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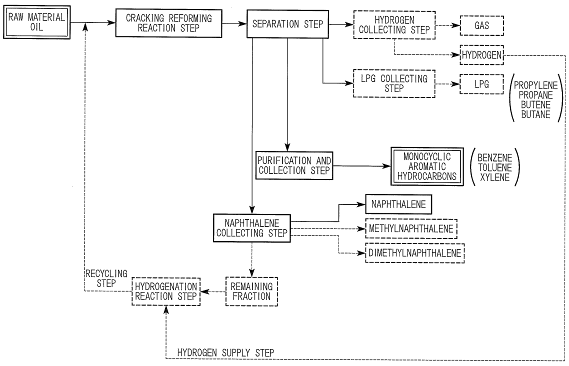
(54) METHOD FOR MANUFACTURING AROMATIC HYDROCARBON

(57) Disclosed is a method for producing aromatic hydrocarbons, the method including a cracking reforming reaction step of bringing a feedstock having a 10 vol% distillation temperature of 140°C or higher and a 90 vol% distillation temperature of 380°C or lower, into contact with a catalyst for monocyclic aromatic hydrocarbon production containing a crystalline aluminosilicate to cause the feedstock to react with the catalyst, and thereby obtaining a product including monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and a heavy oil fraction having 9 or more carbon numbers; a separation step of respectively separating the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and the heavy oil fraction having 9 or more carbon numbers from the product obtained from the cracking reforming reaction step; a purification and collecting step of purifying the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers thus separated in the separation step, and collecting the hydrocarbons; and a naphthalene collecting step of separating naphthalene compounds that include at least naphthalene, from the heavy oil fraction having 9 or more carbon numbers thus separated in the separation step, and collecting the naphthalene compounds.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing aromatic hydrocarbons.
Priority is claimed on Japanese Patent Application No. 2010-205903, filed September 14, 2010, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002] Light cycle oil (hereinafter, referred to as "LCO"), which is a cracked light oil produced by a fluid catalytic cracking (hereinafter, referred to as "FCC") units, contains a large amount of polycyclic aromatic hydrocarbons and has been utilized as light oil or heavy oil. However, in recent years, investigations have been conducted to obtain, from LCO, monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers (for example, benzene, toluene, xylene, ethylbenzene and the like), which can be utilized as high octane value gasoline base materials or petrochemical feedstocks and have a high added value.
For example, Patent Documents 1 to 3 suggest methods for producing monocyclic aromatic hydrocarbons from polycyclic aromatic hydrocarbons that are contained in LCO and the like in a large amount, by using a zeolite catalyst.

Prior Art Documents

Patent Document

[0003]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. H03-2128
[Patent Document 2] Japanese Unexamined Patent Application, First Publication No. H03-52993
[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. H03-26791

DISCLOSURE OF INVENTION

Technical Problem

[0004] However, in regard to the methods described in Patent Documents 1 to 3, it cannot be said that the yield of monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers is sufficiently high.
Furthermore, in recent years, new effective utilization of LCO is anticipated. Specifically, in addition to efficient production of monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers, such as benzene, toluene, xylene and ethylbenzene, it is expected to produce other chemical products as effective by-products, by the same process or only by adding a new process to part of the process.

[0005] The invention was achieved in view of the circumstances described above, and it is an object of the invention to provide a method for producing aromatic hydrocarbons, by which monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers can be produced in high yields from a feedstock containing polycyclic aromatic hydrocarbons, and also, other chemical products, for example, aromatic hydrocarbons other than the monocyclic aromatic hydrocarbons, can be produced.

Solution to Problem

[0006] The present inventors conducted thorough investigations in order to achieve the object described above, and as a result, they obtained the following findings.
Since LCO contains a large amount of polycyclic aromatic hydrocarbons, if this is subjected to a cracking reforming reaction treatment, a relatively large amount of a heavy oil fraction having 9 or more carbon numbers can also be obtained in addition to the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers. In regard to this heavy oil fraction, an investigation has been conducted to merely find that the heavy oil fraction may be collected as a light oil/kerosene base material, or may be recycled as a feedstock of the monocyclic aromatic hydrocarbons.

[0007] Thus, the present inventors analyzed in detail the components of the heavy oil fraction in order to promote effective utilization of the heavy oil fraction, and as a result, the inventors found that the heavy oil fraction contains a large proportion of naphthalene or alkylnaphthalenes. Further, based on such findings, the inventors further conducted investigations regarding the production of naphthalene as a chemical product, in parallel to the production of the monocyclic aromatic hydrocarbons, and as a result, the inventors achieved the invention.

[0008] That is, the method for producing aromatic hydrocarbons of the invention includes:

a cracking reforming reaction step of bringing a feedstock having a 10 vol% distillation temperature of 140°C or higher and a 90 vol% distillation temperature of 380°C or lower, into contact with a catalyst for monocyclic aromatic hydrocarbon production containing a crystalline aluminosilicate to cause the feedstock to react with the catalyst, and thereby obtaining a product including monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and a heavy oil fraction having 9 or more carbon numbers;
a separation step of respectively separating the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and the heavy oil fraction having 9 or more carbon numbers from the product obtained from the cracking reforming reaction step;
a purification and collecting step of purifying the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers thus separated in the separation step, and collecting the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers; and
a naphthalene collecting step of separating naphthalene compounds that include at least naphthalene, from the heavy oil fraction having 9 or more carbon numbers thus separated in the separation step, and collecting the naphthalene compounds.

[0009] Furthermore, in regard to the method for producing aromatic hydrocarbons, the naphthalene collection step is preferably a step of separating and collecting methylnaphthalene and/or dimethylnaphthalene, and naphthalene.
Furthermore, the method for producing aromatic hydrocarbons preferably includes:

a hydrogenation reaction step of hydrogenating the fraction remaining after naphthalene compounds have been separated in the naphthalene collecting step and obtaining a hydrogenation reaction product; and
a recycling step of recycling the hydrogenation reaction product to the cracking reforming reaction step.
Also, in regard to the method for producing aromatic hydrocarbons, the apparatus for separating and collecting naphthalene compounds including naphthalene in the naphthalene collecting step is preferably a distillation apparatus.

[0010] Furthermore, in regard to the method for producing aromatic hydrocarbons, it is preferable that the crystalline aluminosilicate contain, as main components, a zeolite with medium-sized pores and/or a zeolite with large-sized pores.
Furthermore, in regard to the method for producing aromatic hydrocarbons, it is preferable to set the reaction temperature employed when the feedstock and the catalyst for monocyclic aromatic hydrocarbon production in the cracking reforming reaction step, to a temperature ranging from 400°C to 650°C.
Also, in regard to the method for producing aromatic hydrocarbons, it is preferable to set the reaction pressure employed when the feedstock and the catalyst for monocyclic aromatic hydrocarbon production in the cracking reforming reaction step, to a pressure ranging from 0.1 MPaG to 1.5 MPaG.
Furthermore, in regard to the method for producing aromatic hydrocarbons, it is preferable to set the contact time for bringing the feedstock into contact with the catalyst for monocyclic aromatic hydrocarbon production in the cracking reforming reaction step, to a period ranging from 1 to 300 seconds.

Advantageous Effects of Invention

[0011] According to the method for producing aromatic hydrocarbons of the invention, monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers can be produced with a relatively high yield from a feedstock including polycyclic aromatic hydrocarbons, and in addition, naphthalene compounds including naphthalene can be produced as other chemical products.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1 is a diagram for explaining an embodiment of the method for producing aromatic hydrocarbons of the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0013] Hereinafter, the method for producing aromatic hydrocarbons of the invention will be described in detail.
FIG. 1 is a diagram for explaining an embodiment of the method for producing aromatic hydrocarbons of the invention,

and the method for producing aromatic hydrocarbons of the present embodiment is a method for producing monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers from a feedstock, and also producing naphthalene compounds including naphthalene.

