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(54) Title: PROCESS FOR PRODUCING A HYDROPROCESSING CATALYST, AND METHOD FOR HYDROPROCESSING A HYDROCARBON OIL USING SAID CATALYST

(57) Abstract: To provide a hydroprocessing catalyst for hydrocarbon oils, having hydroprocessing (hydrogenation, desulfurization, denitrification and carbon residue removal) performance more excellent the conventional catalysts, and also to provide a method for hydroprocessing a hydrocarbon oil using the catalyst. A process for producing a hydroprocessing catalyst for hydrocarbon oils, loaded with a group 6 element and a group 8 to 10 element of the periodic table and an organic additive, comprising the steps of depositing a boron compound on the pore surfaces of an inorganic porous carrier mainly composed of alumina; calcining to obtain a boron-loaded intermediate product; adding at least one of the group 6 elements of the periodic table by 10 to 40 mass% based on the mass of the oxide catalyst, at least one of the group 8 to 10 elements of the periodic table by 0.5 to 20 mass% based on the mass of the oxide catalyst, and an organic additive by 0.15 to 3 times the moles in total of the group 6 element and the group 8 to 10 element of the periodic table respectively to said intermediate product; and drying.

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Description

Title of Invention: PROCESS FOR PRODUCING A HYDROPROCESSING CATALYST, AND METHOD FOR HYDROPROCESSING A HYDROCARBON OIL USING SAID CATALYST

Technical Field

[0001] The present invention relates to a process for producing a hydroprocessing catalyst used to remove impurities such as sulfur nitrogen and carbon residue contained in a hydrocarbon oil, and method for using the catalyst.

Background Art

[0002] In recent years, global efforts have been being made worldwide to improve air environment, and in this connection, the hydroprocessing catalysts used for hydrorefining distillate oils for use as major fuels have been being required to be further enhanced in performance. Usually hydroprocessing catalysts for hydrocarbon oils are generally obtained by loading inorganic heat-resistant carriers such as alumina and silica with hydrogenation activity metals such as molybdenum, cobalt and nickel. However, in more recent years, various efforts have been being made to modify the carriers and to develop novel metal loading methods in order to further improve the catalyst performance.

[0003] Patent document 1 discloses a hydroprocessing catalyst for heavy oils, in which boron is used to accelerate activity. This catalyst can be obtained by impregnating an alumina carrier with boron, calcining, further impregnating the impregnated and the calcined carrier with hydrogenation activity metals such as molybdenum and cobalt, and calcining for further loading. Since boron is added, the catalyst activity is enhanced to some extent, but owing to the strong interaction between carrier and the hydrogenation activity metals caused in the calcined catalyst, the intended catalytic activity cannot be sufficiently induced in the state of use.

[0004] Patent document 2 discloses a catalyst for hydrodesulfurizing and hydrodenitrifying a hydrocarbon oil, in which an oxide catalyst carrier formed of a boria-alumina is loaded with a group VI a metal and a group VIII metal of the periodic table and a dihydric alcohol, and also a process for producing the catalyst. In this case, since the boria-alumina carrier is prepared by a kneading method, it is difficult to highly disperse boria into the carrier, particularly into the pore surfaces of the carrier. As a result, this process has a problem that the catalyst activity cannot be sufficiently enhanced.

[0005] Patent document 3 discloses that when the ultra-deep desufurization of a hydrocarbon feedstock is performed, a catalyst in which a commonly used oxide carrier contains a group VIB metal, a group VIII metal and an organic additive is used. Though the document refers to a mixture consisting of alumina and boria as an applicable catalyst carrier, the document does not refer to the optimum ratio of alumina and boria or a method for preparing the mixture at all. Therefore, the properties of the boria-containing carrier contributing to the catalytic activity are not known.

[0006] Patent document 4 discloses a catalyst in which an inorganic oxide carrier is loaded with a group 6 metal and a group 8 metal of the periodic table, phosphorus and carbon, and a hydroprocessing catalyst for gas oils. As applicable carriers, alumina alone and composite oxide consisting of alumina and 0.5 mass% to less than 20 mass% of zeolite, boria, silica, etc. are referred to. The document states that these composite oxide carriers are advantageous for imparting the acid sites, for highly dispersing molybdenum, and for stacking layers of molybdenum disulfide when the catalyst is used. However, with regard to the method for producing a composite oxide catalyst, the document merely refers to an example in which zeolite is compounded by a kneading method. A kneading method has the same problem as stated for the patent document 2, and the compounding by boria using a kneading method cannot be expected to allow efficient modification of the alumina carrier.

[0007] Patent document 5 discloses a process for producing a hydroprocessing catalyst for gas oils, comprising the steps of impregnating a porous inorganic oxide carrier with a group 6 metal and a group 8 base metal of the periodic table and a saccharide, and irradiating the impregnated carrier with microwaves for drying.

The patent document 5 also enumerates alumina-boria, alumina-silica-boria, etc. as carriers preferred in view of large specific surface area and pore volume. However, the document does not disclose the particular properties of the carriers or methods for preparing them at all.

[0008] Patent document 6 discloses a hydroprocessing catalyst obtained by loading a composite oxide carrier of alumina-phosphorus with boron and further loading the loaded carrier with a group VIA metal and a group VIII metal of the periodic table, lanthanoid and a water soluble organic compound. This catalyst has such problems that expensive lanthanoid is essential as a catalyst component, and that a first peak (diameter 70 to 100 Angstrom) and a second peak (diameter 100 to 200 Angstrom) difficult to control are necessary in the pore size distribution of the catalyst. Therefore, the practical application of the catalyst as an industrial catalyst is difficult.

Citation List

Patent Literature

[0009]

PLT 1

[0010] US Patent 4,724,226

PLT 2

[0011] JP 6-210182 A

PLT 3

[0012] JP 2000-313890 A

PLT 4

[0013] WO 2004/054712 A

PLT 5

[0014] JP 2004-344754 A

PLT 6

[0015] JP 2006-314916 A

Summary of Invention

Technical Problem

[0016] The problem to be solved by this invention is to provide a process for producing a hydroprocessing catalyst for hydrocarbon oils, having excellent hydroprocessing (hydrogenation, desulfurization, denitrification and carbon residue removal) performance, and also to provide a method of hydroprocessing a hydrocarbon oil using the catalyst.

