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## (54) METHOD FOR PRODUCING HYDROTREATED OIL AND METHOD FOR PRODUCING CATALYTIC CRACKED OIL

(57) There is provided a method for producing hydrotreated oil comprising: a step of passing heavy hydrocarbon oil through a reactor filled with a hydrotreating catalyst to obtain hydrotreated oil, wherein the hydrotreating catalyst contains phosphorus, an iron group element, and a group 6 element; the ratio $C_2/C_1$ of a content $C_2$ of the iron group element to a content $C_1$ of phosphorus in the hydrotreating catalyst is less than 0.60 in a molar ratio; and the average pore diameter of the hydrotreating catalyst is larger than 7.5 nm and smaller than 9.5 nm.

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## Description

### Technical Field

**[0001]** The present invention relates to a production method for obtaining hydrotreated oil from heavy hydrocarbon oil, and to a production method for obtaining catalytic cracked oil from heavy hydrocarbon oil.

### Background Art

**[0002]** Until now, in oil refineries in Japan, fluid catalytic cracking (FCC) unit has been playing a central role in gasoline production for addressing demand for gasoline and promoting conversion of heavy hydrocarbon oil into light oil. Further, in recent years, interest has been high in the FCC unit as a process for producing a light hydrocarbon oil having high added value from heavy hydrocarbon oil, and a feed oil in which oil residue such as an atmospheric residual fraction is mixed in addition to a conventional vacuum gas oil fraction has also been used as a feed oil for FCC, seeking for higher economical efficiency.

**[0003]** Since heavy metals such as vanadium and nickel are contained in addition to sulfur and nitrogen in the atmospheric residue, a catalyst is put in a heavy oil direct desulfurization unit serving as a pretreatment unit of an FCC unit, and the atmospheric residue is reacted under high-temperature high-pressure conditions to be subjected to demetallization, desulfurization, and denitrogenation treatment.

**[0004]** Incidentally, zeolite has been generally used for the FCC catalyst used in an FCC unit, and a reduction in the amount of nitrogen poisoning the zeolite, particularly the amount of basic nitrogen, has been desired in the feed oil for FCC. That is, if it is possible to reduce the amount of nitrogen in the feed oil for FCC, the performance of the FCC catalyst will be sufficiently exhibited, and the efficiency of gasoline production will probably be improved. However, it has been considered until now that the denitrogenation reaction will also proceed when the desulfurization reaction proceeds in the direct desulfurization unit of heavy hydrocarbon oil, and there has been no particular technology of improving denitrogenation activity.

**[0005]** Although the content of nitrogen contained in heavy hydrocarbon oil has been desired to be reduced, a reduction in the content of sulfur has been considered the main object, and much attention has been given to the development of a demetallization catalyst serving as a protection of a desulfurization catalyst for removing sulfur.

**[0006]** For example, in Non Patent Literature 1, there is described that while an improvement in desulfurization activity and denitrogenation activity is found by impregnating and supporting phosphorus, pore volume of the catalyst tends to be reduced to cause rapid metal poisoning to reduce catalyst life.

**[0007]** Until now, a large number of reports have been made on the method for hydrotreating a feed oil for FCC. For example, in Patent Literatures 1 and 2, there is proposed a hydrotreating method of obtaining a feed oil for FCC by hydrotreating vacuum gas oil, atmospheric residue, and the like, the method including a first step of performing desulfurization and denitrogenation treatment at a relatively high reaction temperature and a second step of performing nuclear hydrogenation of two or more cyclic aromatics at a lower reaction temperature.

**[0008]** Further, in Patent Literature 3, there is proposed a method of improving desulfurization activity and denitrogenation activity by using a catalyst containing phosphorus.

**[0009]** However, in an actual direct desulfurization unit, in order to obtain a desired desulfurized production oil, an operation of maintaining the sulfur content in the production oil at a constant level has been performed, and unless a catalyst in which only the denitrogenation activity is improved is used, the content of nitrogen in the production oil has not been reduced. Therefore, even though a hydrotreating catalyst having improved desulfurization activity and denitrogenation activity was used in the above method, the content of nitrogen in the production oil could not be reduced in actual operation.

### Citation List

### Patent Literature

**[0010]**

Patent Literature 1: Japanese Unexamined Patent Publication No. H8-012978
Patent Literature 2: Japanese Unexamined Patent Publication No. H8-183964
Patent Literature 3: Japanese Unexamined Patent Publication No. 2000-351978

## Non Patent Literature

**[0011]** Non Patent Literature 1: J. Japan Petrol. Inst., 23, (2), 110 (1980)

## Summary of Invention

### Technical Problem

**[0012]** From the above circumstances, a catalyst in which denitrogenation activity is higher than desulfurization activity, so called a catalyst in which denitrogenation selectivity is high, and a hydrotreating method using the same are desired.

**[0013]** In view of the above conventional situation, an object of the present invention is to provide a method for producing hydrotreated oil, the method being able to efficiently obtain a hydrotreated oil suitably desulfurized and denitrogened as a feed oil for FCC from heavy hydrocarbon oil. Further, another object of the present invention is to provide a method for producing catalytic cracked oil, the method being able to efficiently obtain the catalytic cracked oil by using the hydrotreated oil obtained in the above production method as a feed oil for FCC.

### Solution to Problem

**[0014]** As a result of intensive and extensive researches for developing a method for efficiently producing a highly desulfurized and denitrogened feed oil for FCC from heavy hydrocarbon oil, the present inventors have found that a hydrotreated oil suitably desulfurized and denitrogened as a feed oil for FCC can be produced while maintaining a suitable catalyst life by using a hydrotreating catalyst having specific composition and a specific average pore diameter, and have come to propose the present invention.

**[0015]** That is, one aspect of the present invention relates to a method for producing hydrotreated oil and a method for producing catalytic cracked oil to be described below.