[0014] That is, the method for producing aromatic hydrocarbons of the present embodiment preferably includes, as shown in FIG. 1:

(a) a cracking reforming reaction step of bringing a feedstock into contact with a catalyst for monocyclic aromatic hydrocarbon production to cause the feedstock to react with the catalyst, and obtaining a product including monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and a heavy oil fraction having 9 or more carbon numbers;
(b) a separation step of separating the product produced in the cracking reforming reaction step into plural fractions;
(c) a hydrogen collecting step of collecting hydrogen that is produced as a by-product in the cracking reforming reaction step from the gas components separated in the separation step;
(d) an LPG collecting step of collecting LPG that is produced as a by-product in the cracking reforming reaction step from a liquid fraction separated in the separation step;
(e) a purification and collection step of purifying and collecting monocyclic aromatic hydrocarbons from a liquid fraction separated in the separation step;
(f) a naphthalene collecting step of separating and collecting naphthalene compounds including at least naphthalene, from a heavy oil fraction having 9 or more carbon numbers that is obtainable from the liquid fraction separated in the separation step;
(g) a hydrogen supply step of supplying the hydrogen collected in the hydrogen collecting step to a hydrogenation reaction step;
(h) a hydrogenation reaction step of hydrogenating the fraction remaining after naphthalene compounds have been separated in the naphthalene collecting step; and
(i) a recycling step of recycling the hydrogenation reaction product obtained in the hydrogenation reaction step to the cracking reforming reaction step.
It should be noted, among the steps of (a) to (i), the steps of (a), (b), (e) and (f) are essential steps for the invention related to claim 1 of the invention, and the other steps are optional steps.

[0015] Hereinafter, the various steps will be specifically described.

<Cracking reforming reaction step>

[0016] In the cracking reforming reaction step, a feedstock is brought into contact with a catalyst for monocyclic aromatic hydrocarbon production, polycyclic aromatic hydrocarbons are partially hydrogenated by a hydrogen transfer reaction from saturated hydrocarbons by using the saturated hydrocarbons included in the feedstock as a hydrogen donating source, and the polycyclic aromatic hydrocarbons are converted to monocyclic aromatic hydrocarbons by ring-opening. Furthermore, conversion to monocyclic aromatic hydrocarbons can also be achieved by cyclizing and dehydrogenating saturated hydrocarbons obtainable from the feedstock or in a cracking step. Also, monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers can also be obtained by cracking monocyclic aromatic hydrocarbons having 9 or more carbon numbers. Thereby, a product including monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and a heavy oil fraction having 9 or more carbon numbers is obtained. This product includes, in addition to the monocyclic aromatic hydrocarbons and the heavy oil fraction, hydrogen, methane, ethane, ethylene, LPG (propane, propylene, butane, butene and the like), and the like. Furthermore, the heavy oil fraction includes large amounts of naphthalene, methylnaphthalene, and dimethylnaphthalene. Meanwhile, in the present specification, these naphthalene, methylnaphthalene and dimethylnaphthalene are collectively described as "naphthalene compounds".

[0017] In the cracking reforming reaction step, components such as naphthenobenzenes, paraffins and naphthenes in the feedstock can be eliminated by producing monocyclic aromatic hydrocarbons, and polycyclic aromatic hydrocarbons can be converted mainly to naphthalene compounds with a high added value, such as naphthalene, methylnaphthalene and dimethylnaphthalene, which have fewer side chains, by cleaving alkyl side chains simultaneously with the conversion of polycyclic aromatic hydrocarbons to monocyclic aromatic hydrocarbons. That is, in the present cracking reforming reaction step, monocyclic aromatic hydrocarbons can be produced with high yield, and at the same time, other components having a boiling point close to that of naphthalene compounds can be reduced as much as possible. Therefore, when the amount of production of naphthalene compounds having short side chains is increased, and the content ratio of naphthalene compounds in the oil produced by the cracking reforming reaction is increased, collection of naphthalene compounds that will be described below can be efficiently carried out.

[0018] Light cycle oil or the like that is used as a main feedstock originally contains a large proportion of naphthalene compounds, but at the same time, contains large proportions of other components such as naphthenobenzenes and paraffins. Therefore, the content ratio of naphthalene compounds relative to the total amount of the feedstock is small, and it is very difficult to directly separate and purify naphthalene compounds from the feedstock. In the case of performing separation and purification of naphthalene compounds from the feedstock, high energy consumption type processes such as crystallization should be employed, which is not preferable.

[0019] The present cracking reforming reaction step enables the proportion of useful aromatic hydrocarbons that can be collected, to be increased to a large extent as described above.

(Feedstock)

[0020] The feedstock that is used in the present embodiment is an oil having a 10 vol% distillation temperature of 140°C or higher and a 90 vol% distillation temperature of 380°C or lower. Since oil having a 10 vol% distillation temperature of lower than 140°C is light, monocyclic aromatic hydrocarbons are produced by very light fraction, and the oil is not suitable for the present embodiment. Furthermore, when an oil having a 90 vol% distillation temperature of higher than 380°C is used, not only the yield of monocyclic aromatic hydrocarbons is lowered, but also the amount of coke deposition on the catalyst for monocyclic aromatic hydrocarbon production increases, and the catalytic activity tends to undergo a rapid decrease.

[0021] The 10 vol% distillation temperature of the feedstock is preferably 150°C or higher, and the 90 vol% distillation temperature of the feedstock is preferably 360°C or lower. On the other hand, the upper limit of the 10 vol% distillation temperature and the lower limit of the 90 vol% distillation temperature of the feedstock are not particularly limited, but from the viewpoint that monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and naphthalene compounds can be efficiently produced, the 10 vol% distillation temperature is preferably 210°C or lower, and the 90 vol% distillation temperature is preferably 240°C or higher.

[0022] Meanwhile, the 10 vol% distillation temperature and 90 vol% distillation temperature as used herein mean values measured according to JIS K2254 "Petroleum products - Distillation test methods".

Examples of the feedstock having a 10 vol% distillation temperature of 140°C or higher and a 90 vol% distillation temperature of 380°C or lower include LCO produced by a FCC units, a hydrogenated purified oil of LCO, other cracked light oils such as hydrogenated cracked light oil and thermally cracked light oil, coal liquefied oil, heavy oil hydrogenated cracked purified oil, straight run kerosene, straight run light oil, coker kerosene, coker light oil, and purified oil obtained by hydrogenation cracking oil sand.

[0023] Furthermore, if the feedstock contains a large amount of polycyclic aromatic hydrocarbons, the yield of monocyclic aromatic hydrocarbons decreases. Therefore, the content of polycyclic aromatic hydrocarbons (polycyclic aromatic content) in the feedstock is preferably 50 vol% or less, and more preferably 40 vol% or less. However, as will be described below, when it is intended to further increase the yield of naphthalene (or naphthalene compounds) produced together with the monocyclic aromatic hydrocarbons, the polycyclic aromatic content in the feedstock may be adjusted to, for example, 50 vol% or more. However, even in that case, the content of aromatic hydrocarbons having 3 or more rings is preferably set to 30 vol% or less, and more preferably set to 15 vol% or less.

The term polycyclic aromatic content as used herein means the total value of the content of bicyclic aromatic hydrocarbons (bicyclic aromatic content) and the content of aromatic hydrocarbons with 3 or more rings (tricyclic or higher-cyclic aromatic content), which are measured according to JPI-5S-49 "Petroleum products - Hydrocarbon type test methods - high performance liquid chromatographic method", or analyzed by an FID gas chromatographic method. Hereinbelow, when the contents of polycyclic aromatic hydrocarbons, bicyclic aromatic hydrocarbons, and tricyclic or higher-cyclic aromatic hydrocarbons are expressed in vol%, the content was measured by the method of JPI-5S-49, while when the content is expressed in mass%, the content was measured by an FID gas chromatographic method.