Solution to Problem

[0017] In view of the abovementioned problems of the prior art, the inventors made an intensive study with attention paid especially to the efficient modification of the pore surfaces of the catalyst carrier, and as a result, they found that the catalyst obtained by loading hydrogenation activity components and an organic additive into an inorganic porous carrier mainly composed of the alumina loaded with boron by specific method is very effective for hydroprocessing hydrocarbon oils.

[0018] This invention is a process for producing a hydroprocessing catalyst for hydrocarbon oils, loaded with a group 6 element and a group 8 to 10 element of the periodic table and an organic additive, comprising the steps of depositing a boron compound on the pore surfaces of an inorganic porous carrier mainly composed of alumina, calcining to obtain a boron-loaded intermediate product, adding at least one of the group 6 elements of the periodic table by 10 to 40 mass% based on the mass of the oxide catalyst, at least one of the group 8 to 10 elements of the periodic table by 0.5 to 20 mass% based on the mass of the oxide catalyst, and an organic additive by 0.15 to 3 times the moles in total of the group 6 element and the group 8 to 10 element of the periodic table respectively to said intermediate product, and drying.

[0019] Further, in the method for producing a hydroprocessing catalyst of this invention, an impregnation method is used as the deposition method for obtaining the boron-loaded intermediate product, and the loaded amount of boron is 0.3 to 10 mass% based on the mass of the oxide of the intermediate product. Further, the group 6 element of the periodic table is at least one selected from chromium, molybdenum and tungsten, and the group 8 to 10 element of the periodic table is at least on selected from iron, cobalt and nickel. In addition, in the process for producing a hydroprocessing catalyst, the organic additive is at least one selected from the group consisting of polyhydric alcohols, saccharides, carboxylic acids, amino acids and chelating agents.

[0020] Furthermore, this invention is a method for hydroprocessing a hydrocarbon oil, comprising the step of the bringing a hydrocarbon oil and the abovementioned hydroprocessing catalyst into contact with each other under a reaction temperature of 300 to 450 degrees C, at a hydrogen partial pressure of 1 to 15 MPa, at a liquid hourly space velocity of 0.1 to 10 hr^{-1} and a hydrogen/oil ratio of 50 to 1,200 Nm^3/kl.

Advantageous Effects of Invention

[0021] If the hydroprocessing catalyst of this invention is used, impurities such as sulfur, nitrogen and carbon residue can be more efficiently removed from a hydrocarbon oil than using conventional catalysts, to raise the grade of the hydrocarbon oil. Further, the hydrocarbon oil processed by the hydroprocessing catalyst of this invention is useful also as a feedstock for a catalytic reforming unit, a fluid catalytic cracking unit, a hydrocracking unit, etc. Therefore, this invention allows advanced use of hydrocarbon oils.

Description of Embodiments

[0022] This invention is explained below in detail. The inorganic porous carrier mainly composed of alumina in this invention (hereinafter referred to as "the alumina-based carrier") is composed of at least 90 mass% or more, preferably 95 mass% or more of alpha, theta, delta, kappa, eta, gamma, chi or other alumina, or alumina hydrate such as bayerite, gibbsite, boehmite or pseudo boehmite, or an arbitrary mixture or composite compound consisting of the foregoing. Among them, gamma, delta, theta or eta-alumina is preferred, and gamma-alumina is especially preferred. The impurities considered to enter in the alumina-based carrier production process include iron oxide, sodium oxide, sulfuric acid ions, chloride ions, other compounds, etc., and it is desirable to keep the total amount of impurities at 5 mass% or less, preferably 3 mass% or less (based on the mass of the carrier).

The alumina-based carrier can also be alumina alone. However, for adjusting the mechanical strength and acidity of the carrier, as required, silica, silica-alumina, titania, zirconia, phosphorus pentoxide, magnesia, zinc oxide, ceria, rare earth element oxide, kaolinite, montmorillonite, talc, saponite, sepiolite, attapulgite, natural or synthetic zeolite or any of mixtures thereof can also be compounded with alumina by 0.1 to 10 mass%, preferably 0.3 to 8 mass% based on the mass of the carrier, by a commonly used method (such as kneading method or impregnation method).

[0023] Meanwhile, to exhibit optimum performance as a catalyst, it is preferred that the alumina-based carrier has the following physical properties.

That is, the preferred physical properties are a pore volume of 0.5 to 1.2 ml/g, an average pore diameter of 8 to 13nm and a specific surface area of 150 to 400m^2/g. The alumina-based carrier can be prepared by a commonly used method, for example, comprising the steps of obtaining alumina hydrate by a neutralization reaction using an acidic alumina compound and/or a basic aluminum compound or a hydrolysis reaction of an aluminum alkoxide, kneading, molding, drying, calcining, etc. Otherwise, a commercially available alumina hydrate powder or alumina-based carrier can also be used.

Meanwhile, when the alumina-based carrier is also prepared or used, it is necessary to take the pore structure of the completed catalyst as described later into consideration.

[0024] A boron compound is deposited on the pore surface of the abovementioned alumina-based carrier, and the boron-deposited carrier is calcined to obtain a boron-loaded intermediate product.

The deposition in this case means that the boron compound is physically or chemically adsorbed by the pore surfaces of the carrier.

As the deposition method, an impregnation method, vapor deposition method, coating method, spraying method, etc. can be applied. In view of easy control of the loaded amount, the simplicity of operation, etc., an impregnation method is preferred.

For impregnation, applicable are various methods such as an adsorption method (the carrier is immersed into a boron compound solution, to adsorb boron by not larger than the saturated adsorption amount), equilibrium adsorption method (similar to the adsorption method, but a solution containing not smaller than the saturated adsorption amount of boron is used as the boron compound solution, and the excessive amount is filtered away), pore filling method (a boron solution is made to be adsorbed by the pores of the carrier by an amount equal to the pore volume of the carrier), incipient wetness method (while the pore volume of the carrier is measured, the carrier is impregnated with a boron compound solution), evaporation-to-dryness method (the carrier is immersed into a boron compound solution, and the mixture is heated with stirring on a hot bath or the like, to evaporate the solvent) and spray method (a boron compound solution is sprayed under reduced pressure for impregnation). Among these methods, in view of operation convenience, the pore filling method is especially preferred. By using any of the abovementioned methods, boron can be efficiently dispersed on the surfaces of the alumina-based carrier.

