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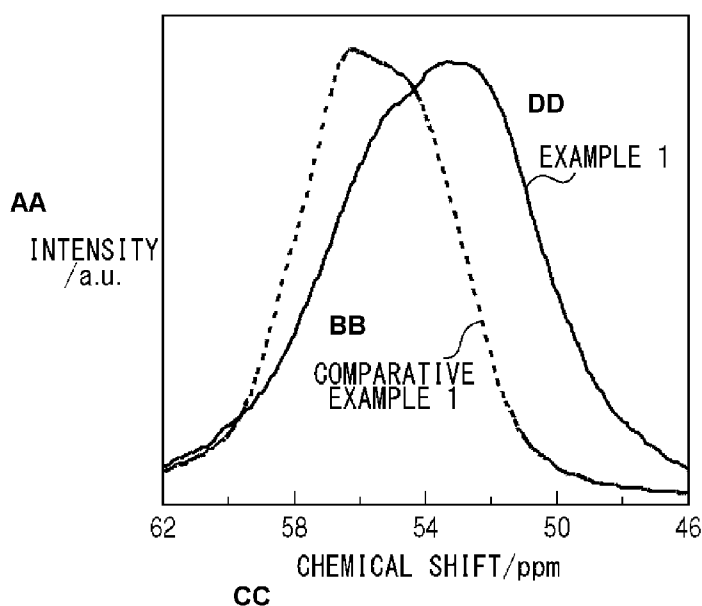
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(54) Title: CATALYST FOR PRODUCING UNSATURATED HYDROCARBON, METHOD OF PRODUCING THE CATALYST, AND METHOD OF PRODUCING UNSATURATED HYDROCARBON

[Fig. 1]

(57) Abstract: A catalyst according to an embodiment contains crystalline aluminosilicate. An aluminum atom contained in the crystalline aluminosilicate has a peak apex in the 50-54 ppm region of a spectrum within the 46-62 ppm range of a chemical shift obtained by ^{27}Al -MAS NMR measurement.



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Description

Title of Invention: CATALYST FOR PRODUCING UN-SATURATED HYDROCARBON, METHOD OF PRODUCING THE CATALYST, AND METHOD OF PRODUCING UN-SATURATED HYDROCARBON

Technical Field

[0001] The present invention relates to both a method of producing a catalyst for producing an unsaturated hydrocarbon to be used in producing an unsaturated hydrocarbon by performing catalytic cracking using naphtha as a raw material, and a method of producing an unsaturated hydrocarbon by using the catalyst.

Background Art

[0002] Although cracking of naphtha is the mainstream for obtaining basic raw materials for petrochemical industry, the carbon dioxide emission rate in this process is high, which is estimated to be approximately one third of the whole petrochemical industry. Accordingly, it is a very important issue in the petrochemical industry to convert the cracking process of naphtha currently performed into a process in which energy and resources can be saved.

[0003] In the cracking process of naphtha, the naphtha is usually heated to 800[degree] or higher. Theoretically, catalytic cracking of naphtha can be performed at a lower temperature, and the reaction can be performed at approximately 650[degree] in the catalytic cracking process using a catalyst. Advantages, occurring not only due to a reduction in the temperature, but also due to a reduction in the basic unit by an improvement in the selectivity for useful products, such as ethylene, propylene, butenes, and BTX, and due to energy saving in a separation process by a reduction in by-products, such as methane, can be expected. Further, a degree of freedom in selecting the products to be produced can be potentially increased in the catalytic cracking process using a catalyst, while the degree thereof in the conventional cracking reaction, occurring by changing operational factors, is not that wide.

[0004] A solid acid catalyst having "acidity" is desirable for the catalyst to be used in the catalytic cracking of naphtha. Many solid acid catalysts have been conventionally proposed, and among them, a zeolite catalyst used in an FCC process is one of the most typical solid acid catalysts. The most characteristic property of the zeolite catalyst is that "it is a crystal having regular pores with a specific size", and accordingly there is the possibility that a cracked product having a molecular size corresponding to the pore size may be produced at a desired ratio. By applying a catalytic cracking process using

a zeolite catalyst as an alternative for the existing cracking process, it can be expected that the efficiency in producing olefins and aromatic compounds, etc., (in particular, propylene, benzene, xylene, etc.), which are key products highly demanded in industrial fields, may be improved (see NPL 1 to 7).

- [0005] Because there are many industrial and economical advantages as an alternative method for the cracking of naphtha, as stated above, various proposals are made with respect to a catalytic cracking method using a solid acid. For example, a catalyst blend for a fluid catalytic cracking process of producing propylene, the catalyst blend including: a first catalyst containing a molecular sieve having a large pore size; a second catalyst containing a molecular sieve having a middle or small pore size; and further a small amount of a metal, is disclosed (see PTL 1). In addition, a technique for producing a light olefin by using a catalyst composed of: a water-insoluble metal salt; a phosphate compound; and a molecular sieve having the skeleton of -Si-OH-Al- group, etc., is disclosed (see PTL 2).