(Reaction mode)

[0024] Examples of the reaction mode employed when the feedstock is brought into contact with a catalyst for monocyclic aromatic hydrocarbons to react therewith, include a fixed bed, a mobile bed, and a fluidized bed. According to the present embodiment, since heavy oil components are used as a feedstock, a fluidized bed which is capable of continuously removing the coke component adhering to the catalyst and is capable of stably carrying out the reaction is preferred. Particularly, a continuously regenerative type fluidized bed in which a catalyst is circulated between a reactor and a regenerator so that reaction-regeneration can be continuously repeated, is particularly preferred. When brought into contact with the catalyst for monocyclic aromatic hydrocarbon production, the feedstock is preferably in a gas phase. Furthermore, the feedstock may also be diluted with a gas as necessary.

(Catalyst for monocyclic aromatic hydrocarbon production)

[0025] The catalyst for monocyclic aromatic hydrocarbon production contains a crystalline aluminosilicate.

[Crystalline aluminosilicate]

[0026] From the viewpoint of further increasing the yield of monocyclic aromatic hydrocarbons, the crystalline aluminosilicate is preferably a zeolite with medium-sized pores and/or a zeolite with large-sized pores.
The zeolite with medium-sized pores is a zeolite having a 10-membered ring skeletal structure, and examples of the zeolite with medium-sized pores include zeolites having AEL type, EUO type, FER type, HEU type, MEL type, MFI type, NES type, TON type, and WEI type crystal structures. Among these, MFI type zeolite is preferred from the viewpoint that the yield of monocyclic aromatic hydrocarbons can be further increased.
The zeolite with large-sized pores is a zeolite having a 12-membered ring skeletal structure, and examples of the zeolite with large-sized pores include zeolites having AFI type, ATO type, BEA type, CON type, FAU type, GME type, LTL type, MOR type, MTW type, and OFF type crystal structures. Among these, from the viewpoint that the total yield of monocyclic aromatic hydrocarbons and aliphatic hydrocarbons having 3 to 4 carbon numbers can be further increased, BEA type zeolite is preferred.

[0027] However, as will be described below, when it is intended to further increase the yield of naphthalene (or naphthalene compounds) that are produced together with monocyclic aromatic hydrocarbons, a catalyst containing a crystalline aluminosilicate other than the MFI type or BEA type zeolite described above may also be used.

[0028] Furthermore, the crystalline aluminosilicate may also contain a zeolite with small-sized pores, having a 10-membered or fewer-membered ring skeletal structure, and a zeolite with ultra-large-sized pores, having a 14-membered or more-membered ring skeletal structure, in addition to the zeolite with medium-sized pores and the zeolite with large-sized pores.
Here, examples of the zeolite with small-sized pores include zeolites having ANA type, CHA type, ERI type, GIS type, KFI type, LTA type, NAT type, PAU type and YUG type crystal structures.
Examples of the zeolite with ultra-large-sized pores include zeolites having CLO type and VPI type crystal structures.

[0029] When the cracking reforming reaction step is carried out as a fixed bed reaction, the content of the crystalline aluminosilicate in the catalyst for monocyclic aromatic hydrocarbon production is preferably 60 mass% to 100 mass%, more preferably 70 mass% to 100 mass%, and particularly preferably 90 mass% to 100 mass%, when the total amount of the catalyst for monocyclic aromatic hydrocarbon production is designated as 100 mass%. When the content of the crystalline aluminosilicate is 60 mass% or more, the yield of monocyclic aromatic hydrocarbons can be sufficiently increased. Furthermore, the yield of naphthalene compounds can also be raised to a relatively high level.

[0030] When the cracking reforming reaction step is carried out by a fluidized bed reaction, the content of the crystalline aluminosilicate in the catalyst for monocyclic aromatic hydrocarbon production is preferably 20 mass% to 60 mass%, more preferably 30 mass% to 60 mass%, and particularly preferably 35 mass% to 60 mass%, when the total amount of the catalyst for monocyclic aromatic hydrocarbon production is designated as 100 mass%. When the content of the crystalline aluminosilicate is 20 mass% or more, the yield of monocyclic aromatic hydrocarbons can be sufficiently increased. Furthermore, the yield of naphthalene compounds can also be raised to a relatively high level. Meanwhile, when the content of the crystalline aluminosilicate is more than 60 mass%, the content of a binder that can be incorporated into the catalyst is decreased, and the catalyst may not be suitable for fluidized bed applications.

[Phosphorus and boron]

[0031] The catalyst for monocyclic aromatic hydrocarbon production preferably contains phosphorus and/or boron. When the catalyst for monocyclic aromatic hydrocarbon production contains phosphorus and/or boron, a decrease in the yield of monocyclic aromatic hydrocarbons over time can be prevented, and coke production on the catalyst surface can be suppressed.

[0032] Examples of the method for incorporating phosphorus to the catalyst for monocyclic aromatic hydrocarbon production include a method of supporting phosphorus on a crystalline aluminosilicate, a crystalline aluminogallosilicate or a crystalline aluminozincosilicate, by an ion exchange method, an impregnation method or the like; a method of incorporating a phosphorus compound at the time of zeolite synthesis and substituting a portion in the skeleton of a crystalline aluminosilicate with phosphorus; and a method of using a crystallization accelerator containing phosphorus at the time of zeolite synthesis. The phosphate ion-containing aqueous solution used at that time is not particularly limited, but solutions prepared by dissolving phosphoric acid, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, and other water-soluble phosphates in water at arbitrary concentrations can be preferably used.

[0033] Examples of the method of incorporating boron into the catalyst for monocyclic aromatic hydrocarbon production include a method of supporting boron on a crystalline aluminosilicate, a crystalline aluminogallosilicate or a crystalline aluminozincosilicate, by an ion exchange method, an impregnation method or the like; a method of incorporating a boron compound at the time of zeolite synthesis and substituting a portion of the skeleton of a crystalline aluminosilicate with boron; and a method of using a crystallization accelerator containing boron at the time of zeolite synthesis.

[0034] The content of phosphorus and/or boron in the catalyst for monocyclic aromatic hydrocarbon production is preferably 0.1 mass% to 10 mass%, relative to the total weight of the catalyst, and the lower limit is more preferably 0.5 mass% or more, while the upper limit is more preferably 9 mass% or less, and particularly preferably 8 mass% or less. When the content of phosphorus and/or boron relative to the total weight of the catalyst is 0.1 mass% or more, a decrease in the yield of monocyclic aromatic hydrocarbons over time can be prevented, and when the content is 10 mass% or less, the yield of monocyclic aromatic hydrocarbons can be increased.

[Gallium and zinc]

[0035] In the catalyst for monocyclic aromatic hydrocarbon production, gallium and/or zinc can be incorporated as necessary. When gallium and/or zinc is incorporated, the production proportion of monocyclic aromatic hydrocarbons can be further increased.

The form of gallium incorporation in the catalyst for monocyclic aromatic hydrocarbon production may be a form in which gallium is incorporated into the lattice skeleton of a crystalline aluminosilicate (crystalline aluminogallosilicate), a form in which gallium is supported on a crystalline aluminosilicate (gallium-supporting crystalline aluminosilicate), or both of them.

[0036] The form of zinc incorporation in the catalyst for monocyclic aromatic hydrocarbon production may be a form in which zinc is incorporated into the lattice skeleton of a crystalline aluminosilicate (crystalline aluminozincosilicate), a form in which zinc is supported on a crystalline aluminosilicate (zinc-supporting crystalline aluminosilicate), or both of them.

The crystalline aluminogallosilicate and crystalline aluminozincosilicate have a structure in which SiO_4, AlO_4 and GaO_4/ZnO_4 structures exist in the skeletal structure. Furthermore, the crystalline aluminogallosilicate and crystalline aluminozincosilicate are obtained by, for example, gel crystallization based on hydrothermal synthesis, a method of inserting gallium or zinc into the lattice skeleton of a crystalline aluminosilicate, or a method of inserting aluminum into the lattice skeleton of a crystalline gallosilicate or a crystalline zincosilicate.

[0037] The gallium-supporting crystalline aluminosilicate is a material in which gallium is supported on a crystalline aluminosilicate according to a known method such as an ion exchange method or an impregnation method. The gallium source that is used at that time is not particularly limited, but examples thereof include gallium salts such as gallium nitrate and gallium chloride, and gallium oxide.