Meanwhile, the pore surfaces used in this specification refer to the surfaces of the pores formed in the clearances among the primary particles and secondary particles of the alumina and the like constituting the carrier, and include not only the apparent outer surfaces of the carrier but also all the pore surfaces existing inside carrier.

[0025] Usually for modifying the carrier using boron or the like, a kneading method is popularly used since the operation is simple.

However, it is difficult to sufficiently disperse the additive by a kneading method, and a long time is needed for obtaining a desired dispersion degree. Further, even if the additive could be dispersed to a certain dispersion degree by kneading, most of the added boron is incorporated into the carrier skeleton not contributing to the catalytic reaction. Therefore, in order to highly disperse boron on the pore surfaces of the carrier as intended in the present application, it is necessary to add a large amount of boron. Therefore, a kneading method is less efficient in view of both the added amount and the operation time, and cannot be considered to be a preferred addition method. Another boron addition method is a coprecipitation method. In this method, when the alumina-based carrier is prepared, an alumina compound and a boron compound as raw materials are coprecipitated to obtain boron-containing alumina hydrate. However, this method is not practical, since it has a problem that most of boron is incorporated into the carrier skeleton as in a kneading method, and in addition, has another problem that added boron flows out due to poor coprecipitation.

[0026] The added amount of boron to be loaded into the carrier is 0.3 to 10 mass% as the oxide based on the mass of the boron-loaded intermediate product. A preferred range is 0.5 to 9 mass%, and an especially preferred range is 0.5 to 8 mass%. If the added amount is less than 0.3 mass%, the effect of addition is insufficient.

Even if the added amount is more than 10 mass%, there is no increment in catalytic activity. Further, the large amount is not adequate, since the larger loaded amount of boron decreases the pore volume of the intermediate product, making it difficult to load the hydrogenation activity components, etc. in the subsequent step.

Meanwhile, the loaded amount of boron can be adequately adjusted depending on the use of the catalyst. In the case where the catalyst is mainly used for hydrogenation reaction or denitrification reaction, the upper limit in the loaded amount of boron is 10 mass%. However, if the catalyst is mainly used for desufurization, the loaded amount of boron is in a range from 0.3 to 4 mass%. A preferred range is 0.5 to 3.9 mass%. In the case of desulfurization activity, if the loaded amount of boron is more than 4 mass%, the activity declines. The optimum range of the loaded amount of boron is different from reaction to reaction as described above, and this difference is considered to be attributable to the difference between the reaction mechanism of desulfurization and the reaction mechanism of denitrification.

[0027] The usable boron compound is not especially limited, and various boron compounds can be used. Examples of the usable boron compound include inorganic boron compounds such as orthoboric acid, metaboric acid, hypoboric acid, ammonium borate and diborane, and organic boron compounds such as dimethylaminoborane, triethylborane, tributylborane, trimethyl borate, triethyl borate and tricyclohexyl borate, etc. Any one of these compounds can be used alone or two or more of them can also be used in an arbitrary combination.

In the case where any of these boron compounds is loaded by a impregnation method, usable is an aqueous solution, alcohol solution (methanol, ethanol, denatured alcohol, propanol, isopropanol, etc.), aqueous alcohol solution, aqueous ammonia solution, or an aqueous solution of salt or adduct with a water soluble alkylamine (methylamine, ethylamine, propylamine, isopropylamine, butylamine, N,N-dimethylamine, N,N-diethylamine, N,N-dipropylamine, trimethylamine, triethylamine, etc.) or with a water soluble alkanolamine (monoethanolamine, diethanolamine, triethanolamine, propanolamine, isopropanolamine, butanolamine, isobutanolamine, N-methylethanolamine, N-methyldiethanolamine, etc.), respectively with an adequate concentration. The impregnation operation of any of these solutions can be performed at a time or sequentially or in several times, in response to the pore volume of the alumina-based carrier and the solution concentration.

[0028] After the boron compound is deposited on the pore surfaces of the alumina-based carrier, the boron-deposited carrier is dried as required and subsequently calcined to load the boron compound in to the carrier as an oxide.

The calcination temperature can be set as appropriate considering the decomposition temperature of the boron compound. Usually if the boron-deposited carrier is calcined in air at a temperature of 300 to 850 degrees C, preferably 400 to 650 degrees C for 0.1 to 3 hours, preferably 0.5 to 2 hours, a boron-loaded intermediate product loaded with boron oxide can be obtained.

[0029] Then, hydrogenation activity components and an organic additive are added to the boron-loaded intermediate product, and the mixture dried for loading the components. The addition method is not especially limited, and any of various industrial methods such as an impregnation method, coating method and spray method can be used. However, in view of working convenience and addition efficiency, an impregnation method is preferred. As the impregnation method, any of various methods described before can be used, but in view of working convenience, the pore filling method is preferred. The order of adding the hydrogenation activity components and organic additive(s) is not especially limited, and they can be added sequentially or simultaneously. In the case of an impregnation method, a solution with the respective components dissolved in any of various polar organic solvents, water or a mixture consisting of water and polar organic solvent can be used. The most preferred solvent is water.

[0030] Among the hydrogenation activity components to be loaded into the carrier, the group 6 element of the periodic table is at least one selected from chromium, molybdenum and tungsten. Any one of these elements can be used alone, but in response to the reactivity of the feedstock and to the operation conditions of the reaction unit, two or more elements can also be used as a combination. Examples of the combination include chromium-molybdenum, chromium-tungsten, molybdenum-tungsten and chromium-molybdenum-tungsten.

The loaded amount is 10 to 40 mass% as the total of the oxides of all the group 6 elements of the periodic table based on the mass of the oxide catalyst. As preferred range is 15 to 35 mass%, and a more preferred range is 20 to 30 mass%. If the amount is less than 10 mass%, the catalytic activity is insufficient, and even if it is more than 40 wt%, there is no increment of activity. The raw materials of the group 6 elements of the periodic table include chromates, molybdates, tungstates, trioxides, halides, heteropoly-acids, heteropoly-acid salts, etc.