Citation List

Patent Literature

- [0006] [PTL 1]Japanese Patent Application Publication No. 2010-167349
[PTL 2]Japanese Patent Application Publication (Translation of PCT Application)
No. 2009-511658

Non Patent Literature

- [0007] [NPL 1]Report of Next-Generation Chemical Process Technology Development
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Disclosure of Invention

Solution to Problem

- [0008] As stated above, it is assumed that, in the reaction process of catalytic cracking of naphtha, a reaction using a solid acid catalyst is performed mainly in order to reduce the reaction temperature and to improve the selection rate; however, in using a solid acid catalyst, it becomes an issue to suppress the degradation of the catalyst. The causes for the degradation of the catalyst include deactivation due to carbon accumulation on the catalyst during the reaction and deactivation accompanying a change

in the catalyst structure.

[0009] The present invention has been made in view of these issues, and a purpose of the invention is to provide a technique in which degradation of a catalyst used in catalytic cracking of naphtha can be suppressed and the catalyst can be used in a longer period of time.

Means for Solving the Problem

[0010] As a result of intensive study on the aforementioned issues, the present inventors have found a method of producing a catalyst whose degradation can be suppressed by changing the coordinate number of aluminum contained in crystalline aluminosilicate (hereinafter, the method sometimes being referred to as a method of preparing a catalyst), the crystalline aluminosilicate being a catalyst for the catalytic cracking of naphtha; and then they have completed the present invention.

[0011] An embodiment of the present invention is a catalyst for producing an unsaturated hydrocarbon by catalytic cracking of naphtha, in which the catalyst comprises crystalline aluminosilicate that has a peak apex in the 50-54 ppm region of a spectrum within the 46-62 ppm range of a chemical shift obtained by ^{27}Al -MAS NMR measurement.

[0012] In the catalyst for producing an unsaturated hydrocarbon according to the aforementioned embodiment, the crystalline aluminosilicate may have a 10-membered or 12-membered ring structure. In addition, the crystalline aluminosilicate may be MFI-type zeolite or BEA-type zeolite.

[0013] Another embodiment of the present invention is a method of producing the catalyst for producing an unsaturated hydrocarbon by catalytic cracking of naphtha, according to any one of the aforementioned embodiments, and the method comprises exposing crystalline aluminosilicate, which is a raw material, to an inert gas at a high-temperature of 400 to 1000[degree].

[0014] Still another embodiment of the present invention is a method of producing the catalyst for producing an unsaturated hydrocarbon by catalytic cracking of naphtha, according to any one of the aforementioned embodiments, and the method comprises impregnating crystalline aluminosilicate, which is a raw material, with an alkaline solution.

[0015] Still another embodiment of the present embodiment is a method of producing the catalyst for producing an unsaturated hydrocarbon by catalytic cracking of naphtha, according to any one of the aforementioned embodiments, and the method comprises exposing crystalline aluminosilicate, which is a raw material, to water vapor at a high-temperature of 500 to 900[degree].

[0016] Still another embodiment of the present invention is a method of producing the catalyst for producing an unsaturated hydrocarbon by catalytic cracking of naphtha,

according to any one of the aforementioned embodiments, and the method comprises impregnating crystalline aluminosilicate, which is a raw material, with an acidic aqueous solution.

- [0017] Still another embodiment of the present invention is a method of producing an unsaturated hydrocarbon, in which naphtha is catalytically cracked by using the catalyst for producing an unsaturated hydrocarbon, according to any one of the aforementioned embodiments.

Advantage of the Invention

- [0018] According to the present invention, degradation of a catalyst used in catalytic cracking of naphtha can be suppressed and the catalyst can be used in a longer period of time.

Brief Description of Drawings

- [0019] [fig.1]Fig. 1 shows ^{27}Al -MAS NMR spectra of the catalysts of Example 1 and Comparative Example 1;
[fig.2]Fig. 2 shows ^{27}Al -MAS NMR spectra of the catalysts of Examples 2, 3 and Comparative Example 2;
[fig.3]Fig. 3 shows ^{27}Al -MAS NMR spectra of the catalysts of Examples 4, 5 and Comparative Example 3; and
[fig.4]Fig. 4 shows ^{27}Al -MAS NMR spectra of the catalysts of Examples 6, 7 and Comparative Example 4.