The zinc-supporting crystalline aluminosilicate is a compound in which zinc is supported on a crystalline aluminosilicate according to a known method such as an ion exchange method or an impregnation method. The zinc source that is used at that time is not particularly limited, but examples thereof include zinc salts such as zinc nitrate and zinc chloride, and zinc oxide.

[0038] When the catalyst for monocyclic aromatic hydrocarbon production contains gallium and/or zinc, the content of gallium and/or zinc in the catalyst for monocyclic aromatic hydrocarbon production is preferably 0.01 mass% to 5.0 mass%, and more preferably 0.05 mass% to 1.5 mass%, relative to 100 mass% of the total amount of the catalyst. When the content of gallium and/or zinc is 0.01 mass% or greater, the production proportion of monocyclic aromatic hydrocarbons can be further increased. When the content is 5.0 mass% or less, the yield of monocyclic aromatic hydrocarbons can be further increased.

[Shape]

[0039] The catalyst for monocyclic aromatic hydrocarbon production is produced into, for example, a powder form, a particulate form, a pellet form or the like according to the reaction mode. For example, in the case of a fluidized bed, the catalyst is produced in a powder form, and in the case of a fixed bed, the catalyst is produced in a particulate form or a pellet form. The average particle size of the catalyst used in a fluidized bed is preferably 30 μm to 180 μm, and more preferably 50 μm to 100 μm. Furthermore, the apparent density of the catalyst used in a fluidized bed is preferably 0.4 g/cc to 1.8 g/cc, and more preferably 0.5 g/cc to 1.0 g/cc.

[0040] Meanwhile, the average particle size represents the particle size for a proportion of 50 mass% in a particle size distribution obtained by classification using sieves, and the apparent density is a value measured by the method of JIS Standards R9301-2-3.

In the case of obtaining a particulate or pellet-like catalyst, an oxide which is inert to the catalyst is incorporated as a binder as necessary, and the mixture may be molded by using various molding machines.

When the catalyst for monocyclic aromatic hydrocarbon production contains an inorganic oxide such as a binder, a binder containing phosphorus may also be used.

(Reaction temperature)

[0041] The reaction temperature at the time of bringing the feedstock into contact with the catalyst for monocyclic aromatic hydrocarbon production to react therewith is not particularly limited, but the reaction temperature is preferably 400°C to 650°C, and more preferably 450°C to 650°C. When the reaction temperature is 400°C or higher, the reaction of the feedstock can be facilitated. When the reaction temperature is from 450°C to 650°C, the yield of monocyclic aromatic hydrocarbons can be sufficiently increased, and the yield of naphthalene compounds can also be raised to a relatively high level.

(Reaction pressure)

[0042] The reaction pressure employed when the feedstock is brought into contact with the catalyst for monocyclic aromatic hydrocarbon production to react therewith is preferably set to 1.5 MPaG or less, and more preferably to 1.0 MPaG or less. When the reaction pressure is 1.5 MPaG or less, by-production of light gas can be suppressed, and also, pressure resistance of the reaction apparatus can be lowered. Furthermore, when the reaction pressure is from 0.1 MPaG to 1.5 MPaG, the yield of monocyclic aromatic hydrocarbons can be sufficiently increased, and the yield of naphthalene compounds can also be raised to a relatively high level.

(Contact time)

[0043] The contact time between the feedstock and the catalyst for monocyclic aromatic hydrocarbon production is not particularly limited so long as the desired reaction substantially proceeds. However, for example, the time for gas passage on the catalyst for monocyclic aromatic hydrocarbon production is preferably 1 second to 300 seconds, and the lower limit is more preferably 5 seconds or longer, while the upper limit is more preferably 150 seconds or shorter. When the contact time is 1 second or longer, the reaction can be achieved reliably, and when the contact time is 300 seconds or shorter, accumulation of carbon substances on the catalyst caused by coking or the like can be suppressed. Also, the amount of light gas generated by cracking can be suppressed. Furthermore, the yield of monocyclic aromatic hydrocarbons can be sufficiently increased, and the yield of naphthalene compounds can also be raised to a relatively high level.

<Separation step>

[0044] In the separation step, the product produced in the cracking reforming reaction step is separated into multiple fractions.

In order to separate the product into plural fractions, known distillation apparatuses and gas-liquid separation apparatuses may be used. Examples of the distillation apparatuses include apparatuses that are capable of separating by distillation of multiple fractions by a multistage distillation apparatus such as a stripper. Examples of the gas-liquid separation apparatuses include apparatuses each equipped with a gas-liquid separating tank, a product inlet pipe for introducing the product into the gas-liquid separating tank, a gas component discharge pipe provided in the upper part of the gas-liquid separating tank, and a liquid component discharge pipe provided in the lower part of the gas liquid separating tank.

[0045] In the separation step, it is preferable to separate at least gas components and a liquid fraction, and the liquid fraction may be further separated into plural fractions. An example of the separation step may be a form of process by which the reaction product is separated into gas components mainly including components having 4 or fewer carbon numbers (for example, hydrogen, methane, ethane, and LPG) and a liquid fraction. Furthermore, another example of the separation step may be a form of process by which the reaction product is separated into gas components including components having 2 or fewer carbon numbers (for example, hydrogen, methane and ethane) and a liquid fraction. Furthermore, another example of the separation step may be a form of process by which the liquid fraction is separated into LPG, a fraction containing monocyclic aromatic hydrocarbons, and a heavy oil fraction. Furthermore, another example of the separation step may be a form of process by which the liquid fraction is separated into LPG (for example, propylene, propane, butene, and butane), a fraction containing monocyclic aromatic hydrocarbons, and plural heavy oil fractions. Furthermore, when a fluidized bed is employed as the reaction mode for the cracking reforming reaction step, the catalyst powder and the like to be incorporated may be removed in the present step. However, for the heavy oil fraction, naphthalene compounds may be separated singly, or the heavy oil fraction may also be collectively fractionated without separating into plural fractions. The boiling point range of the fraction containing monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers is preferably 78°C to 150°C, and the boiling point range of the heavy oil fraction primarily containing naphthalene compounds is preferably 210°C to 270°C.

<Purification and collection step>

[0046] The purification and collection step purifies and collects the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers obtained in the separation step.

In this purification and collection step, the liquid fraction is sufficiently fractionated in the separation step, and when monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers are separated into benzene/toluene/xylene, a step of purifying and collecting the respective components is employed. Furthermore, when the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers are collectively fractionated, a step of collecting these monocyclic aromatic hydrocarbons, subsequently separating the hydrocarbons into benzene/toluene/xylene, and then purifying and collecting the respective components is employed.

[0047] In the case where the liquid fraction is not satisfactorily fractionated in the separation step, and when the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers are collected, the liquid fraction contains a large proportion of a fraction other than the monocyclic aromatic hydrocarbons, these fractions may be separated and supplied to, for example, the hydrogenation reaction step or naphthalene collection step that will be described below. Particularly, among the fractions other than monocyclic aromatic hydrocarbons, a fraction heavier than the monocyclic aromatic hydrocarbons (a heavy oil fraction having 9 or more carbon numbers) is preferably supplied to the naphthalene collection step. This is because the heavy oil fraction having 9 or more carbon numbers contains polycyclic aromatic hydrocarbons as a main component, and contains a large proportion of naphthalene or alkylnaphthalenes in particular.

<Naphthalene collecting step>

[0048] In the naphthalene collecting step, naphthalene compounds including at least naphthalene are separated and collected from a heavy oil fraction having 9 or more carbon numbers obtainable from the liquid fraction separated in the separation step.

In this naphthalene collecting step, in the case where the heavy oil fraction separated in the separation step is separated into a heavy oil fraction primarily containing naphthalene compounds in particular and a heavy oil fraction other than that, the heavy oil fraction containing naphthalene compounds is purified, and thus naphthalene compounds are separated and collected. Furthermore, in the separation step, when the heavy oil fraction having 9 or more carbon numbers is collectively fractionated without dividing the heavy oil fraction having 9 or more carbon numbers into plural fractions, the heavy oil fraction is separated into a fraction containing naphthalene compounds, specifically naphthalene compounds including naphthalene, methylnaphthalene and dimethylnaphthalene, and a fraction other than that, and the naphthalene compounds including at least naphthalene are purified and collected.