[0031] The group 8 to 10 elements of the periodic table as hydrogenation activity components include iron, cobalt and nickel.

Any of these elements can be used alone, but two or more of them can be used as a combination in response to the reactivity of the feedstock and to the operation conditions of the reaction unit. Examples of the combination include iron-cobalt, iron-nickel, cobalt-nickel and iron-cobalt-nickel.

The loaded amount is 0.5 to 15 mass% as the total of the oxides of all the group 8 to 10 elements of the periodic table based on the mass of the oxide catalyst. A preferred range is 1 to 10 mass%, and a more preferred range is 2 to 6 mass%. If the loaded amount is less than 0.5 mass%, the catalytic activity is insufficient, and even if the amount is more than 15 mass%, there is no increase of activity. The compounds of iron, cobalt and nickel used for loading include oxides, hydroxides, halides, sulfates, nitrates, carbonates, organic acid salts, etc.

[0032] In the case where an impregnation solution of the hydrogenation activity components is prepared, as required, ammonia water, hydrogen peroxide water, nitric acid, sulfuric acid, hydrochloric acid, phosphoric acid and hydrofluoric acid, etc. can be added for adjusting the pH of the solution, for enhancing the stability of the solution, and for enhancing the hydrogenation activity of the catalyst. Meanwhile, phosphoric acid can also be added as a catalyst component, and in this case, the added amount is in a range from 0.5 to 15 mass% as the oxide based on the mass of the oxide catalyst. A preferred range is 1 to 10 mass%, and a more preferred range is 2 to 8 mass%. The phosphoric acid that can be added is orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid, phosphonic acid, diphosphonic acid, phosphinic acid, polyphosphoric acid, any of organic salts thereof, any of inorganic salts thereof, etc. Meanwhile, as the impregnation solution of hydrogenation activity components, an impregnation solution containing the group 6 element of the periodic table and an impregnation solution containing the group 8 to 10 element of the periodic table can be prepared, or an impregnation solution containing both the elements can also be prepared.

[0033] The organic additive refers to a water soluble organic compound that can be selected from polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, isopropylene glycol, dipropylene glycol, tripropylene glycol, butanediol (1,2-, 1,3- 1,4- or 2,3-butanediol), pentanediol (for example 1,5-pentanediol, including other isomers), 3-methyl-1,5-pentanediol, neopentyl glycol, hexanediol (for example, 1,2- or 1,6-hexanediol, including other isomers), hexylene glycol, polyvinyl alcohol, polyethylene glycol (average molecular weight 200 to 600), polypropylene glycol (water soluble), glycerol, triemethylolethane, trimethylolpropane, hexanetriol (for example 1,2 6-hexanetriol, including other isomers), erythritol and pentaerythritol, ethers thereof (monoethers, diethers and triethers selected from arbitrary combination of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, water soluble), esters of the aforementioned polyhydric alcohols or the aforementioned ethers (monoesters, diesters and trimesters of formic acid, acetic acid, etc., water soluble), saccharides such as glucose, fructose, isomerized sugar, galactose, maltose, lactose, sucrose, trehalose, starch, dextrin, pectin, glycogen and curdlan, carboxylic acids such as formic cid, acetic acid, propionic acid, oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid, tartaric acid, citric acid(anhydrous, monohydrate), malic acid, gluconic acid and glutaric acid, salts thereof (salts of alkali metals such as lithium, sodium and potassium, salts of alkaline earth metals such as beryllium, magnesium and calcium, ammonium salts, etc.), amino acids such as aspartic acid, alanine, arginine, glycine and glutamic acid, salts thereof (salts of alkali metals such as lithium, sodium and potassium, salts of alkaline earth metals such as beryllium, magnesium and calcium, ammonium salts, etc.), various chelating agents such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), ethylenediaminetetraacetic acid (EDTA), hydroxyethylthylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), triethyltetraminehexaacetic acid (TTHA), hydroxyethyliminodiacetic acid (HIDA), 1,3-propanediaminetetraacetic acid (PDTA), 1,3-diamino-2-hydroxypropanetetraacetic acid (PDTA-OH), trans-1, 2-cyclohexanediaminetetraacetic acid (CyDTA), glycoletherdiaminotetraacetic acid (GEDTA), nitrilotriacetic acid (NTA), dihydroxyethylglycine (DHEG) and (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS), etc. Any one of these organic additives can be used alone or, as appropriate, two or more of them can also be used as a combination.

[0034] The added amount of the organic additive is 0.15 to 3 times the moles in total of the group 6 element of the periodic table and the group 8 to 10 element of the periodic table. A preferred range is 0.2 to 2.5 times. If the amount is less than 0.15 times the moles of the elements, the effect of enhancing the catalytic performance cannot be seen. Even if the amount is more than 3 times the moles of the elements, there is no increment of activity.

Meanwhile, with regard to the relation with the addition of the hydrogenation activity components, there is no limit in the order of adding the hydrogenation activity components and the organic additive. The solution of the organic additive can be added before or after adding the solution(s) of the hydrogenation activity components, or a solution containing the organic additive and the hydrogenation activity components can also be added at a time.

Further, the solution of the hydrogenation activity components or the solution of the organic additive or the solution of the hydrogenation activity components and the organic additive can be added at a time or in multiple times in response to the viscosity of the solution and to the pore volume (water adsorbing amount) of the boron-loaded intermediate product.

[0035] After the hydrogenation activity components and the organic additive have been added, the mixture is dried to load the group 6 element of the periodic table, the group 8 to 10 element of the periodic table and the organic additive into the boron-loaded intermediate product. Since the mixture is merely dried without being calcined when the abovementioned components are loaded into the intermediate product, a catalyst more excellent in activity than the conventional calcined catalysts can be obtained.

In this treatment of drying, it is desirable that the organic additive remains unchanged in its basic skeletal structure (the addition and elimination of crystal water, hydrogen ions, hydroxide ions, ammonium ions, etc. are not considered) while at least a part thereof interacts (intermolecular force, hydrogen bond, covalent bond, ionic bond, coordination bond, etc.) with the hydrogenation activity components.

