approximately 25°C for one hour. Subsequently, the product was blow-dried under a stream of nitrogen, and a muffle furnace was then used to dry the product at 120°C for approximately one hour, and then the product was calcinated at 500°C for 4 hours, thus obtaining a catalyst D.

5 The catalyst D had a specific surface area of 224 m²/g, a pore volume of 0.39 ml/g, and a mean pore diameter of 81 Å.

[0077]

[Comparative Example 1]

With the exception of replacing the zeolite 1 from Example 1 with the zeolite 5, a
 10 zeolite-alumina complex carrier (zeolite/alumina mass ratio = 7/93, pore volume = 0.63 ml/g, specific surface area = 334 m²/g, mean pore diameter = 71 Å) having the same shape as the carrier of Example 1 was obtained in the same manner as that described for Example 1. Next, 50.0 g of this zeolite-alumina complex carrier was placed in a round-bottom flask, the entire volume of the same impregnation solution as that used in
 15 Example 1 was added to the flask, impregnation was performed in the same manner as Example 1, and the product was blow-dried, dried, and calcinated in the same manner as that described for Example 1 to obtain a catalystX.

The catalyst X had a specific surface area of 223 m²/g, a pore volume of 0.37 ml/g, and a mean pore diameter of 82 Å.

20 [0078]

The elemental analysis values for the catalysts A to D and the catalyst X are shown in Table 2, and the properties of the respective catalysts are shown in Table 3. In Table 3, "SA" represents the specific surface area (m²/g), "PV" represents the pore volume (ml/g), "MPD" represents the mean pore diameter (Å), "PSD" represents the pore
 25 distribution (%) (the percentage of the total pore volume accounted for by pores having a

size of $\text{MPD} \pm 15 \text{ \AA}$, and "CBD" represents the compacted bulk density (g/ml). As illustrated in Tables 2 and 3, the catalysts A to D and the catalyst X all had substantially the same chemical composition and physical shape.

[0079]

5 [Table 2]

	Carrier		Impregnated material				
	(mass % relative to total mass of carrier)		(mass % relative to total mass of catalyst)				
	Zeolite	Zeolite percentage	CoO	MoO ₃	P ₂ O ₅	Co/(Co+Mo)	P/Mo
Example 1 Catalyst A	Zeolite 1	7	4.9	20.2	3.3	0.20	0.16
Example 2 Catalyst B	Zeolite 2	7	5.3	20.5	3.1	0.21	0.15
Example 3 Catalyst C	Zeolite 3	7	5.0	20.2	2.7	0.20	0.13
Example 4 Catalyst D	Zeolite 4	7	5.1	19.9	2.9	0.20	0.15
Comparative Example 1 Catalyst X	Zeolite 5	7	4.9	20.2	3.3	0.20	0.16

[0080]

[Table 3]

	SA (m ² /g)	PV (ml/g)	MPD ($\text{\AA}$)	PSD $\pm 15 \text{ \AA}$ (%)	CBD (g/ml)
Catalyst A	227	0.40	80	84	0.86
Catalyst B	223	0.43	81	86	0.85
Catalyst C	220	0.38	83	80	0.86
Catalyst D	224	0.39	81	85	0.86
Catalyst X	223	0.37	82	81	0.85

[0081]

[Straight-run Gas Oil Hydrotreatment Reaction 1]

Using the catalysts A to D and the catalyst X prepared in Examples 1 to 4 and Comparative Example 1 respectively, a hydrotreatment of a straight-run gas oil having
 5 the properties shown below was performed in the manner described below.

First, the catalyst was packed in a high-pressure flow reactor to form a fixed-bed catalyst layer, and treatment was then performed under the conditions listed below.

Next, a mixed fluid containing the feedstock heated to reaction temperature and a hydrogen-containing gas was introduced into the upper section of the reactor, and a
 10 hydrogenation reaction was allowed to proceed under the conditions listed below. A mixed fluid containing the product oil and a gas flowed out from the lower section of the reactor, and the product oil was separated in a gas-liquid separator.