Meanwhile, in order to separate the heavy oil fraction into multiple fractions, a known distillation apparatus (distillation column) such as that used in the separation step may be used.

[0049] Since the components having a boiling point close to that of the naphthalene compounds in the oil produced by a cracking reforming reaction have been reduced to a large extent by going through the cracking reforming reaction step, in the present naphthalene collecting step, naphthalene can be separated with high purity, purified and collected by using only a known distillation apparatus such as that used in the separation step. For example, naphthalene can be purified to a purity of about 80% to 98% and then can be collected. Meanwhile, the purity of naphthalene thus collected is determined on the basis of reduction of the number and the production amount of components having a boiling point close to that of naphthalene that remains in the cracking reforming reaction step, and the performance of the distillation apparatus. When naphthalene is collected with a purity of 95% or higher, the naphthalene can be dealt with as a product which is generally distributed as crude naphthalene and has a commercial value, and in regard to naphthalene with a purity of less than 95%, for example, about 80% to 95%, this can be made into crude naphthalene as a chemical product by performing a purification treatment later and increasing the purity to 95% or higher. Furthermore, a fraction having a purity of 95% or higher can also be subjected to a further purification treatment and can be converted to naphthalene with higher purity. Examples of the purification treatment methods in this case include crystallization.

[0050] In the naphthalene collecting step, so long as naphthalene can be separated and collected, naphthalene compounds other than naphthalene may be collectively separated, purified and collected as alkylnaphthalenes, or may be individually separated, purified and collected as methylnaphthalene, dimethylnaphthalene and the like. In this case, methylnaphthalene and dimethylnaphthalene are respectively purified to a purity of about 80% to 95% and collected. Thereafter, the components are respectively purified to a purity demanded as chemical products.

[0051] Here, in this naphthalene collecting step, a fraction other than the desired naphthalene, methylnaphthalene and dimethylnaphthalene is also obtained. This fraction is sent out of the system, and for example, after treatments such as purification are carried out as necessary, the fraction is used as a base material for light oil/kerosene. Alternatively, the fraction is sent to the hydrogenation reaction step that will be described below, and after this step, the fraction is recycled.

[0052] Meanwhile, in the present embodiment shown in FIG 1, the naphthalene collecting step is composed of a single step. In the naphthalene collecting step, first, the step may be divided into multiple steps by providing a step of separating and collecting naphthalene from a heavy oil fraction having 9 or more carbon numbers, and then providing steps of respectively fractionating and collecting methylnaphthalene, dimethylnaphthalene and the like, and naphthalene, methylnaphthalene and dimethylnaphthalene may be respectively fractionated and collected. Furthermore, a fraction other than these is used as a base material for light oil/kerosene, or is subjected to a hydrogenation reaction step or the like and then supplied to the feedstock for recycling.

<Hydrogenation reaction step>

[0053] In this hydrogenation reaction step, a portion or the entirety of the remaining fraction obtained after naphthalene has been separated in the naphthalene collecting step is supplied to this hydrogenation reaction step, and this fraction is hydrogenated. Here, if only naphthalene is separated and collected in the naphthalene collecting step, and alkylnaphthalenes such as methylnaphthalene and dimethylnaphthalene are not separated and collected, these alkylnaphthalenes constitute the "remaining fraction obtained after naphthalene has been separated" as described above, and are supplied to the hydrogenation reaction step. Meanwhile, the remaining fraction obtained after naphthalene compounds have been separated, which was not supplied to the hydrogenation reaction step, may also be used as a fuel base material for light oil/kerosene and the like.

[0054] Specifically, the remaining fraction obtained by naphthalene compounds have been separated in the naphthalene collecting step, and hydrogen are supplied to a hydrogenation reactor, and at least a portion of the polycyclic aromatic hydrocarbons included in the remaining fraction obtained after naphthalene compounds have been separated is subjected to hydrogenation by using a hydrogenation catalyst.

The polycyclic aromatic hydrocarbons are not particularly limited, but it is preferable to hydrogenate the polycyclic aromatic hydrocarbons until the number of aromatic rings becomes 1 or less on the average. When the polycyclic aromatic hydrocarbons are hydrogenated until the number of aromatic rings becomes 1 or less on the average, when the polycyclic aromatic hydrocarbons are recycled to the cracking reforming reaction step, the hydrogenation reaction product can be easily converted to monocyclic aromatic hydrocarbons.

[0055] Furthermore, in order to further increase particularly the yield of monocyclic aromatic hydrocarbons, the content of polycyclic aromatic hydrocarbons in the hydrogenation reaction product obtainable in the hydrogenation reaction step is preferably adjusted to 20 mass% or less, and more preferably 10 mass% or less. The content of polycyclic aromatic hydrocarbons in the hydrogenation reaction product is preferably smaller than the content of polycyclic aromatic hydrocarbons in the feedstock, and the content can be reduced as the amount of the hydrogenation catalyst is increased, and as the reaction pressure is increased.

However, it is not necessary to carry out the hydrogenation treatment until the entirety of the polycyclic aromatic hydrocarbons becomes saturated hydrocarbons. Excessive hydrogenation tends to cause an increase in the amount of hydrogen consumption and an increase in the amount of heat generation.

[0056] Furthermore, when it is intended to prioritize an enhancement of the yield of naphthalene (naphthalene compounds) to an enhancement of the yield of monocyclic aromatic hydrocarbons, the content of polycyclic aromatic hydrocarbons in the hydrogenation reaction product obtainable in the hydrogenation reaction step is preferably adjusted to 20 mass% or more.

In the present embodiment, hydrogen produced as a by-product in the cracking reforming reaction step can also be utilized. That is, hydrogen is collected in the hydrogenation collecting step that will be described below from the gas components obtained in the separation step, and in the hydrogen supply step, the collected hydrogen is supplied to the hydrogenation reaction step.

[0057] Regarding the reaction mode for the hydrogenation reaction step, a fixed bed is suitably employed.

As the hydrogenation catalyst, known hydrogenation catalysts (for example, a nickel catalyst, a palladium catalyst, a nickel-molybdenum-based catalyst, a cobalt-molybdenum-based catalyst, a nickel-cobalt-molybdenum-based catalyst, and a nickel-tungsten-based catalyst) can be used.

The reaction temperature may vary depending on the hydrogenation catalyst used, but the reaction temperature is usually set to the range of 100°C to 450°C, more preferably 200°C to 400°C, and even more preferably 250°C to 380°C.

[0058] The reaction pressure may vary depending on the hydrogenation catalyst or feedstock used, but the reaction pressure is preferably set to the range of 0.7 MPa to 13 MPa, more preferably set to 1 MPa to 10 MPa, and particularly preferably set to 1 MPa to 7 MPa. When the reaction pressure is adjusted to 13 MPa or less, a hydrogenation reactor having a low durability pressure can be used, and the cost of equipment can be reduced.

On the other hand, the reaction pressure is preferably 0.7 MPa or greater in view of the yield of the hydrogenation reaction.

The amount of hydrogen consumption is preferably 3000 scfb (506 Nm^3/m^3) or less, more preferably 2500 scfb (422 Nm^3/m^3) or less, and even more preferably 1500 scfb (253 Nm^3/m^3) or less.

On the other hand, the amount of hydrogen consumption is preferably 300 scfb (50 Nm^3/m^3) or greater in view of the yield of the hydrogenation reaction.

The liquid hourly space velocity (LHSV) is preferably set to from 0.1 h^{-1} to 20 h^{-1}, and more preferably set to from 0.2 h^{-1} to 10 h^{-1}. When the LHSV is set to 20 h^{-1} or less, polycyclic aromatic hydrocarbons can be sufficiently hydrogenated at a lower hydrogenation reaction pressure. On the other hand, when the LHSV is set to 0.1h^{-1} or higher, an excessive increase in the size of hydrogenation reactors can be avoided.