As the yardstick of the remaining rate of the organic additive, it is preferred that the rate of the mass decreased when the completed catalyst is heated in air at 550 degrees C for 1 hour is 5 to 55 mass%. A more preferred range is 10 to 50 mass%. If the rate of mass decrease is less than 5 mass%, the loaded organic additive has, for example, volatilized or decomposed, and since the interaction with the hydrogenation activity components is insufficient, the catalytic activity cannot be enhanced. If the rate is more than 55 mass%, the large amount of water produced in the presulfidation step drives away the organic additive, and the catalytic activity cannot be enhanced.

[0036] As far as the interaction between the organic additive and the hydrogenation activity components as described above can be maintained, the drying method is not especially limited. For example, any of various industrial methods such as hot gas drying in air or in an inert gas, far infrared drying, conductive heat transfer drying, ultraviolet drying, microwave drying, freeze drying or reduced pressure drying can be applied. The drying conditions are not especially limited either and can be set, appropriately for adaptation to the volatilization or decomposition condition of the organic additive. The simplest drying method is hot gas drying, and in this case, for example, the mixture can be dried in air or in an inert gas (nitrogen gas, rare gas, carbonic acid gas or low oxygen atmosphere, etc.) at 30 to 250 degrees C (as the temperature of the material to be dried, not the atmospheric temperature), preferably 50 to 220 degrees C, more preferably 80 to 200 degrees C for 0.1 to 3 hours.

[0037] It is desirable that the completed catalyst has the following physical properties and pore structure, so that the catalyst can exhibit good catalytic performance.

The average pore diameter is 8.5 to 16 nm, preferably 9 to 15 nm. If the average pore diameter is less than 8.5 nm, the diffusion of hydrocarbon oil into the pores is insufficient, and if the diameter is more than 16 nm, the specific surface area declines to lower the catalytic performance.

Further, it is preferred that the total pore volume is 0.3 to 1.1 ml/g. A more preferred range is 0.32 to 1.0 ml/g. A total pore volume of 0.3 ml/g or less is insufficient for diffusing the hydrocarbon oil into the pores, and if the volume is more than 1.1 ml/g the absolute weight of the catalyst loaded into the reactor is so light that sufficient catalytic performance cannot be exhibited.

As an indicator showing the uniformity of the catalyst pores, it is desirable that the pore structure of the catalyst is such that the volume of the pores with their diameters kept in a range of between the average pore diameter +1.5 nm and -1.5nm accounts for 60 to 95% of the total pore volume. A preferred range is 65 to 90%, and a more preferred range is 70 to 85%. If the volume of the pores with their diameters as specified above accounts for less than 50%, micro pores not contributing to the reaction and large pores reducing the surface area increase relatively, if the volume of the pores with their diameters as specified above accounts for more than 95%, the diffusion of the hydrocarbon oil molecules with long molecular lengths into the pores is inhibited to lower the catalytic activity.

Meanwhile, the pore size distribution of the catalyst of this invention is a mono-peak distribution with the average pore diameter at the center. The distribution is not a multi-peak distribution having a peak in the pore diameter range smaller than the average pore diameter or a peak in the pore diameter range larger than the average pore diameter or peaks in both the ranges, in addition to the peak of the average pore diameter.

It is desirable that the specific surface area is 100 to 300 m^2/g. A more preferred range is 120 to 280 m^2/g. If the specific surface area is less than 100 m^2/g, the catalytic performance is insufficient, and if it is more than 300 m^2/g, the average pore diameter is so small that pore plugging or the like is liable to occur during the reaction.

[0038] Meanwhile, in this invention, the values of the pore structure (pore volume, average pore diameter, pore size distribution, etc.) are obtained by the mercury penetration method (contact angle 140 degrees, surface tension 480 dyn/cm), and the value of the specific surface area is obtained by the BET method. For measuring the pore structure and the specific surface area of a carrier, completed catalyst, etc. and for measuring the loaded amount of hydrogenation activity components, each sample is treated in air at 450 degrees C for 1 hour to remove the water and organic material contained therein, before measurement. In the meantime, for measuring the loaded amount of hydrogenation activity components, an X-ray fluorescence spectrometer is used.

[0039] The hydroprocessing catalyst of this invention can be loaded into the reactor as it is. However, as required, a hydrocarbon oil, for example, a non-hydroprocessed oil such as naphtha, kerosene, gas oil, heavy gas oil or vacuum gas oil, an oil obtained by hydroprocessing any of the non-hydroprocessed oils, lubricating oil or an oil obtained by arbitrarily mixing the oils enumerated above can be used to form a protective film on the surface of the catalyst for preventing the reduction of the catalyst by high temperature hydrogen gas in the startup step of the hydroprocessing unit, or for preventing or easing the volatilization or alteration of the organic additive loaded into the catalyst, before the catalyst is loaded into the reactor.

The protective film can be formed by adding any of the abovementioned hydrocarbon oils to the completed catalyst loaded with the organic additive. The added amount is 20 to 500% of the volume of the hydrocarbon oil required for saturating the pore volume of the completed catalyst. A preferred range is 30 to 200%, and a more preferred range is 50 to 125%.

[0040] Meanwhile, the catalyst is usually used after it has been presulfided. The presulfiding operation can be performed inside or outside the reactor. The presulfidation can be performed by a liquid phase sulfidation method in which a kerosene or gas oil fraction or an oil obtained by mixing said fraction with an adequate amount of a sulfidizing agent such as carbon disulfide, butanethiol, dimethyl disulfide (DMDS) or di-tertiary nonyl polysulfide (TNPS) is used in a heated state in hydrogen atmosphere, or by a gas phase sulfidation method in which a sulfidation agent such as hydrogen sulfide or carbon disulfide is used in a heated hydrogen gas stream.

[0041] The hydrocarbon oil to be hydroprocessed by the catalyst of this invention is a distillate oil with a 90% boiling point of 560 degrees C or lower, preferably 540 degrees C or lower and an initial boiling point of 100 degrees C or higher, preferably 150 degrees C or higher based on the ASTM D-2887 or D-2887 extended method. As examples of the distillate oil, petroleum naphtha, straight-run kerosene, straight-run gas oil, heavy gas oil, vacuum gas oil, heavy vacuum gas oil, etc. can be enumerated. Further examples include the kerosene and gas oil fractions (light cycle oil, coker gas oil, etc.) obtained from a hydrocracking unit, thermal cracking unit and fluid catalytic cracking unit, the kerosene and gas oil fractions derived from a heavy oil direct desulfurization unit, distillate oils derived from coal or animal or plant biomass, and oils obtained by arbitrarily mixing the distillate oils enumerated above.