(1) A method for producing hydrotreated oil comprising: a step of passing heavy hydrocarbon oil through a reactor filled with a hydrotreating catalyst to obtain hydrotreated oil, wherein the hydrotreating catalyst contains phosphorus, an iron group element, and a group 6 element; the ratio $C_2/C_1$ of the content $C_2$ of the iron group element to the content $C_1$ of phosphorus in the hydrotreating catalyst is less than 0.60 in a molar ratio; the average pore diameter of the hydrotreating catalyst is larger than 7.5 nm and smaller than 9.5 nm.

(2) The production method according to the above (1), wherein, in the hydrotreating catalyst, the ratio $C_2/C_3$ of the content $C_2$ of the iron group element to the content $C_3$ of the group 6 element is less than 0.45 in a molar ratio, and the ratio $C_1/C_3$ of the content $C_1$ of the phosphorus to the content $C_3$ of the group 6 element is larger than 0.23 in a molar ratio.

(3) A method for producing catalytic cracked oil comprising: a step of obtaining hydrotreated oil by the production method according to the above (1) or (2); and a step of obtaining catalytic cracked oil by fluid catalytic cracking of the hydrotreated oil.

### Advantageous Effects of Invention

**[0016]** According to the present invention, there is provided a method for producing hydrotreated oil, the method being able to efficiently obtain hydrotreated oil suitably desulfurized and denitrogened as a feed oil for FCC from heavy hydrocarbon oil. Further, according to the present invention, there is provided a method for producing catalytic cracked oil, the method being able to efficiently obtain catalytic cracked oil.

## Description of Embodiments

**[0017]** Suitable embodiments of the present invention will be described below.

**[0018]** The method for producing hydrotreated oil according to the present embodiment comprises a step of passing heavy hydrocarbon oil through a reactor filled with a hydrotreating catalyst to obtain hydrotreated oil.

**[0019]** In the present embodiment, the hydrotreating catalyst contains phosphorus, an iron group element, and a group 6 element. In the present specification, the iron group element represents metal elements belonging to group 8, group 9, and group 10 elements of the fourth period of the periodic table, and the group 6 element represents metal elements belonging to group 6 elements of the periodic table. Examples of the iron group element include iron (Fe), cobalt (Co), and nickel (Ni), and examples of the group 6 element include chromium (Cr), molybdenum (Mo), and tungsten (W).

**[0020]** In the present embodiment, the ratio $C_2/C_1$ (molar ratio) of the content $C_2$ of the iron group element to the content $C_1$ of phosphorus in the hydrotreating catalyst is less than 0.60. Further, the average pore diameter of the hydrotreating catalyst is larger than 7.5 nm and smaller than 9.5 nm.

**[0021]** In the production method according to the present embodiment, a hydrotreated oil suitably desulfurized and denitrogened as a feed oil for FCC can be efficiently obtained from heavy hydrocarbon oil.

**[0022]** In the present embodiment, since the hydrotreating catalyst has specific metal composition and a specific average pore diameter, good catalyst life and excellent denitrogenation activity are obtained in the hydrotreatment of heavy hydrocarbon. Therefore, according to the production method according to the present embodiment, even in the operation in which the content of sulfur in the production oil is set to a constant level like before, denitrogenation efficiently proceeds in addition to desulfurization, and a hydrotreated oil in which nitrogen content is sufficiently reduced can be obtained. That is, in the production method according to the present embodiment, a hydrotreated oil suitably denitrogened as a feed oil for FCC can be efficiently produced as compared with conventional direct desulfurization methods.

<Feed oil>

**[0023]** The feed oil used in the method for producing hydrotreated oil according to the present embodiment may be any oil as long as it is heavy hydrocarbon oil. In the present specification, the heavy hydrocarbon oil refers to that containing a fraction whose boiling point under normal pressure is 380°C or more.

**[0024]** The heavy hydrocarbon oil may be, for example, atmospheric distillation residue and vacuum distillation residue, and may be solvent deasphalted oil, visbreaking oil, and the like obtained by using them as a feedstock. Further, the heavy hydrocarbon oil may contain vacuum gas oil, a residue from a fluid catalytic cracking (FCC) unit, and the like.

**[0025]** The solvent deasphalted oil may be, for example, a heavy hydrocarbon oil in which the content of a fraction whose boiling point is 550°C or more is 70 mass% or more.

**[0026]** The method for producing the solvent deasphalted oil is not particularly limited, but it can be obtained, for example, by solvent deasphalting using a chain saturated hydrocarbon having 3 to 6 carbon atoms as a solvent. Specific examples of the solvent include propane, normal butane, isobutane, normal pentane, isopentane, and normal hexane. The solvent may be used singly or in combination. Further, a solvent containing a chain saturated hydrocarbon having 5 or 6 carbon atoms in an amount of 50 vol% or more is suitably used as the solvent in solvent deasphalting, and according to such a solvent, the solvent deasphalted oil tends to be obtained at a high extraction ratio of 60 vol% or more or 70 vol% or more. Note that the residue after extraction is separated as a pitch.

**[0027]** In the heavy hydrocarbon oil used as a feed oil, it is preferable that the content of sulfur be 5.0 mass% or less, and it is more preferable that the content of sulfur be 4.0 mass% or less. When the content of sulfur is in this range, the content of sulfur in the resulting hydrotreated oil will be sufficiently reduced, and the content of sulfur in the catalytic cracked oil to be obtained later will also be suitably reduced. Note that although the lower limit of the content of sulfur in the heavy hydrocarbon oil is not particularly limited, the lower limit may be, for example, 0.6 mass% or more, and may be 0.8 mass% or more. According to the production method according to the present embodiment, even when a heavy hydrocarbon oil having such a content of sulfur is used as a feed oil, the heavy hydrocarbon oil will be sufficiently desulfurized by hydrotreatment, and the content of sulfur in the hydrotreated oil will be sufficiently reduced.

**[0028]** The content of nitrogen in the heavy hydrocarbon oil may be, for example, 0.05 mass% or more, and may be 0.07 mass% or more. In the production method according to the present embodiment, since the hydrotreating catalyst has excellent denitrogenation activity, even when a heavy hydrocarbon oil containing nitrogen as described above is used as a feed oil, the heavy hydrocarbon oil will be sufficiently denitrogened by hydrotreatment, and the content of nitrogen in the hydrotreated oil will be sufficiently reduced. Further, the content of nitrogen in the heavy hydrocarbon oil may be, for example, 0.35 mass% or less, and may be 0.30 mass% or less. When the content of nitrogen is in this range, the nitrogen in the resulting hydrotreated oil tends to be more significantly reduced.