<Hydrogen collecting step>

[0059] In the hydrogen collecting step, hydrogen is collected from the gas components obtained in the separation step. Regarding the method for collecting hydrogen, there are no particular limitations so long as hydrogen and other gases that are included in the gas components obtained in the separation step can be separated, and examples thereof include a pressure swing adsorption method (PSA method), a low temperature separation processing method, and a membrane separation method.
Conventionally, the amount of hydrogen collected in the hydrogen collecting step is larger than the amount required for hydrogenating the heavy oil fraction or the light oil/kerosene fraction described above.

<Hydrogen supply step>

[0060] In the hydrogen supply step, hydrogen obtained in the hydrogen collecting step is supplied to the hydrogenation reactor of the hydrogenation reaction step. The amount of hydrogen supplied at that time is adjusted according to the amount of the remaining fraction obtained after naphthalene compounds have been separated in the naphthalene collecting step, which is supplied to the hydrogenation reaction step. Furthermore, if necessary, the hydrogen pressure is regulated.
By including such a hydrogen supply step as that of the present embodiment, the remaining fraction obtained after naphthalene compounds have been separated in the naphthalene collecting step described above can be hydrogenated by using the hydrogen produced as a by-product in the cracking reforming reaction step, and efficient operation of the apparatus can be promoted.

<Recycling step>

[0061] In the recycling step, the hydrogenation reaction product is mixed with the feedstock, and the mixture is recycled to the cracking reforming reaction step. The hydrogenation reaction product is a product obtained by allowing the remaining fraction obtained after naphthalene compounds have been separated in the naphthalene collecting step, to react in the hydrogenation reaction step.
When such a hydrogenation reaction product is recycled to the cracking reforming reaction step, monocyclic aromatic hydrocarbons or naphthalene compounds can be obtained by using the heavy oil fraction (excluding naphthalene compounds), which is a by-product, as a feedstock. Therefore, not only the amount of by-product can be reduced, but also, the amount of monocyclic aromatic hydrocarbons or naphthalene compounds produced can be increased. Furthermore, since saturated hydrocarbons are also produced by hydrogenation, the hydrogen transfer reaction can be accelerated in the cracking reforming reaction step. From these matters, the general yield of monocyclic aromatic hydrocarbons relative to the amount of the feedstock supplied can be increased, and also, the yield of naphthalene compounds can also be increased.
Meanwhile, when the remaining fraction obtained by separating naphthalene compounds in the naphthalene collecting step is recycled directly to the cracking reforming reaction step without performing a hydrogenation treatment, since the reactivity of polycyclic aromatic hydrocarbons is low, an increase in the yield of monocyclic aromatic hydrocarbons can be hardly expected. However, an increase in the yield of naphthalene compounds can be promoted.

<LPG collecting step>

[0062] In the LPG collecting step, LPG that is produced as a by-product in the cracking reforming reaction step is collected from the liquid fraction separated in the separation step.
In this LPG collecting step, a liquid fraction having 3 or 4 carbon numbers, that is, propylene, propane, butene and butane are purified and collected as LPG In the oil produced by the cracking reforming reaction in the method for producing aromatic hydrocarbons of the present embodiment, unlike the products of hydrogenation cracking and the like in conventional petroleum purification processes, more of olefins such as propylene and butene are present. Therefore, if necessaty, collection of olefins by hydrogenation or rectification can also be achieved.

[0063] As explained above, in the method for producing aromatic hydrocarbons of the present embodiment, monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers can be produced with a relatively high yield from a feedstock containing polycyclic aromatic hydrocarbons, and as other chemical products, naphthalene compounds including naphthalene, or olefin compounds such as propylene, propane, butene and butane can also be produced.

[0064] Particularly, in regard to naphthalene, it has been conventional in general to produce naphthalene according to a crystallization method by which coal tar distillate oil is cooled, and thereby crystals are precipitated. However, the crystallization method requires complicated steps, and there is a problem that the production cost is high.
In contrast to this, the method for producing aromatic hydrocarbons of the present embodiment can obtain naphthalene

with a relatively high purity, only by adding a naphthalene collecting step, or if necessary, a naphthalene compound separation and collection step to the process for producing monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers. Therefore, in regard to the production cost for naphthalene (or naphthalene compounds), when the portion for producing monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers is deducted, the production cost is markedly decreased as compared with conventional methods according to a crystallization method. Therefore, naphthalene (or naphthalene compounds) can be provided at low cost.

[Other embodiments]

[0065] The invention is not intended to be limited to the embodiment examples described above, and various modifications can be made to the extent that the gist of the invention is maintained.
For example, in regard to the method shown in FIG. 1, a hydrogenation reaction step of hydrogenating a portion of the liquid components separated in the separation process may be provided between the separation process and the purification and collection process. In the purification and collection step, the hydrogenation reaction product obtained in the hydrogenation reaction step may be distilled, and monocyclic aromatic hydrocarbons may be purified and collected. Furthermore, a portion of the heavy oil fraction separated in the separation step may also be supplied to the hydrogenation reaction step without going through the naphthalene collecting step, and the portion may also be hydrogenated and recycled to the cracking reforming reaction process.
Furthermore, in these methods or in the method shown in FIG. 1, regarding hydrogen used in the hydrogenation reaction step, hydrogen obtained in a known hydrogen production method may be used instead of the hydrogen produced as a by-product in the cracking reforming reaction step, or hydrogen produced as a by-product in another contact cracking method may also be used.

EXAMPLES

[0066] Hereinafter, the invention will be more specifically described based on Examples and Comparative Examples, but the invention is not intended to be limited by these Examples.

[Preparation Example for catalyst for monocyclic aromatic hydrocarbon production]

[0067] Preparation of catalyst containing Ga and phosphorus-supported crystalline aluminosilicate:

> A solution (A) containing sodium silicate (J sodium silicate No. 3, SiO_2: 28 mass% to 30 mass%, Na: 9 mass% to 10 mass%, balance water, manufactured by Nippon Chemical Industrial Co., Ltd.): 1706.1 g and water: 2227.5 g, and a solution (B) containing $Al2(SO_4)_3 .14\text{-}18\ H_2O$ (reagent grade, manufactured by Wako Pure Chemical Industries, Ltd.): 64.2 g, tetrapropylammonium bromide: 369.2 g, H_2SO_4 (97 mass%): 152.1 g, NaCl: 326.6 g and water: 2975.7 g were each prepared.

Subsequently, while the solution (A) was stirred at room temperature, the solution (B) was slowly added to the solution (A). The mixture thus obtained was vigorously stirred for 15 minutes in a mixer, and the gel was crushed to obtain a milky homogenously fine state.
Subsequently, this mixture was placed in an autoclave made of stainless steel, and a crystallization operation was carried out under self-pressure under the conditions of a temperature of 165°C, a time of 72 hours, and a stirring speed of 100 rpm. After completion of the crystallization operation, the product was filtered to collect a solid product, and washing and filtration was repeated 5 times by using about 5 liters of deionized water. The solid obtained by filtration was dried at 120°C, and the solid was calcined at 550°C for 3 hours under a stream of air.
It was confirmed by an X-ray diffraction analysis (model name: Rigaku RINT-2500V) that the calcination product thus obtained had an MFI structure. Furthermore, the SiO_2/Al_2O_3 ratio (molar ratio) obtained by a fluorescence X-ray analysis (model name: Rigaku ZSX101e) was 64.8. Furthermore, the content of the aluminum element contained in the lattice structure calculated from these results was 1.32 mass%.
Subsequently, a 30 mass% aqueous solution of ammonium nitrate was added at a ratio of 5 mL per 1 g of the calcination product thus obtained, and the mixture was heated and stirred at 100°C for 2 hours, subsequently filtered and washed with water. This operation was repeated 4 times, and then the mixture was dried at 120°C for 3 hours. Thus, an ammonium type crystalline aluminosilicate was obtained.
Thereafter, calcination was carried out for 3 hours at 780°C, and thus a proton type crystalline aluminosilicate was obtained.
Subsequently, 120 g of the proton type crystalline aluminosilicate thus obtained was impregnated with 120 g of an aqueous solution of gallium nitrate such that 0.4 mass% (a value calculated relative to 100 mass% of the total mass of

the crystalline aluminosilicate) of gallium would be supported, and the resultant was dried at 120°C. Thereafter, the product was calcined at 780°C for 3 hours under an air stream, and thus a gallium-supported crystalline aluminosilicate was obtained.