Meanwhile, it is desirable that the content of metals such as vanadium and nickel in the feedstock to be processed is 5 mass ppm or less, preferably 1 mass ppm or less, and that the carbon residue content is 1 mass% or less, preferably 0.9 mass% or less. A heavy oil such as long residue, short residue, solvent deasphalted oil, coal liquefaction oil, shale oil or tar sand oil can also be mixed with the distillate oil to be hydroprocessed, for fulfilling the aforementioned metal content and carbon residue content.

[0042] The hydroprocessing catalyst of this invention can be used for any of various hydroprocessing reactions such as hydroprocessing, hydrodesulfurization, hydrodenitrification, hydrodeoxygenation, hydrometallization, carbon residue removal, hydrocracking and hydroisomerization of a hydrocarbon oil in the presence of hydrogen in a reactor of fixed bed, ebullating bed or moving bed.

The reaction conditions in the case where a hydroprocessing unit is used depend on the feedstock to be hydroprocessed, but are usually a hydrogen partial pressure of 1 to 15 MPa, preferably 3 to 10 MPa, a hydrogen/oil ratio of 50 to 1,200 Nm^3/kl, preferably 100 to 1,000 Nm^3/kl, a liquid hourly space velocity of 0.1 to $10h^{-1}$, preferably 0.5 to 8 h^{-1} and a reaction temperature of 300 to 450 degrees C, preferably 320 to 430 degrees C.

This invention is explained below more particularly based on the following examples, though this invention is not limited thereto or thereby.

(Preparation of catalysts)

Example 1

[0043] Water was added to pseudo-boehmite, and the mixture was kneaded by a kneading machine for 30 minutes and extrusion-molded.

The molding was calcined in air at 720 degrees C for 1.5 hours, to obtain a gamma-alumina carrier with a specific surface area of 245 m^2/g, a pore volume of 0.71 ml/g and an average pore diameter of 10.4 nm.

The carrier was impregnated with an aqueous boric acid-ammonia solution by pore filling method, and the impregnated carrier was calcined in air at 530 degrees C for 1 hour to obtain a boron-loaded intermediate product loaded with 0.5 mass% of boron based on the mass of the oxide of the intermediate product.

The intermediate product was impregnated with an aqueous solution containing molybdenum trioxide, basic nickel carbonate, phosphoric acid and diethylene glycol (the amount of diethylene glycol was 0.75 times the moles in total of molybdenum and nickel) by pore filling method, to let the completed catalyst contain 20 mass% of molybdenum trioxide, 4 mass% of nickel oxide and 7 mass% of phosphorus pentoxide respectively based on the mass of the oxide of the completed catalyst.

The impregnated carrier was dried in hot air for 2 hours with the temperature of the impregnated carrier kept at 120 degrees C, to obtain a catalyst A. The physical properties and chemical composition of the catalyst A are shown in Table 1.

Example 2

[0044] A catalyst B was prepared according to the same method as that of Example 1, except that the amount of boron loaded in the boron-loaded intermediate product was 1.1 mass%. The physical properties and chemical composition of the catalyst B are shown in Table 1.

Example 3

[0045] A catalyst C was prepared according to the same method as that of Example 1, except that the amount of boron loaded in the boron-loaded intermediate product was 2.6 mass%. The physical properties and chemical composition of the catalyst C are shown in Table 1.

Example 4

[0046] A catalyst D was prepared according to the same method as that of Example 1, except that the amount of boron loaded in the boron-loaded intermediate product was 3.6 mass%. The physical properties and chemical composition of the catalyst D are shown in Table 1.

Example 5

[0047] A catalyst E was prepared according to the same method as that of Example 1, except that the amount of boron loaded in the boron-loaded intermediate product was 7.7 mass%. The physical properties and chemical composition of the catalyst E are shown in Table 1.

Example 6

[0048] An aqueous phosphoric acid solution was added to the pseudo-boehmite used for preparing the gamma-alumina carrier of Example 1, and the mixture was kneaded for 30 minutes using a kneading machine and extrusion-molded. The molding was calcined in air at 730 degrees C for 1.5 hours to obtain a phosphorus-alumina carrier containing 7 mass% of phosphorus as the oxide, with a specific surface area of 275 m^2 /

g, a pore volume of 0.70 ml/g and an average pore diameter of 9.9 nm.

The alumina-phosphorus carrier was impregnated with an aqueous boric acid-monoethanolamine solution by pore filling method, and the impregnated carrier was calcined in air at 530 degrees C for 1 hour to obtain a boron-loaded intermediate product loaded with 3.0 mass% of boron based on the mass of the oxides of the boron-loaded intermediate product.

The intermediate product was impregnated with an aqueous solution containing molybdenum trioxide, basic nickel carbonate, phosphoric acid, diethylene glycol and citric acid monohydrate as organic additives (the amounts of the organic additives were respectively 0.25 times the moles in total of molybdenum and nickel) by pore filling method, to let the completed catalyst contain 20 mass% of molybdenum trioxide, 4 mass% of nickel oxide and 7 mass% of phosphorus pentoxide respectively based on the mass of the oxide of the completed catalyst.

The impregnated carrier was dried in hot air for 2 hours with the temperature of the impregnated carrier kept at 120 degrees C, to obtain a catalyst F. The physical properties and chemical composition of the catalyst F are shown in Table 1.

Example 7

[0049] A boron-loaded intermediate product was obtained according to the same method as that of Example 3 and was impregnated with an aqueous solution containing molybdenum trioxide, basic cobalt carbonate, phosphoric acid and diethylene glycol (the amount of diethylene glycol was 0.75 times the moles in total of molybdenum and cobalt) by pore filling method, to let the completed catalyst contain 20 mass% of molybdenum trioxide, 4 mass% of cobalt oxide and 7 mass% of phosphorus pentoxide respectively based on the mass of the oxides of the completed catalyst. Then, according to the same method as that of Example 3, a catalyst G was obtained. The physical properties and chemical composition of the catalyst G are shown in Table 1.