Best Mode for Carrying out the Invention

- [0020] Preferred embodiments of the present invention will be described hereinafter, but the invention should not be limited to these embodiments. It will be appreciated by those skilled in the art that various variations may be made thereto without departing from the spirit and scope of the invention.
- [0021] The catalyst obtained by a production method according to the present invention can be preferably used as a catalyst for catalytically cracking naphtha, i.e., components composed of hydrocarbons each having a boiling point of 35 to 180[degree] to produce an unsaturated hydrocarbon.
- [0022] Hereinafter, a catalyst and a method of producing the catalyst, according to an embodiment, will be specifically described.
- [0023] <Crystalline Aluminosilicate>
The catalyst according to the embodiment contains crystalline aluminosilicate. An aluminum atom contained in the crystalline aluminosilicate has a peak apex in the 50-54 ppm region of a spectrum within the 46-62 ppm range of a chemical shift obtained by using ^{27}Al -MAS NMR. It is further preferable that the peak apex is located in the 51-53 ppm region. It can be inferred that the shift of such a peak apex is

originated from an anisotropic 4-coordinated aluminum created by alteration of the coordination state of the aluminum.

[0024] The crystalline aluminosilicate preferably has a 10-membered or 12-membered ring structure, and more preferably has an MFI structure or a BEA structure.

[0025] The crystalline aluminosilicate preferably has $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 1 to 1000, more preferably has that of 5 to 800, and most preferably has that of 10 to 500.

[0026] The shape of the crystalline aluminosilicate is not limited. Specific examples of the shape include a powder-like shape, a spherical shape, a pellet-like shape, etc. An optimal shape may be selected in accordance with the type and reactor, etc., of the catalytic cracking reaction of naphtha.

[0027] The size of the crystalline aluminosilicate is not particularly limited. When the catalytic cracking of naphtha is performed in a tubular fixed bed reactor for gas phase reaction and the crystalline aluminosilicate having a spherical shape is used, the particle size is preferably within a range of 0.05 to 20 mm, and more preferable within a range of 0.2 to 5 mm. If the particle size is smaller than 0.05 mm, a large pressure loss is generated when a gas is flowing through the particles, thereby causing the fear that the gas may not be circulated effectively. On the other hand, if the particle size is larger than 20 mm, a reaction gas cannot be diffused into the catalyst, thereby causing the fear that the efficiency of the catalyst reaction may be decreased.

[0028] The pore of the crystalline aluminosilicate preferably has a diameter of 0.1 to 1000 nm, and more preferably has a diameter of 3 to 200 nm. The specific surface area of the crystalline aluminosilicate, obtained by BET measurement, is preferably within a range of 10 to 1000 m^2/g , and more preferably within a range of 50 to 700 m^2/g .

[0029] <Method of Changing Coordination State of Aluminum>

Commercially-available zeolite (e.g., H-ZSM-5 (made by ZEOLYST International)) can be used as crystalline aluminosilicate (hereinafter, referred to as material crystalline aluminosilicate) that is a material of the crystalline aluminosilicate according to the embodiment. Examples of a method of changing the coordination state of aluminum in the material crystalline aluminosilicate to obtain the catalyst according to the embodiment, include a method of exposing the material crystalline aluminosilicate to an inert gas at a high-temperature, a method of impregnating that with an alkaline aqueous solution, a method of exposing that to water vapor at a high-temperature, and a method of impregnating that with an acidic aqueous solution. Alternatively, two or more methods selected from these methods may be combined together, such as the case where, after being exposed to water vapor at a high-temperature, the material crystalline aluminosilicate is impregnated with an acidic aqueous solution.

[0030] <Method of Exposing to Inert Gas at High-Temperature>

The crystalline aluminosilicate according to the embodiment can be obtained by

exposing the material crystalline aluminosilicate to an inert gas. In the method of exposing the material crystalline aluminosilicate to an inert gas at a high-temperature, the type of the inert gas to be used is not particularly limited, but nitrogen, helium, argon, or the like, can be used as the inert gas. The purity of the inert gas is preferably 99% or higher, and more preferably 99.9% or more. The temperature at which the material crystalline aluminosilicate is exposed within a range of 400 to 1000[degree], and more preferably 600[degree] or higher and 900[degree] or lower. The material crystalline aluminosilicate may be exposed to the inert gas while the gas is flowing or is being stopped. When the gas is made to flow, it is needed to control the temperature of the gas so as not to be greatly changed depending on the flow rate of the gas with which the material crystalline aluminosilicate is brought into contact. It is preferable to expose the material crystalline aluminosilicate to the inert gas for a period of time longer than or equal to 24 hours. The pressure of a supply gas is not particularly limited, but is preferably within a range of 0.0 to 1 MPaG (gauge pressure), and more preferably within a range of 0.0 to 0.3 MPaG, from the viewpoint of safety.