**[0029]** In heavy hydrocarbon oil, the content of basic nitrogen may be, for example, 0.02 mass% or more, and may be 0.03 mass% or more. In the production method according to the present embodiment, since the hydrotreating catalyst has excellent denitrogenation activity, even when a heavy hydrocarbon oil containing basic nitrogen as described above is used as a feed oil, the heavy hydrocarbon oil will be sufficiently denitrogened by hydrotreatment, and the content of basic nitrogen in the hydrotreated oil will be sufficiently reduced. Further, the content of basic nitrogen in the heavy hydrocarbon oil may be, for example, 0.12 mass% or less, and may be 0.10 mass% or less. When the content of basic nitrogen is in this range, the basic nitrogen in the resulting hydrotreated oil tends to be more significantly reduced.

**[0030]** Heavy hydrocarbon oil may contain heavy metals such as nickel and vanadium. It is preferable that the content of heavy metals in the heavy hydrocarbon oil be, for example, 200 massppm or less, and it is more preferable that the content of heavy metals be 100 massppm or less. When the content of heavy metals is as described above, a reduction in the catalyst life of a hydrotreating catalyst due to metal poisoning can be sufficiently suppressed.

**[0031]** Further, in heavy hydrocarbon oil, the content of heavy metals may be more than 3 massppm, and may be 5 massppm or more. Even when a heavy hydrocarbon oil containing heavy metals is used as a feed oil, a reduction in the catalyst life of a hydrotreating catalyst can be sufficiently suppressed by filling the upstream side of a reactor with a demetallization catalyst. Note that the content of heavy metals in a heavy hydrocarbon oil after demetallization may be, for example, 12 massppm or less, and may be 15 massppm or less.

**[0032]** Heavy hydrocarbon oil may contain asphaltene. The content of asphaltene in heavy hydrocarbon oil may be, for example, 0.05 mass% or more, and may be 2.0 mass% or more. Further, the content of asphaltene in heavy hydrocarbon oil may be, for example, 3.0 mass% or less, and may be 4.0 mass% or less.

**[0033]** In the present specification, the content of sulfur in heavy hydrocarbon oil represents a value determined according to JIS K2541 "Crude oil and petroleum products -- Determination of sulfur content". Further, the content of nitrogen in heavy hydrocarbon oil represents a value determined according to JIS K2541 "Crude oil and petroleum products -- Determination of nitrogen content". Further, the content of basic nitrogen in heavy hydrocarbon oil represents a value measured according to UOP testing method No. 269-90. Further, the content of heavy metals in heavy hydrocarbon oil represents a value measured by X-ray fluorescence analysis. Further, the content of asphaltene in heavy hydrocarbon oil represents a value measured according to IP143 as heptane insolubles.

<Hydrotreating Catalyst>

**[0034]** A hydrotreating catalyst contains phosphorus, an iron group element, and a group 6 element, and the ratio $C_2/C_1$ (molar ratio) of the content $C_2$ of the iron group element to the content $C_1$ of phosphorus in the hydrotreating catalyst is less than 0.60. Further, the average pore diameter of the hydrotreating catalyst is larger than 7.5 nm and smaller than 9.5 nm.

**[0035]** The hydrotreating catalyst may be that comprising an inorganic oxide carrier and an active component supported by the inorganic oxide carrier. Here, the active component contains phosphorus, an iron group element, and a group 6 element.

**[0036]** A refractory inorganic oxide carrier is suitable as the inorganic oxide carrier, and examples include alumina, silica, titania, magnesia, zirconia, boron oxide, zinc oxide, and zeolite (for example, Y zeolite, ZSM-5 zeolite, and the like), and mixtures thereof.

**[0037]** The active component supported by the inorganic oxide carrier may contain components other than phosphorus, an iron group element, and a group 6 element; and, for example, the active component may contain platinum and the like.

**[0038]** It is preferable that the hydrotreating catalyst contain cobalt and/or nickel as an iron group element, and it is more preferable that the hydrotreating catalyst contain nickel.

**[0039]** It is preferable that the hydrotreating catalyst contain molybdenum and/or tungsten as a group 6 metal, and it is more preferable that the hydrotreating catalyst contain molybdenum.

**[0040]** The content of phosphorus in the hydrotreating catalyst may be, for example, 0.1 mass% or more, and it is preferable that the content of phosphorus be 1.0 mass% or more. Further, the content of phosphorus may be, for example, 4.0 mass% or less, and it is preferable that the content of phosphorus be 3.0 mass% or less.

**[0041]** The content of an iron group element in the hydrotreating catalyst may be, for example, 1.0 mass% or more, and it is preferable that the content of an iron group element be 1.5 mass% or more. Further, the content of an iron group element may be, for example, 3.5 mass% or less, and it is preferable that the content of an iron group element be 3.0 mass% or less.

**[0042]** The content of a group 6 element in the hydrotreating catalyst may be, for example, 5.0 mass% or more, and it is preferable that the content of a group 6 element be 6.0 mass% or more. Further, the content of a group 6 element may be, for example, 12.0 mass% or less, and it is preferable that the content of a group 6 element be 11.0 mass% or less.

**[0043]** Note that, in the present specification, the content of phosphorus, an iron group element, and a group 6 element represents a value measured by ICP emission spectroscopy.

**[0044]** In the hydrotreating catalyst, the ratio $C_2/C_1$ (molar ratio) of the content $C_2$ of an iron group element to the content $C_1$ of phosphorus is less than 0.60; it is preferable that the ratio $C_2/C_1$ be less than 0.55; and it is more preferable that the ratio $C_2/C_1$ be less than 0.53. In such a hydrotreating catalyst, denitrogenation activity tends to be further improved. Further, it is preferable that the ratio $C_2/C_1$ be 0.20 or more, and it is more preferable that the ratio $C_2/C_1$ be 0.25 or more. According to the hydrotreating catalyst having such a ratio $C_2/C_1$, desulfurization activity tends to be further improved.