Comparative Example 1

[0050] A catalyst H was obtained according to the same method as that of Example 1, except that boron was not added. The physical properties and chemical composition of the catalyst H are shown in Table 2.

Comparative Example 2

[0051] A catalyst I was obtained according to the same method as that of Example 6, except that boron was not added. The physical properties and chemical composition of the catalyst I are shown in Table 2.

Comparative Example 3

[0052] A slurry with boric acid suspended in water was added to the pseudo-boehmite used for preparing the gamma-alumina carrier of Example 1, and the mixture was kneaded for 30 minutes by a kneading machine and extrusion-molded. The molding was calcined in air at 770 degrees C for 1.5 hours to obtain a boron-alumina carrier containing 2.6 mass% of boron as the oxide, with a specific surface area of 262 m^2/g, a pore volume of 0.70 ml/g and an average pore diameter of 10.0nm. Molybdenum, nickel, phosphorus and diethylene glycol were added to the boron-alumina carrier according to the same method as that of Example 1, to prepare a catalyst J. The physical properties and chemical composition of the catalyst J are shown in Table 2.

Comparative Example 4

[0053] The catalyst obtained in Example 3 was calcined in air at 450 degrees C for 1.5 hours to prepare a catalyst K. The physical properties and chemical composition of the catalyst K are shown in Table 2.

Comparative Example 5

[0054] A catalyst L was obtained according to the same method as that of Example 7, except that boron was not added. The physical properties and chemical composition of the catalyst L are shown in Table 2.

[0055]

[Table 1]

Properties of prepared catalysts (examples)

		Example 1	Example 2	Example 3	Example 4
		Catalyst A	Catalyst B	Catalyst C	Catalyst D
MoO_3	mass%	20.2	19.8	20.0	20.2
CoO	mass%	-	-	-	-
NiO	mass%	3.9	4.0	4.1	4.1
P_2O_5	mass%	7.0	7.1	7.2	7.2
$B_2O_3$1)	mass%	0.5	1.1	2.6	3.6
Al_2O_3	mass%	Balance	Balance	Balance	Balance
Total pore volume	ml/g	0.37	0.37	0.35	0.35
Average pore diameter	nm	11.9	12.0	12.0	11.8
Specific surface area	m^2/g	147	142	134	129
Pore volume rate 2)	%	74.3	73.7	72.8	73.6
Number of peaks of pore size distribution	-	1	1	1	1
Mass decrease rate	mass%	16.0	16.2	15.7	16.1

1) Based on the mass of the boron-loaded intermediate product (calculated value)

2) Rate of the volume of the pores with their diameters kept in a range of ± 1.5 nm of the average pore diameter to the total pore volume.

		Example 5	Example 6	Example 7
		Catalyst E	Catalyst F	Catalyst G
MoO_3	mass%	20.0	20.3	20.2
CoO	mass%	-	-	4.0
NiO	mass%	4.1	4.0	-
P_2O_5	mass%	7.4	7.3	6.9
$B_2O_3$1)	mass%	7.7	3.0	2.6
Al_2O_3	mass%	Balance	Balance	Balance
Total pore volume	ml/g	0.33	0.41	0.37
Average pore diameter	nm	11.5	11.8	12.9
Specific surface area	m^2/g	118	131	132
Pore volume rate 2)	%	78.5	78.3	73.4
Number of peaks of pore size distribution	-	1	1	1
Mass decrease rate	mass%	17.9	17.3	16.5

[0056]

[Table 2]

Properties of prepared catalysts (comparative examples)

		Compara. Example 1	Compara. Example 2	Compara. Example 3	Compara. Example 4	Compara. Example 5
		Catalyst H	Catalyst I	Catalyst J	Catalyst K	Catalyst L
MoO_3	mass%	19.9	21.1	21.0	20.0	19.7
CoO	mass%	-	-	-	-	4.4
NiO	mass%	4.0	4.0	4.1	4.1	-
P_2O_5	mass%	7.0	7.1	7.5	7.2	7.3
B_2O_3 1)	mass%	-	-	2.6	2.6	-
Al_2O_3	mass%	Balance	Balance	Balance	Balance	Balance
Total pore volume	ml/g	0.37	0.45	0.38	0.35	0.43
Average pore diameter	nm	11.6	13.3	13.0	12.0	12.2
Specific surface area	m^2/g	152	151	131	134	176
Pore volume rate 2)	%	75.2	73.4	81.5	72.8	74.1
Number of peaks of pore size distribution	-	1	1	1	1	1
Mass decrease rate	mass%	16.1	16.2	16.9	1.30	14.7

1) Based on the mass of the boron-loaded intermediate product (calculated value)

2) Rate of the volume of the pores with their diameters kept in a range of ± 1.5 nm of the average pore diameter to the total pore volume.

[0057] (Hydrogenation activity tests)

1. Vacuum gas oil hydroprocessing test

A small fixed bed flow reactor was packed with any of the catalysts of Examples 1 to 6 and Comparative Examples 1 to 4, and subsequently a sulfurized oil (corresponding to a total sulfur content of 2.5 mass%) obtained by adding dimethyl disulfide to the gas oil of Table 5 was used to perform presulfidation.

Then, the vacuum gas oil with the properties shown in Table 3 was experimentally hydroprocessed under the conditions of Table 4. The sulfur content and nitrogen content of the produced oil obtained in the test were measured respectively by the X-ray fluorescence method and the oxidative decomposition and chemiluminescence method, and the relative volume activity values were obtained based on expressions (1) to (3). The test tests are shown in Table 7.