[0031] <Method of Impregnating with Alkaline Solution>

The crystalline aluminosilicate according to the embodiment can be obtained by impregnating the material crystalline aluminosilicate with an alkaline solution. The pH of the alkaline solution at normal temperature is preferably $14 \leq \text{pH} < 14.3$, and more preferably $14 \leq \text{pH} < 14.3$. Examples of the alkaline solution include solutions of alkaline compounds, such as hydroxides of alkali metals or alkaline earth metals and silicates of alkali metals or alkaline earth metals. Lithium, sodium, and potassium are used as the alkaline metals. Magnesium, calcium, barium, and strontium are used as the alkaline earth metals. Sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, strontium hydroxide, sodium metasilicate, and potassium metasilicate are preferably used.

[0032] The alkaline solution is preferably used in a concentration of 1 to 1000 mmol/L, and more preferably used in a concentration of 5 to 200 mmol/L, based on 1 g of the material crystalline aluminosilicate to be used. Examples of a solvent of the alkaline solution include water, methanol, and ethanol, etc., and among them, water is preferable.

[0033] A method of impregnating the material crystalline aluminosilicate with the alkaline solution is not particularly limited. The method includes, for example: (I) a method in which carriers are immersed in a large amount of the alkaline solution for a while, followed by taking out the carriers impregnated with an adsorption amount of the alkaline solution; and (II) a method in which an alkaline compound is dissolved in a solvent such that the concentration thereof is adjusted so as to be equal to an adsorption amount for carriers, followed by the carriers being impregnated with the

solution. The method (II) is more preferable from the viewpoint of a reduction in the amount of effluent to be treated.

[0034] <Method of Exposing to Water Vapor at High-Temperature>

The crystalline aluminosilicate according to the embodiment can be obtained by exposing the material crystalline aluminosilicate to water vapor. When the material crystalline aluminosilicate is exposed to water vapor, a method in which evaporated water vapor is introduced in advance or a method in which water vapor is made to accompany the inert gas, is preferable. When made to accompany the inert gas, the concentration of the water vapor is not particularly limited. The temperature at which the material crystalline aluminosilicate is exposed to the water vapor is preferably within a range of 400 to 900[degree], and more preferably within a range of 500 to 700[degree]. When the material crystalline aluminosilicate is exposed to water vapor, the pressure of the water vapor is not particularly limited, but is preferably smaller than 1 MPaG from the viewpoint of safety.

[0035] This method is adopted for stabilizing, in advance, the coordinate number of aluminum, in order to prevent the catalyst from being permanently degraded by the aluminum being desorbed during the reaction due to the water vapor at a high-temperature. Accordingly, it is needed to perform the method in a pretreatment process or before naphtha, a raw material, is introduced into a reactor.

[0036] <Method of Impregnating with Acidic Aqueous Solution>

The crystalline aluminosilicate according to the embodiment can be obtained by impregnating the material crystalline aluminosilicate with an acidic aqueous solution. The pH of the acidic aqueous solution is preferably within a range of $0.01 \leq \text{pH} < 4$, and more preferably within a range of $0.1 \leq \text{pH} < 2$. Examples of the acid contained in the acidic aqueous solution include, for example: inorganic acids, such as nitric acid, hydrochloric acid, sulfuric acid, hydrofluoric acid, and phosphoric acid; and organic acids, such as citric acid, oxalic acid, formic acid, acetic acid, and tartaric acid. The period of time during which the material crystalline aluminosilicate is impregnated with the acidic aqueous solution can be appropriately set in accordance with the pH of the acidic aqueous solution, and when the pH is, for example, 1, the period of time is 1 hour.

[0037] <Metal-Carrying Crystalline Aluminosilicate>

The material crystalline aluminosilicate may be a metal-carrying crystalline aluminosilicate on which a metal for suppressing carbon accumulation or a metal for controlling acidity are carried. Examples of the metal to be carried include a platinum group, nickel, alkali metals, and alkaline earth metals.

[0038] The carried metal may be a reduced metal or an ionized metal. Examples of a reducing agent for reducing the carried metal include hydrazine, hydrogen, ethylene,

and carbon monoxide, etc. The carried metal can be reduced by contacting the carried metal with the reducing agent in a liquid phase or gas phase.

[0039] Liquid-phase reduction may be performed in a non-aqueous system using alcohols or hydrocarbons, or in an aqueous system. Examples of the reducing agent include carboxylic acid and a salt thereof, aldehyde, hydrogen peroxide, sugars, polyhydric phenol, diborane, amine, hydrazine, etc. Examples of the carboxylic acid and the salt thereof exemplarily include oxalic acid, potassium oxalate, formic acid, potassium formate, and ammonium citrate; and example of the sugars includes glucose. Examples of the preferred reducing agents include hydrazine, formaldehyde, acetaldehyde, hydroquinone, sodium boron hydride, potassium citrate, etc., and among them, hydrazine is most preferable.