**[0045]** In the hydrotreating catalyst, it is preferable that the ratio $C_1/C_3$ (molar ratio) of the content $C_1$ of phosphorus to the content $C_3$ of a group 6 element be larger than 0.23; it is more preferable that the ratio $C_1/C_3$ be larger than 0.40; and it is further preferable that the ratio $C_1/C_3$ be larger than 0.50. In such a hydrotreating catalyst, denitrogenation activity tends to be further improved. Further, it is preferable that the ratio $C_1/C_3$ be less than 1.5, and it is more preferable that the ratio $C_1/C_3$ be less than 1.0. In such a hydrotreating catalyst, metal tolerance tends to be further improved.

**[0046]** In the hydrotreating catalyst, it is preferable that the ratio $C_2/C_3$ (molar ratio) of the content $C_2$ of an iron group element to the content $C_3$ of a group 6 element be less than 0.45; it is more preferable that the ratio $C_2/C_3$ be less than 0.44; and it is further preferable that the ratio $C_2/C_3$ be less than 0.42. In such a hydrotreating catalyst, the ratio (denitrogenation selectivity) of denitrogenation activity to desulfurization activity tends to be much higher, and a highly denitrogened hydrotreated oil tends to be easily obtained.

**[0047]** The average pore diameter of the hydrotreating catalyst is larger than 7.5 nm; it is preferable that the average pore diameter be larger than 7.6 nm; and it is more preferable that the average pore diameter be larger than 7.8 nm. In such a hydrotreating catalyst, the catalyst life tends to be significantly improved by the improvement in metal tolerance performance.

**[0048]** Further, the average pore diameter of the hydrotreating catalyst is less than 9.5 nm; it is preferable that the average pore diameter be less than 9.2 nm; and it is more preferable that the average pore diameter be less than 9.0 nm. In such a hydrotreating catalyst, denitrogenation selectivity tends to be further improved, and a highly denitrogened hydrotreated oil tends to be easily obtained.

**[0049]** Note that in the present specification, the average pore diameter of a hydrotreating catalyst represents a value measured by a nitrogen adsorption method.

**[0050]** It is preferable that the specific surface area of a hydrotreating catalyst be 150 $m^2/g$ or more; it is more preferable that the specific surface area be 200 $m^2/g$ or more; it is preferable that the specific surface area be 350 $m^2/g$ or less; and it is more preferable that the specific surface area be 320 $m^2/g$ or less. In such a hydrotreating catalyst, further excellent denitrogenation activity tends to be obtained in combination with sufficient desulfurization performance.

**[0051]** As a hydrotreating catalyst, a new catalyst, a regenerated catalyst, and the like may be used without particular limitation.

<Demetallization Catalyst>

**[0052]** In the method for producing hydrotreated oil according to the present embodiment, a reactor may be further filled with a catalyst other than the above hydrotreating catalyst. For example, when a heavy hydrocarbon oil used as a feed oil contains heavy metals, the reactor may be filled with a demetallization catalyst on the upstream side of the hydrotreating catalyst. That is, the reactor may be filled with a demetallization catalyst in the preceding stage, and may be filled with a hydrotreating catalyst in the subsequent stage.

**[0053]** The demetallization catalyst is not particularly limited as long as it can remove at least a part of heavy metals in heavy hydrocarbon oil.

**[0054]** Suitable examples of the demetallization catalyst include that comprising an inorganic oxide carrier and an active component supported by the inorganic oxide carrier. A refractory inorganic oxide carrier is preferred as the inorganic oxide carrier, and examples include alumina, silica, alumina-silica, boron oxide, and zinc oxide, and mixtures thereof. Further, examples of the active component include group 6 elements such as molybdenum and tungsten and iron group elements such as cobalt and nickel. Further, the inorganic oxide carrier may further contain phosphorus.

**[0055]** In the demetallization catalyst, it is preferable that the average pore diameter measured by a nitrogen adsorption method be 10 nm or more, and it is more preferable that the average pore diameter be 12 nm or more. In such a demetallization catalyst, more excellent demetallization activity tends to be obtained. Further, it is preferable that the average pore diameter of the demetallization catalyst be 25 nm or less, and it is more preferable that the average pore diameter be 23 nm or less. In such a demetallization catalyst, more excellent hydrotreating activity and catalyst strength tend to be obtained.

**[0056]** It is preferable that the pore volume of the demetallization catalyst be 0.6 mL/g or more; it is more preferable that the pore volume of the demetallization catalyst be 0.65 mL/g or more; it is preferable that the pore volume of the demetallization catalyst be 1.0 mL/g or less; and it is more preferable that the pore volume of the demetallization catalyst be 0.9 mL/g or less. In such a demetallization catalyst, sufficient catalyst life and catalyst strength tend to be obtained, and more stable operation tends to be achieved.

**[0057]** As a demetallization catalyst, a new catalyst, a regenerated catalyst, and the like may be used without particular limitation. Further, the filling proportion of the demetallization catalyst in the reactor may be arbitrarily changed depending on the operating conditions and the feed oil composition.

**[0058]** The reactor may be further filled with a catalyst other than the demetallization catalyst and the hydrotreating catalyst; for example, the reactor may be filled with a middle stage catalyst in which demetallization activity and desulfurization activity are combined. Various well-known catalysts may be used as such a catalyst.

<Reaction Conditions>

**[0059]** In the method for producing hydrotreated oil according to the present embodiment, the hydrotreated oil is obtained by passing heavy hydrocarbon oil through a reactor filled with a hydrotreating catalyst and performing hydrotreatment of the heavy hydrocarbon oil.

**[0060]** The reaction conditions of the hydrotreatment may be arbitrarily adjusted depending on the target production oil composition (for example, the content of sulfur) and the catalyst activity of the catalyst with which the reactor is filled.