Subsequently, 30 g of the gallium-supported crystalline aluminosilicate thus obtained was impregnated with 30 g of an aqueous solution of diammonium hydrogen phosphate such that 0.7 mass% of phosphorus (a value calculated relative to 100 mass% of the total mass of the crystalline aluminosilicate) would be supported, and the resultant was dried at 120°C. Thereafter, the product was calcined at 780°C for 3 hours under an air stream, and thus a catalyst A containing a crystalline aluminosilicate, gallium and phosphorus was obtained.

Meanwhile, when the production of monocyclic aromatic hydrocarbons is carried out in a fluidized bed reaction mode, the catalyst A further contains a silica binder (the content of the silica binder is 60 mass% relative to the total mass of the catalyst) in addition to the crystalline aluminosilicate, gallium and phosphorus.

(Example 1)

[0068] LCO as indicated in Table 1 (10 vol% distillation temperature: 224.5°C, 90 vol% distillation temperature: 349.5°C), which was a feedstock, was brought into contact with the catalyst A (a catalyst produced by incorporating a silica binder to an MFI type zeolite supporting 0.4 mass% of gallium and 0.7 mass% of phosphorus, in an amount of 60 mass% relative to the total mass of the catalyst) in a fluidized bed reactor under the conditions of a reaction temperature of 550°C, a reaction pressure of 0.1 MPaG, and a contact time of 30 seconds, and was allowed to react therewith, and thus production of monocyclic aromatic hydrocarbons was carried out.

The reaction product oil thus obtained was analyzed by an FID gas chromatographic method, and the amount of impurities between durene (boiling point: 196°C) and naphthalene (boiling point: 218°C) was 1.9 mass% relative to 100 of naphthalene. Furthermore, the amount of impurities between naphthalene and 2-methylnaphthalene (boiling point: 241°C) was 0.6 mass% relative to 100 of naphthalene, and 0.4 mass% relative to 100 of methylnaphthalene. Thus, it was found that there were very few components having a boiling point close to that of naphthalene.

Subsequently, the reaction product oil thus obtained was fractionated in a rectifying column into a gas fraction, a fraction containing monocyclic aromatic hydrocarbons (benzene, toluene and xylene), and a heavy oil fraction having 9 or more carbon numbers (heavy oil fraction 1).

The heavy oil fraction 1 was further distilled in the rectifying column, and was fractionated into a fraction mainly containing naphthalene (boiling point: 218°C) and a fraction other than naphthalene (heavy oil fraction 2).

The yield of the monocyclic aromatic hydrocarbons (benzene, toluene, and crude xylene (xylene including a small amount of ethylbenzene and the like)) obtained by fractionation was 30 mass%, and the yield of the naphthalene fraction was 7 mass%. Meanwhile, the naphthalene purity in the naphthalene fraction was 96 mass%.

[0069]

[Table 1]

Feedstock characteristics				Analysis method
Density @ 15°C		g/cm^3	0.906	JIS K 2249
Dynamic viscosity @ 30°C		mm^2/s	3.640	JIS K 2283
Distillate characteristics	Initial boiling point	°C	175.5	JIS K 2254
	10 vol% distillation temperature	°C	224.5	
	50 vol% distillation temperature	°C	274.0	
	90 vol% distillation temperature	°C	349.5	
	End point	°C	376.0	
Composition analysis	Saturated content	Vol%	35	JPI-5S-49
	Olefin content	Vol%	8	
	Total aromatic content	Vol%	57	
	Monocyclic aromatic content	vol%	23	
	Bicyclic aromatic content	vol%	25	
	Tricyclic or higher-cyclic aromatic content	vol%	9	

(Example 2)

[0070] LCO as indicated in Table 1 (10 vol% distillation temperature: 224.5°C, 90 vol% distillation temperature: 349.°C), which was a feedstock, was brought into contact with the catalyst A (an MFI type zeolite supporting 0.4 mass% of gallium and 0.7 mass% of phosphorus) in a fixed bed reactor under the conditions of a reaction temperature of 550°C, a reaction pressure of 0.3 MPaG, and a contact time of 18 seconds, and was allowed to react therewith, and thus production of monocyclic aromatic hydrocarbons was carried out.
The reaction product oil thus obtained was analyzed by an FID gas chromatographic method, and the amount of impurities between durene (boiling point: 196°C) and naphthalene (boiling point: 218°C) was 2.4 mass% relative to 100 of naphthalene. Furthermore, the amount of impurities between naphthalene and 2-methylnaphthalene (boiling point: 241°C) was 1.6 mass% relative to 100 of naphthalene, and 0.9 mass% relative to 100 of methylnaphthalene. Thus, it was found that there were very few components having a boiling point close to that of naphthalene.
Subsequently, the reaction product oil thus obtained was fractionated in a rectifying column into a gas fraction, a fraction containing monocyclic aromatic hydrocarbons (benzene, toluene and crude xylene), and a heavy oil fraction having 9 or more carbon numbers.
The heavy oil fraction having 9 or more carbon numbers was further distilled in the rectifying column, and was fractionated into a fraction mainly containing naphthalene (boiling point: 218°C) and a fraction other than naphthalene.
The yield of the monocyclic aromatic hydrocarbons (benzene, toluene, and crude xylene) obtained by fractionation was 37 mass%, and the yield of the naphthalene fraction was 9 mass%. Meanwhile, the naphthalene purity in the naphthalene fraction was 95 mass%.

(Example 3)

[0071] The fraction other than naphthalene (heavy oil fraction 2: content of polycyclic aromatic hydrocarbons is 95 mass% or more) obtained in Example 1 was subjected to a hydrogenation reaction by using a commercially available nickel-molybdenum catalyst under the conditions of a reaction temperature of 350°C and a reaction pressure of 5 MPaG. The hydrogenation reaction product thus obtained was 69 mass% of hydrocarbon compounds having one aromatic ring, and 28 mass% of compounds having two or more aromatic rings (polycyclic aromatic hydrocarbons). Thus, compared to the fraction before the hydrogenation reaction, the content of polycyclic aromatic hydrocarbons was reduced to a large extent.

[0072] Subsequently, a feedstock obtained by recycling the hydrogenation reaction product into the LCO indicated in Table 1 in an amount of 0.4 times the mass of LCO, was brought into contact with the catalyst A (a catalyst produced by incorporating a silica binder to an MFI type zeolite supporting 0.4 mass% of gallium and 0.7 mass% of phosphorus, in an amount of 60 mass% relative to the total mass of the catalyst) in a fluidized bed reactor under the conditions of a reaction temperature of 550°C, a reaction pressure of 0.3 MPaG, and a contact time of 30 seconds, and was allowed to react therewith, and thus production of monocyclic aromatic hydrocarbons was carried out.
The yield of monocyclic aromatic hydrocarbons (benzene, toluene and crude xylene) thus obtained was 36 mass%, and as compared with Example 1 in which the hydrogenation reaction product was not recycled, an increase in the yield of monocyclic aromatic hydrocarbons was observed.

[0073] From the results of Examples 1 to 3, it was found that according to the method for producing aromatic hydrocarbons related to the invention, monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers including benzene, toluene and crude xylene are obtained with high yield, and naphthalene of high purity (90 mass% or higher) can be produced.

INDUSTRIAL APPLICABILITY

[0074] According to the method for producing aromatic hydrocarbons of the present invention, not only monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers but also naphthalene compounds including naphthalene can all be produced by using an oil containing polycyclic aromatic hydrocarbons such as LCO.