[0040] The temperature at which a reduction treatment is performed by a liquid phase method is not particularly limited, but the temperature of the metal-carrying crystalline aluminosilicate is preferably within a range of 0 to 200[degree], and more preferably within a range of 10 to 100[degree].

[0041] The reducing agent to be used in gas-phase reduction is selected from olefins consisting of hydrogen gas, carbon monoxide, alcohol, aldehyde, ethylene, propene, and isobutene, etc. The reducing agent to be used in gas-phase reduction is preferably hydrogen gas. In the gas-phase reduction, an inert gas may be added as a diluent. Examples of the inert gas include, for example, helium, argon, and nitrogen.

[0042] The temperature at which a reduction treatment is performed by a gas phase method is not particularly limited, but the metal-carrying crystalline aluminosilicate is heated preferably to a temperature of approximately 30 to 350[degree], and more preferably to a temperature of 100 to 300[degree]. It is advantageous, from the viewpoint of practical use, that the pressure at which the reduction treatment is performed by a gas phase method is within a range of 0.0 to 3.0 MPaG in terms of facilities, but it is not particularly limited thereto. The pressure is more preferably within a range of 0.1 to 1.5 MPaG.

[0043] When a gaseous reducing substance is made to flow, the substance may have any concentration, and if necessary, nitrogen, carbon dioxide, or a rare gas can be used as a diluents. Alternatively, a reduction treatment may be performed under a condition in which ethylene, hydrogen, or the like exists in the presence of evaporated water.

[0044] The metal-carrying crystalline aluminosilicate subjected to a reduction treatment is washed with pure water, etc., if necessary. The washing may be performed in a continuous mode or a batch mode. The temperature at which the washing is performed is preferably within a range of 5 to 200[degree], and more preferably within a range of 15 to 80[degree]. The period of time during which the washing is performed is not particularly limited. A sufficient condition may be selected for the purpose of elimination

of remaining undesirable impurities. Examples of the undesirable impurities include sodium and chlorine. The solvent is dried and removed after the washing.

[0045] <Production of Unsaturated Hydrocarbon>

Subsequently, a process for producing an unsaturated hydrocarbon by using the catalyst according to the embodiment will be described. The method of producing an unsaturated hydrocarbon is suitable for the production of an unsaturated hydrocarbon, in particular, a lower unsaturated hydrocarbon having 2 to 10 carbons. Examples of the lower unsaturated hydrocarbon include ethylene, propylene, butene, pentene, hexene, decene, etc.

[0046] The reaction temperature at which an unsaturated hydrocarbon is produced by catalytically cracking naphtha with the use of the catalyst according to the embodiment is not particularly limited. The temperature at which naphtha is catalytically cracked by using the catalyst according to the embodiment, is preferably within a range of 500 to 800[degree], and more preferably within a range of 600 to 750[degree]. It is advantageous, from the viewpoint of practical use, that the reaction pressure is within a range of 0.0 to 10.0 MPaG in terms of facilities, but the pressure is not particularly limited. The reaction pressure is more preferably within a range of 0.01 to 0.5 MPaG.

[0047] Naphtha is supplied to the reaction system as a raw material. Further, nitrogen, carbon dioxide, steam, a rare gas, or the like, can be used as a diluent, if necessary. The dilute concentration is not particularly limited, but may be one at which an unsaturated hydrocarbon, which is a target product, can be efficiently produced.

[0048] The reaction mixed gas is supplied to the catalyst in a condition in which SV is within a range of 0.01 to 1000 h⁻¹, and more preferably within a range of 0.1 to 100 h⁻¹ in the standard state.

[0049] The reaction form in which naphtha is cracked is not particularly limited, but a publicly-known method, for example, a fixed bed, a fluidized bed, or the like, can be adopted. It is advantageous, from the viewpoint of practical use, that a fixed bed in which a reaction tube having corrosion resistance is filled with the catalyst according to the embodiment is preferably adopted.

Examples

[0050] The present invention will be further specifically described based on the following Examples, but the invention should not be limited only to the following Examples. In Examples, the case where an unsaturated hydrocarbon is obtained by catalytically cracking n-hexane, which is one of the major components of naphtha and used instead of naphtha, is adopted as an example, for easy analyses.

[0051] <Pretreatment>

The material crystalline aluminosilicate used in each of Examples and Comparative Examples was subjected to firing under air at 550[degree] for 10 hours as a pre-

treatment.

<Water>

The water used in each of Examples and Comparative Examples was pure water (ion exchange water).