**[0061]** For example, the reaction temperature of hydrotreatment may be 300°C or more, and may be 350°C or more. By setting such a reaction temperature, the activity of the hydrotreating catalyst with which the reactor is filled tends to be more significantly exhibited. Further, the reaction temperature of hydrotreatment may be, for example, 500°C or less, and may be 450°C or less. By setting such a reaction temperature, the thermal cracking of heavy hydrocarbon oil does not excessively proceed; the operation of a hydrotreating unit can be smoothly performed; and activity degradation of the hydrotreating catalyst can be suppressed.

**[0062]** The hydrogen partial pressure in hydrotreatment may be, for example, 3 MPa or more, and may be 5 MPa or more. By setting such hydrogen partial pressure, hydrogenation reaction tends to sufficiently proceed, and a more highly desulfurized and denitrogened hydrotreated oil tends to be obtained. Further, the hydrogen partial pressure in hydrotreatment may be, for example, 25 MPa or less, and may be 20 Mpa or less. In such hydrogen partial pressure, an increase in equipment construction cost and operating cost tends to be avoided, and an economical advantage tends to be obtained.

**[0063]** The hydrogen/oil ratio in hydrotreatment may be, for example, 400 L/L, and may be 500 L/L. By setting such a hydrogen/oil ratio, the hydrogenation activity of a hydrotreating catalyst tends to be more significantly exhibited. Further, the hydrogen/oil ratio in hydrotreatment may be, for example, 3000 L/L, and may be 1800 L/L. By setting such a hydrogen/oil ratio, excellent economical efficiency can be secured.

**[0064]** The liquid hourly space velocity (LHSV) in hydrotreatment may be, for example, 0.1 $h^{-1}$ or more, and may be 0.2 $h^{-1}$ or more. By setting such a liquid hourly space velocity, excellent economical efficiency can be secured. Further, the liquid hourly space velocity in hydrotreatment may be, for example, 3.0 $h^{-1}$and may be 2.0 $h^{-1}$. By setting such a liquid hourly space velocity, a more highly desulfurized and denitrogened hydrotreated oil tends to be obtained.

## <Hydrotreated Oil>

**[0065]** The hydrotreated oil obtained in the method for producing hydrotreated oil according to the present embodiment is highly desulfurized and denitrogened, and can be suitably used as a feed oil for FCC.

**[0066]** It is preferable that the content of sulfur in hydrotreated oil be 0.15 mass% or less; it is more preferable that the content of sulfur be 0.10 mass% or less; and it is further preferable that the content of sulfur be 0.05 mass% or less.

**[0067]** It is preferable that the content of nitrogen in hydrotreated oil be 0.15 mass% or less; and it is more preferable that the content of nitrogen be 0.13 mass% or less. Further, it is preferable that the content of basic nitrogen be 0.05 mass% or less; and it is more preferable that the content of basic nitrogen be 0.04 mass% or less.

**[0068]** It is preferable that the content of nickel and vanadium in hydrotreated oil be 10 ppm or less, respectively, and it is more preferable that the content of nickel and vanadium be 5 ppm or less, respectively. Such a hydrotreated oil can sufficiently suppress metal poisoning of a catalyst used in the FCC process.

**[0069]** According to the production method according to the present embodiment, a hydrotreated oil suitable for the FCC process can be efficiently and stably produced by a method excellent in economical efficiency.

## <FCC Process>

**[0070]** In the present embodiment, catalytic cracked oil can be efficiently obtained by using the hydrotreated oil obtained in the above production method as a feed oil for FCC. That is, the method for producing catalytic cracked oil according to the present embodiment may comprise a step of obtaining hydrotreated oil by the above method and a step of obtaining catalytic cracked oil by fluid catalytic cracking of the hydrotreated oil.

**[0071]** In the method for producing catalytic cracked oil according to the present embodiment, since the hydrotreated oil obtained in the production method is suitably denitrogened as a feed oil for FCC, catalyst degradation in the fluid catalytic cracking is sufficiently suppressed, and the catalytic cracked oil can be efficiently obtained.

**[0072]** In the present embodiment, the embodiment of fluid catalytic cracking is not particularly limited, but can be performed by a known method.

**[0073]** The catalytic cracked oil obtained in the production method according to the present embodiment can be suitably used for the applications of a gasoline fraction, a gas oil fraction, cokes feed, and chemicals such as propylene and butadiene.

**[0074]** As mentioned above, the suitable embodiments of the present invention have been described, but the present invention is not limited to the above embodiments.

## Examples

**[0075]** Next, the present invention will be described by Examples and Comparative Examples, but the present invention is not intended to be limited to these Examples.

<Preparation of Feed oil>

**[0076]** In the following Examples and Comparative Examples, a mixture in which an atmospheric residue A and a solvent deasphalted oil each having the following composition are mixed in an equal volume was used as a feed oil.

(Atmospheric Residue A)

**[0077]**

Content of sulfur in the atmospheric residue: 2.9 mass%
Content of vanadium in the atmospheric residue: 40 massppm
Content of nickel in the atmospheric residue: 15 massppm
Content of asphaltene in the atmospheric residue: 3.0 mass%
Density of the atmospheric residue at 15°C: 0.9619 g/cm$^3$
Kinematic viscosity of the atmospheric residue at 100°C: 30.5 mm$^2$/s
Content of carbon residue in the atmospheric residue: 9.0 mass%
Content of nitrogen in the atmospheric residue: 0.154 mass%
Content of basic nitrogen in the atmospheric residue: 0.052 mass%

**[0078]** (Solvent Deasphalted Oil)
**[0079]** There was used a solvent deasphalted oil obtained by solvent deasphalting the following vacuum residue at an extraction ratio of 70% using a hydrocarbon solvent containing 90% or more of a hydrocarbon having 5 and 6 carbon atoms. The properties of the solvent deasphalted oil were as follows.