Claims

1. A method for producing aromatic hydrocarbons, the method comprising the steps of:

bringing a feedstock having a 10 vol% distillation temperature of 140°C or higher and a 90 vol% distillation temperature of 380°C or lower, into contact with a catalyst for monocyclic aromatic hydrocarbon production containing a crystalline aluminosilicate to cause the feedstock to react with the catalyst, and thereby obtaining

a product including monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and a heavy oil fraction having 9 or more carbon numbers;
separating respectively the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers and the heavy oil fraction having 9 or more carbon numbers from the product obtained from the cracking reforming reaction step;
purifying the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers thus separated in the separation step, and collecting the monocyclic aromatic hydrocarbons having 6 to 8 carbon numbers; and
separating naphthalene compounds that include at least naphthalene, from the heavy oil fraction having 9 or more carbon numbers thus separated in the separation step, and collecting the naphthalene compounds.

2. The method for producing aromatic hydrocarbons according to Claim 1, wherein the step of collecting naphthalene is a process of separating and collecting methylnaphthalene and/or dimethylnaphthalene, and naphthalene.

3. The method for producing aromatic hydrocarbons according to Claim 1 or 2, further comprising the steps of:

hydrogenating a remaining fraction obtained by separating naphthalene compounds in the step of collecting naphthalene, and obtaining a hydrogenation reaction product; and
recycling the hydrogenation reaction product to the step of cracking reforming reaction.

4. The method for producing aromatic hydrocarbons according to any one of Claims 1 to 3, wherein in the step of collecting naphthalene, the apparatus for separating and collecting naphthalene compounds including naphthalene is a distillation apparatus.

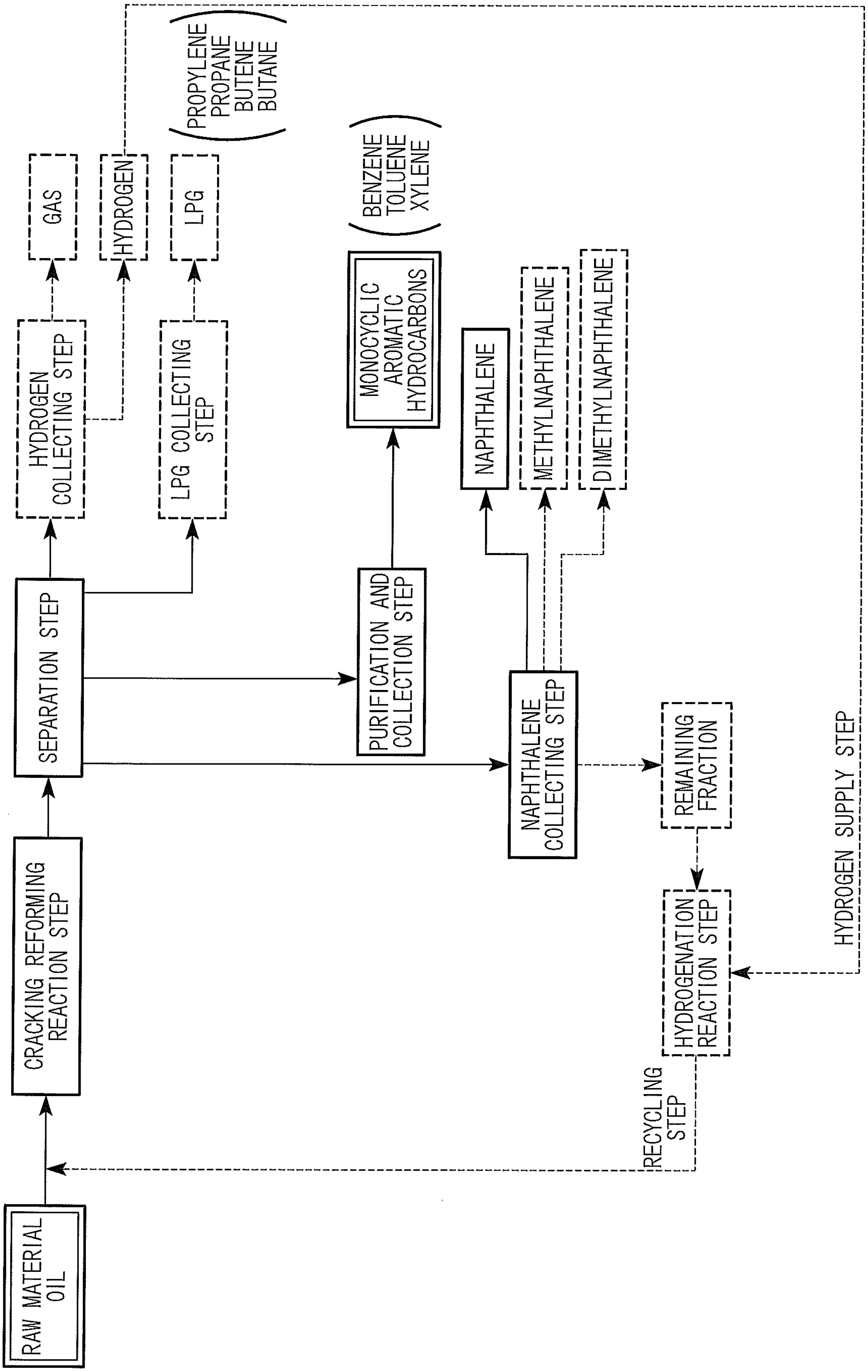
5. The method for producing aromatic hydrocarbons according to any one of Claims 1 to 4, wherein the crystalline aluminosilicate comprises a zeolite with medium-sized pores and/or a zeolite with large-sized pores as main components.

6. The method for producing aromatic hydrocarbons according to any one of claims 1 to 5, wherein the reaction temperature employed when the feedstock is allowed to react with the catalyst for monocyclic aromatic hydrocarbon production in the step of cracking reforming reaction is from 400°C to 650°C.

7. The method for producing aromatic hydrocarbons according to any one of Claims 1 to 6, wherein the reaction pressure employed when the feedstock is allowed to react with the catalyst for monocyclic aromatic hydrocarbon production in the step of cracking reforming reaction is from 0.1 MPaG to 1.5 MPaG.

8. The method for producing aromatic hydrocarbons according to any one of Claims 1 to 7, wherein the contact time for bringing the feedstock into contact with the catalyst for monocyclic aromatic hydrocarbon production in the step of cracking reforming reaction is from 1 second to 300 seconds.

FIG. 1


RAW MATERIAL OIL
CRACKING REFORMING REACTION STEP
SEPARATION STEP
HYDROGEN COLLECTING STEP
GAS
HYDROGEN
LPG COLLECTING STEP
LPG
PROPYLENE
PROPANE
BUTENE
BUTANE
PURIFICATION AND COLLECTION STEP
MONOCYCLIC AROMATIC HYDROCARBONS
BENZENE
TOLUENE
XYLENE
NAPHTHALENE COLLECTING STEP
NAPHTHALENE
METHYLNAPHTHALENE
DIMETHYLNAPHTHALENE
REMAINING FRACTION
HYDROGENATION REACTION STEP
HYDROGEN SUPPLY STEP
RECYCLING STEP

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/070925

A. CLASSIFICATION OF SUBJECT MATTER
C07C7/04(2006.01)i, *C07C15/04*(2006.01)i, *C07C15/06*(2006.01)i, *C07C15/067*(2006.01)i, *C07C15/24*(2006.01)i, *C10G11/05*(2006.01)i, *C07B61/00*(2006.01)n

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)
C07C7/04, C07C15/04, C07C15/06, C07C15/067, C07C15/24, C10G11/05, C07B61/00

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010-001462 A (Cosmo Oil Co., Ltd.), 07 January 2010 (07.01.2010), claims (Family: none)	1-8
A	JP 2009-235248 A (Toray Industries, Inc.), 15 October 2009 (15.10.2009), claims (Family: none)	1-8
A	JP 3-002128 A (Idemitsu Kosan Co., Ltd.), 08 January 1991 (08.01.1991), claims (Family: none)	1-8

☒ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search 31 October, 2011 (31.10.11)	Date of mailing of the international search report 08 November, 2011 (08.11.11)
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INTERNATIONAL SEARCH REPORT

International application No.
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