<Particle Size>

The material crystalline aluminosilicate used in each of Examples and Comparative Examples was granulated to have a particle size of 250 to 500 μm .

<Raw Material Compounds>

n-hexane (made by Wako Pure Chemical Industries, Ltd.) H-ZSM-5 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$ (made by ZEOLYST International, molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ 80:1, MFI structure)

H-ZSM-5 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$ (made by ZEOLYST International, molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ 150:1, MFI structure)

Sodium hydroxide (made by Wako Pure Chemical Industries, Ltd.)

Ammonium nitrate (made by Wako Pure Chemical Industries, Ltd.)

Tetrapropylammonium hydroxide 20 wt% aqueous solution (TPAOH) (made by Tokyo Chemical Industry Co., Ltd.)

Tetraethoxy silane (TEOS) (made by Tokyo Chemical Industry Co., Ltd.)

Aluminum nitrate nonahydrate (made by Wako Pure Chemical Industries, Ltd.)

Hydrochloric acid (made by Wako Pure Chemical Industries, Ltd.)

[0052] (Example 1)

A reaction tube having an inner diameter of 10 mm was filled with 2.5 g of the granulated H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) and heated to 800[degree] at a rate of temperature increase of 5[degree]/min under nitrogen gas flow at a rate of 20 ml/min in an electric tube furnace, and then the reaction tube was kept for 80 hours. Thereafter, the reaction tube was cooled down naturally while nitrogen gas was flowing, and then was calcined in the air at 550[degree] for 10 hours to obtain the catalyst of Example 1.

[0053] (Comparative Example 1)

A reaction tube having an inner diameter of 10 mm was filled with 2.5 g of the granulated H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) and heated to 800[degree] at a rate of temperature increase of 5[degree]/min under air flow at a rate of 20 ml/min in an electric tube furnace, and then the reaction tube was kept for 80 hours. Thereafter, the reaction tube was cooled down naturally while air was flowing, and then was calcined in the air at 550[degree] for 10 hours to obtain the catalyst of Comparative Example 1.

[0054] (Example 2)

An aqueous solution A was obtained by dissolving 8.31 g of tetrapropylammonium hydroxide (TPAOH) solution and 9.37 g of tetraethoxy silane (TEOS) in 74.5 ml of water. After this aqueous solution A was stirred at 80[degree] for 24 hours, an aqueous solution B, obtained by dissolving 0.34 g of aluminum nitrate nonahydrate and 0.18 g

of sodium hydroxide in 3.0 ml of water, was added thereto and the mixture was stirred at 25[degree] for 1 hour. Thereafter, the mixture was transferred into an autoclave having a TeflonTM internal tube to perform hydrothermal synthesis on the mixture at 170[degree] for 24 hours. The obtained compound was calcined at 550[degree] for 10 hours to obtain Na-ZSM-5. The raw material composition was adjusted such that TEOS : TPAOH : Al(NO₃)₃ : NaOH : H₂O = 1 : 0.25 : 0.02 : 0.1 : 100 holds (mass ratio).

[0055] Na-ZSM-5 was added to 100 mL of 0.1 M sodium hydroxide aqueous solution and the mixture was stirred at 60[degree]. Thereafter, the mixture was washed with ion exchange water and dried overnight at 100[degree]. The mixture was subjected to ion exchange by using 1 M ammonium nitrate aqueous solution and calcined at 550[degree] to obtain the catalyst of Example 2.

[0056] (Example 3 and Comparative Example 2)

The catalyst of Example 3 and that of Comparative Example 2 were obtained in the same way as in Example 2, except that 100 mL of 0.2 M sodium hydroxide aqueous solution and 100 mL of 0.05 M sodium hydroxide aqueous solution were respectively used, instead of the 0.1 M sodium hydroxide aqueous solution.

[0057] (Example 4)

A reaction tube having an inner diameter of 10 mm was filled with 3.0 g of the granulated H-ZSM-5 (SiO₂/Al₂O₃ = 150) and heated to 600[degree] at a rate of temperature increase of 5[degree]/min under nitrogen gas flow at a rate of 80 ml/min in an electric tube furnace, and then the reaction tube was kept for 5 hours while 20 vol% water vapor/nitrogen gas were being supplied at a rate of 100 ml/min. Thereafter, the reaction tube was cooled down naturally while nitrogen gas was flowing to obtain the catalyst of Example 4.

[0058] (Example 5)

The catalyst of Example 4 in an amount of 1.3 g was added to 90 ml of 3.0 mol/L hydrochloric acid and stirred at 90[degree] for 1 hour. Thereafter, the mixture was washed with ion exchange water and dried at 100[degree] to obtain the catalyst of Example 5.