Content of sulfur in the vacuum residue: 4.4 mass%
Content of vanadium in the vacuum residue: 98 massppm
Content of nickel in the vacuum residue: 30 massppm
Content of asphaltene in the vacuum residue: 10.4 mass%
Density of the vacuum residue at 15°C: 1.0400 g/cm$^3$
Kinematic viscosity of the vacuum residue at 100°C: 461 mm$^2$/s
Content of carbon residue in the vacuum residue: 24.7 mass%
Content of nitrogen in the vacuum residue: 0.38 mass%
Content of basic nitrogen in the vacuum residue: 0.13 mass%
Content of sulfur in the solvent deasphalted oil: 4.2 mass%
Content of vanadium in the solvent deasphalted oil: 29 massppm
Content of nickel in the solvent deasphalted oil: 9 massppm
Content of asphaltene in the solvent deasphalted oil: 0.2 mass%
Density of the solvent deasphalted oil at 15°C: 1.0037 g/cm$^3$
Kinematic viscosity of the solvent deasphalted oil at 100°C: 419 mm$^2$/s
Content of carbon residue in the solvent deasphalted oil: 15.5 mass%
Content of nitrogen in the solvent deasphalted oil: 0.182 mass%
Content of basic nitrogen in the solvent deasphalted oil: 0.062 mass%

<Example 1>

**[0080]** In Example 1, a catalyst (demetallization catalyst X) (average pore diameter: 18 nm, pore volume: 0.87 mL/g) in which 2.7 mass% of molybdenum (in terms of molybdenum elements) was supported by an alumina carrier was used as a demetallization catalyst. Further, a catalyst A having the composition shown in Table 1 was used as a hydrotreating catalyst. Note that, in Table 1, $C_2/C_3$ represents the ratio of the content $C_2$ of an iron group element to the content $C_3$ of a group 6 element; $C_1/C_3$ represents the ratio of the content $C_1$ of phosphorus to the content $C_3$ of a group 6 element; and $C_2/C_1$ represents the ratio of the content $C_2$ of an iron group element to the content $C_1$ of phosphorus.
**[0081]** The reactor inlet side of a hydrotreating unit was filled with the demetallization catalyst X, and the subsequent stage side of the hydrotreating unit was filled with the equal volume of the catalyst A. Hydrotreatment was performed under the following conditions using this hydrotreating unit.

Hydrogen partial pressure: 14.4 Mpa
Hydrogen/oil ratio: 1000 L/L
LHSV: 0.44 h$^{-1}$

**[0082]** The reaction temperature was changed to 360°C, 380°C, and 400°C; the analysis of sulfur, nitrogen, and heavy metals was performed on the hydrotreated oil obtained under each condition; and based on the analysis results, desulfurization activity (kHDS), denitrogenation activity (kHDN), and demetallization activity (kHDM) were determined. Note that each activity was calculated as an average value of a relative ratio to the reaction rate constant of Comparative Example 4 to be described below by calculating the reaction rate constant at each reaction temperature, assuming that the order of reaction is second order for desulfurization reaction, first order for denitrogenation reaction, and first order for demetallization reaction.

**[0083]** Further, the basic nitrogen removal ratio was calculated from the basic nitrogen concentration in a feed oil and the basic nitrogen concentration in a hydrotreated oil at a reaction temperature of 380°C. Further, the proportion (kHDN/kHDS) of denitrogenation activity to desulfurization activity was defined as HDN selectivity. Further, the time until desulfurization activity decreases to 20% of initial desulfurization activity was measured as an index of catalyst life of hydrotreating catalyst; a relative value to the time in Comparative Example 4 to be described below was determined; and the relative value was defined as a relative metal tolerance.

**[0084]** The desulfurization activity (kHDS), denitrogenation activity (kHDN), demetallization activity (kHDM), basic nitrogen removal ratio, HDN selectivity, and relative metal tolerance determined by the above methods are shown in Table 2.

<Examples 2 to 4>

**[0085]** Hydrotreatment and analysis of the resulting hydrotreated oil were performed in the same manner as in Example 1 except that, as a hydrotreating catalyst, catalysts B to D shown in Table 1 were used instead of the catalyst A. The analysis results were as shown in Table 2.

<Comparative Examples 1 to 4>

**[0086]** Hydrotreatment and analysis of the resulting hydrotreated oil were performed in the same manner as in Example 1 except that, as a hydrotreating catalyst, catalysts E to H shown in Table 1 were used instead of the catalyst A. The analysis results were as shown in Table 2.

[Table 1]

| | | Examples 1 | Example 2 | Example 3 | Example 4 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 |
|---|---|---|---|---|---|---|---|---|---|
| | | Desulfurization catalyst A | Desulfurization catalyst B | Desulfurization catalyst C | Desulfurization catalyst D | Desulfurization catalyst E | Desulfurization catalyst F | Desulfurization catalyst G | Desulfurization catalyst H |
| Mo | (mass%) | 8 | 10 | 8 | 10 | 8 | 12 | 12 | 8 |
| Ni | (mass%) | 2 | 2.5 | 1.5 | 2 | 0.65 | 3 | 2.7 | 2.2 |
| Co | (mass%) | 0 | 0 | 0 | 0 | 135 | 0 | 0.8 | 0 |
| P | (mass%) | 2 | 2.5 | 2 | 2.5 | 0.6 | 2.5 | 1.4 | 0 |
| $C_2/C_3$ | (mol/mol) | 0.4 | 0.4 | 0.31 | 0.32 | 0.4 | 0.4 | 0.49 | 0.45 |
| $C_1/C_3$ | (mol/mol) | 0.78 | 0.78 | 0.78 | 0.78 | 0.23 | 0.65 | 0.36 | 0 |
| $C_2/C_1$ | (mol/mol) | 0.52 | 0.52 | 0.40 | 0.41 | 1.72 | 0.62 | 1.35 | - |
| Average pore diameter | (Å) | 82 | 82 | 82 | 82 | 85 | 75 | 60 | 95 |

[Table 2]

|  |  | Example 1 | Example 2 | Examples 3 | Example 4 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Desulfurization catalyst A | Desulfurization catalyst B | Desulfurization catalyst C | Desulfurization catalyst D | Desulfurization catalyst E | Desulfurization catalyst F | Desulfurization catalyst G | Desulfurization catalyst H |
| kHDS | % | 110 | 117 | 87 | 107 | 133 | 116 | 133 | 100 |
| kHDN | % | 167 | 206 | 161 | 203 | 118 | 189 | 223 | 100 |
| kHDM | % | 85 | 78 | 70 | 75 | 88 | 84 | 51 | 100 |
| Basic nitrogen removal ratio | % | 23 | 30 | 19 | 32 | 11 | 26 | 28 | 5 |
| HDN selectivity | % | 152 | 176 | 185 | 190 | 89 | 163 | 168 | 100 |
| Relative metal tolerance | % | 58 | 50 | 58 | 50 | 67 | 33 | 17 | 100 |

**[0087]** When Examples are compared with Comparative Examples, high denitrogenation selectivity and basic nitrogen removal ratio were obtained in Examples while suppressing significant reduction in catalyst life (relative metal tolerance).