[0082]

Catalyst pretreatment conditions:

15 Pressure: normal pressure

Atmosphere: a stream of hydrogen sulfide (5%) in hydrogen gas

Temperature: increased in a stepwise manner by holding at 150°C for 0.5 hour,
 and then holding at 350°C for one hour

[0083]

20 Hydrogenation reaction conditions:

Reaction temperature: 360°C, or a temperature at which the sulfur content of the product oil was reduced to 200 ppm

Pressure (hydrogen partial pressure): 5 MPa

Liquid hourly space velocity: 1.2 h⁻¹

25 Hydrogen/oil ratio: 250 m³/m³

[0084]

Properties of feedstock:

Oil type: Middle East straight-run gas oil

Specific gravity (15/4°C): 0.8648

5 Distillation properties: initial distillation point 206.0°C, 50% point 319.0°C, 90% point 372.0°C, end point 390.0°C

Sulfur component: 1.44 mass %

Nitrogen component: 170 ppm

Kinematic viscosity (at 30°C): 6.660 cSt

10 Pour point: 2.5°C

Cloud point: 3.0°C

Cetane index: 53.2

Saybolt color: -16

ASTM color: L1.0

15 Aniline point: 74.2°C

[0085]

The reaction results were analyzed using the methods described below.

The reactor was operated at 360°C, and after 6 days had passed, a sample of the product oil was collected and the properties analyzed. Subsequently, for each catalyst, the reactor was operated for 200 days at the temperature required to achieve a product oil sulfur content of 200 ppm. During this operation of producing a product oil with a constant sulfur content, in order to suppress any increase in the sulfur content within the product oil caused by degradation of the catalyst, the operating temperature was adjusted as appropriate during operation.

25 [0086]

[1] hydrodesulfurization rate (HDS) (%):

The desulfurization rate is defined as the proportion of the sulfur content eliminated from the feedstock by converting the sulfur content within the feedstock to hydrogen sulfide via the desulfurization reaction, and can be calculated from the sulfur analysis values for the feedstock and the product oil using the formula shown below.

[2] Desulfurization reaction rate constant (Ks):

Relative to the reduction in the sulfur content (Sp) in the product oil, the desulfurization reaction rate constant (Ks) was defined as the constant for the reaction rate equation that yielded a 1.5 order of reaction. A higher reaction rate constant indicates superior catalytic activity. These results are shown in Table 4.

[0087]

$$\text{Desulfurization rate (\%)} = \frac{(S_f - S_p)}{S_f} \times 100$$

Desulfurization reaction rate constant

$$= 2 \times \left[\frac{1}{\sqrt{(S_p)}} - \frac{1}{\sqrt{(S_f)}} \right] \times (\text{LHSV})$$

In the above formulas, Sf represents the sulfur content (mass %) within the feedstock, Sp represents the sulfur content (mass %) in the reaction product oil, and LHSV represents the liquid hourly space velocity (h⁻¹).

[0088]

Comparative activity (%)

$$= \frac{\text{desulfurization reaction rate constant of each desulfurization catalyst}}{\text{desulfurization reaction rate constant with comparative catalyst X}} \times 100$$

[0089]

[3] A graph plotting the desulfurization reaction rate constant (K_s) calculated in [2] against the crystallite diameter of the zeolite is illustrated in FIG. 1.

[4] Desulfurization reaction rate constant (K_s):

Relative to the reduction in the sulfur content (S_p) in the product oil, the
 5 desulfurization reaction rate constant (K_s) was defined as the constant for the reaction rate equation that calculated to be a 1.5 order of reaction. A higher reaction rate constant indicates superior catalytic activity. These results when the reaction was performed at 360°C are shown in Table 4.