[0058]

[Table 3]

Properties of vacuum gas oil

Sulfur content	mass%	1.91
Nitrogen content	ppm	781
Vanadium	ppm	< 1
Nickel	ppm	< 1
Carbon residue	mass%	0.86
Kinematic viscosity	cSt@50°C	39.9
Density	g/cm^3@15°C	0.9168
Distillation Properties*)		
IBP	°C	311
50%	°C	449
90%	°C	535
FBP	°C	572

*) According to ASTM D-2887 extended method

[0059] [Table 4]

Activity test conditions

Hydrogen partial pressure	MPa	6.0
Reaction temperature	°C	375
Hydrogen/oil ratio	Nl/l	1000
Liquid space velocity	h^{-1}	1.0
Period	h	120

[0060] [Math.1]

Relative volume activity =
(k of any of Examples 1 to 6 and Comparative Examples 1 to 4) / (k of Comparative Example 1) × 100 Expression (1)

Hydrodesulfurization reaction:

$$k = \mathrm{LHSV}/(n-1) \times \{1/Y^{(n-1)} - 1/X^{(n-1)}\} \quad (\text{where } n \neq 1) \qquad \text{Expression (2)}$$

Hydrodenitrification reaction:

$$k = \mathrm{LHSV} \times \ln (X/Y) \quad (\text{where } n = 1) \qquad \text{Expression (3)}$$

[0061] In the above expressions, LHSV is a liquid hourly space velocity; k is a reaction rate constant; n is the order of reaction; X is the mass rate of sulfur or nitrogen component in feedstock; and Y is the mass rate of sulfur or nitrogen component in produced oil. ln expresses a natural logarithm.

[0062] 2. Gas oil hydroprocessing test

The catalyst of Examples 7 or Comparative Example 5 was packed into a small fixed bed flow reactor, and a sulfurized oil (corresponding to a total sulfur content of 2.5 mass%) obtained by adding dimethyl disulfide to the gas oil of Table 5 was used to perform presulfidation. Then, the raw gas oil of Table 5 was subjected to a hydroprocessing test under the conditions of Table 6. The sulfur content of the produced oil obtained in the test was measured by the X-ray fluorescence method, and the relative volume activity values were obtained based on mathematical expressions (2) and (4). The evaluation results are shown in Table 8.

[0063] [Table 5]

Properties of gas oil

Sulfur content	mass%	1.20
Nitrogen content	ppm	109
Density	g/cm^3@15°C	0.8415
Distillation Properties*)		
IBP	°C	180
50%	°C	275
90%	°C	347
FBP	°C	380

*) According to ASTM D-2887 method

[0064] [Table 6]

Activity test conditions

Hydrogen partial pressure	MPa	5.0
Reaction temperature	°C	330
Hydrogen/oil ratio	Nl/l	200
Liquid space velocity	h^{-1}	1.5
Period	h	100

[0065] [Math.2]

Relative volume activity =
(k of any of Examples 7 or Comparative Examples 5) / (k of Comparative Example 5) × 100 Expression (4)

[0066]

[Table 7]

Vacuum gas oil test results

	Example 1 Catalyst A	Example 2 Catalyst B	Example 3 Catalyst C	Example 4 Catalyst D	Example 5 Catalyst E	Example 6 Catalyst F
Relative volume activity of denitirification	104	107	112	110	106	111
Relative volume activity of desulfurization	103	104	105	103	93	104

	Comparative Example 1 Catalyst H	Comparative Example 2 Catalyst I	Comparative Example 3 Catalyst J	Comparative Example 4 Catalyst K
Relative volume activity of denitirification	100	98	100	91
Relative volume activity of desulfurization	100	99	98	100

Order of desulfurization reaction: 1.3rd

Order of denitrification reaction : 1st

[0067] [Table 8]

Gas oil test results

	Example 7 Catalyst G	Comparative Example 5 Catalyst L
Relative volume activity of desulfurization	113	100

Order of desulfurization reaction: 1.3rd

[0068] From the hydroprocessing test results of vacuum gas oil and gas oil (Tables 7 and 8), it can be seen that the boron-added catalysts of this invention show excellent hydrodesulfurization and hydrodenitrification activity compared with conventional boron-less catalyst, boron-kneaded catalyst and calcined boron-added catalyst.

Claims

[Claim 1] A process for producing a hydroprocessing catalyst for hydrocarbon oils, loaded with a group 6 element and a group 8 to 10 element of the periodic table and an organic additive, comprising the steps of depositing a boron compound on the pore surfaces of an inorganic porous carrier mainly composed of alumina, calcining to obtain a boron-loaded intermediate product, adding at least one of the group 6 elements of the periodic table by 10 to 40 mass% based on the mass of the oxide catalyst, at least one of the group 8 to 10 elements of the periodic table by 0.5 to 20mass% based on the mass of the oxide catalyst, and an organic additive by 0.15 to 3 times the moles in total of the group 6 element and the group 8 to 10 element of the periodic table respectively to said intermediate product, and drying.

[Claim 2] The process for producing a hydroprocessing catalyst, according to claim 1, wherein an impregnation method is used as the deposition method for obtaining the boron-loaded intermediate product, and the loaded amount of boron is 0.3 to 10 mass% based on the mass of the oxide of said intermediate product.

[Claim 3] The process for producing a hydroprocessing catalyst, according to claim 1 or 2, wherein the group 6 element of the periodic table is at least one selected from chromium, molybdenum and tungsten, while the group 8 to 10 element of the periodic table is at least one selected from iron, cobalt and nickel.

[Claim 4] The process for producing a hydroprocessing catalyst, according to any one of claims 1 through 3, wherein the organic additive is at least one selected from the group consisting of polyhydric alcohols, saccharides, carboxylic acids, amino acids and chelating agents.

[Claim 5] A method for hydroprocessing a hydrocarbon oil, comprising the step of bringing a hydrocarbon oil and the hydroprocessing catalyst as set forth in any one of claims 1 through 4 into contact with each other at a reaction temperature of 300 to 450 degrees C at a hydrogen partial pressure of 1 to 15 MPa, at a liquid hourly space velocity of 0.1 to 10 hr^{-1} and at a hydrogen/oil ratio of 50 to 1,200 Nm^3/kl.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2010/005678

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J23/85 B01J23/883 B01J27/188 B01J27/19 B01J37/02
B01J35/10

ADD.

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)

B01J C10G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 724 226 A (CHENG WU-CHENG [US] ET AL) 9 February 1988 (1988-02-09)	1-5
Y	* abstract column 3, lines 8-9; examples 2,3,4 table 2 claims 10,13-18 -----	1-5
Y	EP 0 601 722 A1 (SUMITOMO METAL MINING CO [JP]) 15 June 1994 (1994-06-15) * abstract page 3, line 25 - page 4, line 38 ----- -/--	1-5

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 17 November 2010	Date of mailing of the international search report 26/11/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fischbach, Malaika

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INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2010/005678

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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