<Example 5>

**[0088]** A hydrotreating system using a plurality of catalysts was performed to obtain production oil. Further, in order to confirm the reactivity of catalytic cracking reaction of the resulting production oil, a MAT (Micro Activity Test) test was performed on the production oil. Details will be described below.

**[0089]** First, the above demetallization catalyst X, a demetallization catalyst Y (average pore diameter: 18 nm, pore volume: 0.80 mL/g) in which 6 mass% of molybdenum (in terms of molybdenum elements) and 1.5 mass% of nickel (in term of nickel elements) are supported by an alumina carrier, the above desulfurization catalyst E, the above desulfurization catalyst H, and the above desulfurization, catalyst A were prepared. Further, a mixture in which the above solvent deasphalted oil was mixed with an atmospheric residue B to be shown below were mixed in a ratio of 54:46 (volume ratio) was prepared as a feed oil for hydrotreatment.

(Atmospheric Residue B)

**[0090]**

Content of sulfur in the atmospheric residue: 0.92 mass%
Content of vanadium in the atmospheric residue: 11 massppm
Content of nickel in the atmospheric residue: 11 massppm
Content of asphaltene in the atmospheric residue: 0.2 mass%
Density of the atmospheric residue at 15°C: 0.9187 g/cm$^3$
Kinematic viscosity of the atmospheric residue at 100°C: 25.2 mm$^2$/s
Content of carbon residue in the atmospheric residue: 5.1 mass%
Content of nitrogen in the atmospheric residue: 0.170 mass%
Content of basic nitrogen in the atmospheric residue: 0.057 mass%

**[0091]** A reactor in which two reaction towers were coupled was prepared; a first tower was filled with the demetallization catalyst X and the demetallization catalyst Y in this order from the inlet side; and a second tower was filled with the desulfurization catalyst E, the desulfurization catalyst H, and the desulfurization catalyst A in this order from the inlet side. The amounts of the catalysts used were set to X:Y:E:H:A = 3:41:11:12:33 (volume ratio). Hydrotreatment was performed under the following conditions using this reactor. Note that the inlet temperature of the first tower was set to 350°C for 30 days after the start of reaction.

Hydrogen partial pressure: 14.4 Mpa
Hydrogen/oil ratio: 1000 L/L
LHSV: 0.44 h$^{-1}$
Outlet temperature of the first tower = Inlet temperature of the first tower + 8°C
Inlet temperature of the second tower = Inlet temperature of the first tower - 2°C
Outlet temperature of the second tower = Inlet temperature of the second tower + 20°C

**[0092]** 30 days after the start of reaction, when the reaction temperature was adjusted so that the sulfur content at the bottom of production oil (a residue in distillation separation, a fraction having a boiling point of 390°C or more) would be 0.6 mass%, the average of the reaction temperature was 364°C. A fraction having a boiling point of less than 390°C of the production oil was cut to obtain desulfurization oil 5A. The composition of the desulfurization oil 5A was as shown in Table 3. This desulfurization oil 5A was used for the MAT test.

**[0093]** In the MAT test, an FCC feed oil A in which the vacuum gas oil whose composition was shown in Table 3 was mixed with the above desulfurization oil 5A in a ratio of 57:43 (mass ratio) was used as a feed oil. The MAT test was performed under the following conditions. Note that a commercially available FCC catalyst was used as the catalyst. The test results are shown in Table 4.

Reaction temperature: 530°C
Catalyst/oil ratio: 8.5 (weight ratio)
Catalyst weight: 12 g

<Comparative Example 5>

**[0094]** Hydrotreatment was performed in the same manner as in Example 5 except that the first tower of the reactor was filled with the demetallization catalyst X and the demetallization catalyst Y in this order from the inlet side; the second tower of the reactor was filled with the desulfurization catalyst E and the desulfurization catalyst H in this order from the inlet side; the amounts of the catalysts used were set to X:Y:E:H = 22:22:23:33 (volume ratio).

**[0095]** 30 days after the start of reaction, when the reaction temperature was adjusted so that the sulfur content at the bottom of production oil (a residue in distillation separation, a fraction having a boiling point of 390°C or more) would be 0.6 mass%, the average of the reaction temperature was 377°C. A fraction having a boiling point of less than 390°C of the production oil was cut to obtain desulfurization oil 5B. The composition of the desulfurization oil 5B was as shown in Table 3. This desulfurization oil 5B was used for the MAT test.

**[0096]** In the MAT test, an FCC feed oil B in which the vacuum gas oil shown in Table 3 was mixed with the above desulfurization oil 5B in a ratio of 57:43 (mass ratio) was used as a feed oil. The MAT test was performed in the same manner as in Example 5 except that the FCC feed oil B was used as a feed oil. The test results are shown in Table 4.

<Example 6>

**[0097]** The MAT test was performed in the same manner as in Example 5 except that the catalyst/oil ratio was changed to 9.5 (weight ratio). The test results are shown in Table 4.