[0059] (Comparative Example 3)

Untreated H-ZSM-5 (SiO₂/Al₂O₃ = 150) was used as the catalyst of Comparative Example 3.

[0060] (Example 6)

A reaction tube having an inner diameter of 10 mm was filled with 1.5 g of the granulated H-ZSM-5 (SiO₂/Al₂O₃ = 80) and heated to 600[degree] at a rate of temperature increase of 5[degree]/min under nitrogen gas flow at a rate of 160 ml/min in an electric tube furnace, and then the reaction tube was kept for 5 hours while 20 vol%

water vapor/nitrogen gas were being supplied at a rate of 200 ml/min. Thereafter, the reaction tube was cooled down naturally while nitrogen gas was flowing to obtain the catalyst of Example 6.

[0061] (Example 7)

The catalyst of Example 6 in an amount of 1.3 g was added to 78 ml of 3.0 mol/L hydrochloric acid and stirred at 90[degree] for 1 hour. Thereafter, the mixture was washed with ion exchange water and dried at 100[degree] to obtain the catalyst of Example 7.

[0062] (Comparative Example 4)

Untreated H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) was used as the catalyst of Comparative Example 4.

[0063] (^{27}Al -MAS NMR Spectrum Measurement)

^{27}Al -MAS NMR measurement was performed on each of the catalysts of Examples 1 to 7 and Comparative Examples 1 to 4. ECA-600 Spectrometer (^{27}Al resonance frequency: 156.4 MHz) made by JEOL Ltd., was used as the measurement and the external magnetic field was set to be 14.1 T. A sample tube having a diameter of 4 mm was filled with a sample, and the sample rotating frequency of the sample was set to be 17 kHz, the repetition time to be 10 ms, the pulse width to be 90°, and the cumulative number to be 10,000 times. The chemical shift reference was set at -0.54 ppm for alum. Each spectrum is shown in Figs. 1 to 4. Chemical shift values at peak apexes within the 46-62 ppm range of chemical shifts are shown in Table 1.

[Table 1]

CATALYST	CATALYST PRODUCTION METHOD		^{27}Al -MASNMR SPECTRUM	
	RAW MATERIAL	TREATMENT	PEAK APEX ppm	FIG. NO.
EXAMPLE 1	H-ZSM-5 (80)	$\text{N}_2 \rightarrow \text{Air}$	53.18	FIG. 1
COMPARATIVE EXAMPLE 1	H-ZSM-5 (80)	Air	56.19	FIG. 1
EXAMPLE 2	Na-ZSM-5	0.1M NaOH	52.22	FIG. 2
EXAMPLE 3	Na-ZSM-5	0.2M NaOH	52.47	FIG. 2
COMPARATIVE EXAMPLE 2	Na-ZSM-5	0.05M NaOH	55.12	FIG. 2
EXAMPLE 4	H-ZSM-5 (150)	$\text{N}_2 \rightarrow \text{H}_2\text{O}/\text{N}_2$	52.28	FIG. 3
EXAMPLE 5	H-ZSM-5 (150)	$\text{N}_2 \rightarrow \text{H}_2\text{O}/\text{N}_2 \rightarrow \text{HCl}$	51.79	FIG. 3
COMPARATIVE EXAMPLE 3	H-ZSM-5 (150)	NOT PRESENT	54.24	FIG. 3
EXAMPLE 6	H-ZSM-5 (80)	$\text{N}_2 \rightarrow \text{H}_2\text{O}/\text{N}_2$	51.79	FIG. 4
EXAMPLE 7	H-ZSM-5 (80)	$\text{N}_2 \rightarrow \text{H}_2\text{O}/\text{N}_2 \rightarrow \text{HCl}$	52.04	FIG. 4
COMPARATIVE EXAMPLE 4	H-ZSM-5 (80)	NOT PRESENT	54.24	FIG. 4

[0064] It has been confirmed that each of the catalysts of Examples 1 to 7 has a peak apex in the 50-54 ppm region of a spectrum within the 46-62 ppm range of a chemical shift obtained by ^{27}Al -MAS NMR measurement. It has also been confirmed that, on the other hand, in each of the catalysts of Comparative Examples 1 to 4, a peak apex

within the 46-62 ppm range of a chemical shift obtained by ^{27}Al -MAS NMR measurement is located outside the 50-54 ppm range.

[0065] (Evaluation of Catalyst Performance)

A reaction tube (inner diameter: 7 mm) made of InconelTM was filled with 0.36 g of each of the catalysts of Example 1 and Comparative Example 1. n-hexane was introduced at a rate of $\text{SV} = 10 \text{ h}^{-1}$ under the conditions in which the temperature of a catalyst layer was 650[degree] and the reaction pressure was 0.01 MPaG, thereby performing a conversion reaction into ethylene and propylene. At the time, nitrogen gas was used as a dilution medium. A dilution ratio was set such that n-hexane : nitrogen = 23 : 77.