[0090]

10 [Table 4]

	Product oil sulfur content (mass %)	Desulfurization rate (%)	Desulfurization reaction rate constant (K_s)	Comparative activity (%)
Example 1 (Catalyst A)	0.0193	98.7	15.28	171
Example 2 (Catalyst B)	0.0173	98.8	16.25	182
Example 3 (Catalyst C)	0.0241	98.3	13.46	151
Example 4 (Catalyst D)	0.0301	97.9	11.83	133
Comparative Example 1 (Catalyst X)	0.0483	96.6	8.92	100

[0091]

As is evident from Table 4, the catalysts A to D of Examples 1 to 4 exhibited higher desulfurization rates, larger desulfurization reaction rate constants, and extremely
 15 high comparative activities of at least 130% compared with the catalyst X of Comparative Example 1. In particular, whereas the sulfur content of the product oil was approximately 0.05 mass % when the catalyst X was used, when the catalysts A to D

were used, the sulfur content in the product oil was able to be reduced to 0.03 mass % or less.

Further, as illustrated in FIG. 1, it was evident that the crystallite diameter of the zeolite contained within the catalyst had an effect on the desulfurization reaction rate constant of the catalyst, with the desulfurization reaction rate constant reaching a peak value when the crystallite diameter was in the vicinity of 85 to 95 nm, and then falling rapidly when the crystallite diameter was 100 nm or greater.

[0092]

Moreover, Table 5 illustrates the operating temperatures after 100 days and after 200 days of operation. When the catalysts A to D of Examples 1 to 4 were used, the difference between the operating temperature after 100 days and the operating temperature after 200 days was within a range from 1 to 4°C, indicating that even when the operation of producing a product oil with a constant sulfur content was performed for a long period, there was no necessity to significantly increase the operating temperature. In contrast, when the catalyst X of Comparative Example 1 was used, the operating temperature after 200 days needed to be increased more than 10°C from the operating temperature after 100 days. Based on these results, it is clear that the catalyst according to the present invention is able to maintain stable activity over a long period of time.

[0093]

[Table 5]

	Operating temperature after 100 days (°C)	Operating temperature after 200 days (°C)
Example 1 (Catalyst A)	361	363
Example 2 (Catalyst B)	360	361
Example 3 (Catalyst C)	365	368
Example 4 (Catalyst D)	369	373
Comparative Example 1 (Catalyst X)	381	392

[0094]

5 As is evident from the above results, the catalyst according to the present invention exhibits excellent activity in a desulfurization reaction for a hydrocarbon oil such as a gas oil under substantially the same conditions such as hydrogen partial pressure and reaction temperature as those employed in conventional gas oil hydrotreatments. As a result, by using the catalyst according to the present invention, a

10 gas oil base having an extremely low sulfur content, for example a gas oil base having a sulfur content lower than even 0.05 mass %, can be supplied with comparative ease.

What is claimed is:

1. A hydrodesulfurization catalyst for a hydrocarbon oil, the catalyst prepared by impregnating cobalt, molybdenum and phosphorus on a complex oxide carrier
- 5 comprising 80 to 99 mass % of an alumina and 1 to 20 mass % of an HY zeolite, wherein
 based on a total mass of the catalyst, and calculated in terms of oxide content, the catalyst comprises 3 to 6 mass % of cobalt, 16 to 24 mass % of molybdenum, and 0.8 to 4.5 mass % of phosphorus,
 the catalyst has a specific surface area measured by a nitrogen adsorption method
 10 of 210 to 280 m²/g, a pore volume measured by a mercury intrusion method of 0.3 to 0.6 ml/g, a mean pore diameter in a pore distribution measured by the mercury intrusion method of 75 to 95 Å, and a pore volume for pores within a range of ± 15 Å from the mean pore diameter that is at least 75% of total pore volume, and
 the HY zeolite has:
- 15 (a) a SiO₂/Al₂O₃ (molar ratio) of 3 to 10,
 (b) a crystal lattice constant of 2.435 to 2.465 nm,
 (c) a molar ratio of Al within the zeolite framework relative to the total Al content of 0.2 to 0.9, and
 (d) a crystallite diameter of 30 to 100 nm.