[Table 3]

| Feed oil | | Vacuum gas oil | Desulfurized oil 5A | Desulfurized oil 5B | FCC feed oil A | FCC feed oil B |
|---|---|---|---|---|---|---|
| Density (15°C) | | 0.9031 | 0.9468 | 0.9473 | 0.9214 | 0.9217 |
| LCO fraction (GC distillation 343°C-) | mass% | 7.6 | 0.0 | 0.0 | 4.4 | 4.3 |
| VR traction (GC distillation 538°C+) | mass% | 11.0 | 64.4 | 63.3 | 33.8 | 33.3 |
| Carbon residue | mass% | 0.21 | 5.85 | 5.97 | 2.64 | 2.69 |
| Average molecular weight | - | 446 | 723 | 709 | 518 | 554 |
| Nitrogen | mass% | 0.06 | 0.13 | 0.15 | 0.09 | 0.10 |
| Basic nitrogen | mass% | 0.016 | 0.047 | 0.056 | 0.029 | 0.033 |
| Sulfur | mass% | 0.19 | 0.59 | 0.60 | 0.36 | 0.37 |
| Ni | massppm | Less than 1 | 3 | 3 | 1 | 1 |
| V | massppm | Less than 1 | 4 | 3 | 2 | 1 |

**[0098]** Note that, in Table 3, "Density (15°C)" represents the density at 15°C; "LCO fraction" represents the content of a fraction having a boiling point of 221°C or more and less than 343°C; and "VR fraction" represents the content of a fraction having a boiling point of 538°C or more. Further, "Carbon residue", "Nitrogen", "Basic nitrogen", "Sulfur", "Ni", and "V" represent the content of carbon residue, nitrogen, basic nitrogen, sulfur, nickel, and vanadium, respectively. Further, "Average molecular weight" represents the number average molecular weight value of hydrocarbon measured with a GPC unit.

[Table 4]

| | | Examples 5 | Example 6 | Comparative Example 5 |
|---|---|---|---|---|
| Feed oil | | FCC feed oil A | FCC feed oil A | FCC feed oil B |
| Catalyst/Oil | Mass ratio | 8.5 | 9.5 | 8.5 |
| Dry gas | mass% | 3.4 | 3.6 | 3.4 |
| $H_2$ | mass% | 0.1 | 0.1 | 0.1 |

(continued)

| | | Examples 5 | Example 6 | Comparative Example 5 |
|---|---|---|---|---|
| CH4 | mass% | 1.3 | 1.4 | 1.2 |
| C2H4 | mass% | 1.0 | 1.1 | 1.1 |
| C2H6 | mass% | 1.0 | 1.0 | 1.1 |
| LPG | mass% | 12.6 | 12.9 | 12.8 |
| C3H6 | mass% | 4.5 | 4.6 | 4.6 |
| C3H8 | mass% | 1.3 | 1.4 | 1.3 |
| C4H8 | mass% | 3.7 | 3.8 | 3.8 |
| C4H10 | mass% | 3.0 | 3.1 | 3.1 |
| WCCG | mass% | 52.5 | 52.6 | 52.0 |
| LCO | mass% | 16.0 | 15.5 | 15.9 |
| CLO | mass% | 8.3 | 7,9 | 8.4 |
| COKE | mass% | 7.2 | 7.5 | 7.5 |
| TOTAL | mass% | 100.0 | 100.0 | 100.0 |
| Conversion ratio | mass% | 68.5 | 69.1 | 68.2 |

**[0099]** Note that, in Table 4, "Dry gas", "LPG", "WCCG", "LCO", "CLO", and "COKE" represent a hydrocarbon having 1 or 2 carbon atoms, a hydrocarbon having 3 or 4 carbon atoms, a hydrocarbon having 5 or more carbon atoms and a boiling point of less than 221°C, a hydrocarbon having a boiling point of 221 °C or more and less than 343°C, a liquid hydrocarbon having a boiling point of 343°C or more, and a solid product, respectively. Further, "Conversion ratio" represents the proportion of the amount excluding LCO, CLO, and COKE from all the products.

**[0100]** As shown in Table 3, even though the reaction temperature (364°C) where sulfur content is 0.6 mass% was lower in the hydrotreatment of Example 5 than that (377°C) in Comparative Example 5, the amount of basic nitrogen has been reduced than that in Comparative Example 5. Further, as shown in Table 4, the amount of COKE produced in the catalytic cracking reaction of Example 5 has been suppressed as compared with that in Comparative Example 5. Further, as shown in Table 4, a higher conversion ratio than in Comparative Example 5 has been obtained in Example 6 in which the catalyst/feed oil ratio was adjusted so that the amount of COKE produced would be in the same degree as that in Comparative Example 5.

## Claims

1. A method for producing hydrotreated oil comprising:

   a step of passing heavy hydrocarbon oil through a reactor filled with a hydrotreating catalyst to obtain hydrotreated oil, wherein
   the hydrotreating catalyst contains phosphorus, an iron group element, and a group 6 element;
   a ratio $C_2/C_1$ of a content $C_2$ of the iron group element to a content $C_1$ of phosphorus in the hydrotreating catalyst is less than 0.60 in a molar ratio; and
   an average pore diameter of the hydrotreating catalyst is larger than 7.5 nm and smaller than 9.5 nm.

2. The production method according to claim 1, wherein, in the hydrotreating catalyst,
   a ratio $C_2/C_3$ of the content $C_2$ of the iron group element to a content $C_3$ of the group 6 element is less than 0.45 in a molar ratio, and
   a ratio $C_1/C_3$ of the content $C_1$ of phosphorus to the content $C_3$ of the group 6 element is larger than 0.23 in a molar ratio.

3. A method for producing catalytic cracked oil comprising:

   a step of obtaining hydrotreated oil by the production method according to claim 1 or 2; and
   a step of obtaining catalytic cracked oil by fluid catalytic cracking of the hydrotreated oil.

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/065219

A. CLASSIFICATION OF SUBJECT MATTER
*C10G45/08*(2006.01)i, *C10G69/04*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G45/08, C10G69/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

| | | | |
|---|---|---|---|
| Jitsuyo Shinan Koho | 1922-1996 | Jitsuyo Shinan Toroku Koho | 1996-2016 |
| Kokai Jitsuyo Shinan Koho | 1971-2016 | Toroku Jitsuyo Shinan Koho | 1994-2016 |

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | JP 2013-17999 A (Cosmo Oil Co., Ltd.),<br>31 January 2013 (31.01.2013),<br>claim 1; paragraph [0057]; referential example 5; tables 7, 8<br>(Family: none) | 1-3 |
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☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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**INTERNATIONAL SEARCH REPORT**

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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