[0066] Part of the outlet gas passing through the catalyst-filled layer was taken out after a lapse of 1 hour and a lapse of 17 hours since the start of the reaction, so that the composition was analyzed by using: gas chromatography (GC-2014ATT, GC-2014AFF made by Shimadzu Corporation); and columns (DC-200 25% on ShimaliteTM, PorapakTM-N, PorapakTM-Q, Molecular Sieve-5A, ShimaliteTM-Q, FFAP 25% on CW (AW) DMCS, DB-1-60W-THK, CP-AL203/KCL).

[0067] The degradation property of a catalyst was evaluated by using both the n-hexane conversion rate after a lapse of 1 hour and that after a lapse of a predetermined period of time (17 hours or 24 hours), the start of the reaction. The obtained results are shown in Table 2. Herein, the conversion rate was calculated by the following equation:

$$\text{Reduction amount in conversion rate (point)} = \text{Conversion rate}_{\text{after 1 hour}} - \text{Conversion rate}_{\text{after a predetermined period of time}}$$

[Table 2]

CATALYST			EXAMPLE 1	COMPARATIVE EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	COMPARATIVE EXAMPLE 2	EXAMPLE 4	EXAMPLE 5	COMPARATIVE EXAMPLE 3	EXAMPLE 6	EXAMPLE 7	COMPARATIVE EXAMPLE 4
REACTION CONDITIONS OF CATALYTIC CRACKING		TEMPERATURE (°C)	650	650	650	650	650	650	650	650	650	650	650
		PRESSURE (MPaG)	0.01	0.01	0.10	0.10	0.10	0.10	0	0	0	0	0
DILUTE GAS TYPE			N ₂	N ₂	He	He	He	NOT PRESENT	NOT PRESENT	NOT PRESENT	NOT PRESENT	NOT PRESENT	NOT PRESENT
n-HEXANE	SUPPLY SPEED	SV(h ⁻¹)	10	10	69	69	69	20	20	20	20	20	20
	CONVERSION RATE (%)	AFTER A LAPSE OF 1 HRS	99	92	84	85	90	91	98	98	100	93	99
		AFTER A LAPSE OF 17 HRS	90	67				75	81	58	86	78	41
		AFTER A LAPSE OF 24 HRS			70	73	62						
REDUCTION AMOUNT (IN CONVERSION RATE) point			9	25	14	12	29	16	17	40	14	15	58
ETHYLENE	YIELD (%)	AFTER A LAPSE OF 1 HRS	19	18	18	18	21	18	19	19	19	19	19
		AFTER A LAPSE OF 17 HRS	19	13				14	16	11	17	16	11
		AFTER A LAPSE OF 24 HRS			13	15	10						
	SELECTION RATE (%)	AFTER A LAPSE OF 1 HRS	20	20	22	21	15	20	19	19	19	20	20
AFTER A LAPSE OF 17 HRS		21	20				19	19	20	20	20	27	
AFTER A LAPSE OF 24 HRS				19	20	15							
PROPYLENE	YIELD (%)	AFTER A LAPSE OF 1 HRS	18	25	25	23	26	22	19	21	16	23	19
		AFTER A LAPSE OF 17 HRS	23	19				22	24	18	23	23	11
		AFTER A LAPSE OF 24 HRS			25	23	24						
	SELECTION RATE (%)	AFTER A LAPSE OF 1 HRS	18	27	29	27	24	25	20	21	16	25	19
AFTER A LAPSE OF 17 HRS		25	29				30	29	31	27	30	26	
AFTER A LAPSE OF 24 HRS				35	32	39							

[0068] A reaction tube (inner diameter: 4 mm) made of quartz was filled with 10 mg of each of the catalysts of Examples 2, 3 and Comparative Example 2. n-hexane was introduced at a rate of $\text{WHSV} = 69 \text{ h}^{-1}$ under the conditions in which the reaction peak temperature of a catalyst layer was 650[degree] and the reaction pressure was 0.10 MPaG, thereby performing a conversion reaction into ethylene and propylene. At the

time, helium was used as a dilution medium. A dilution ratio was set such that n-hexane : helium = 23 : 77 (vol ratio).

[0069] Part of the outlet gas passing through the catalyst-filled layer was taken out after a lapse of 1 hour and a lapse of 24 hours since the start of the reaction, so that the composition was analyzed by using: gas chromatography (GC-2014Fsc made by Shimadzu Corporation); and a column (CP, SILICA PLOT Fused Silica). The obtained results are shown in Table 2.

[0070] A reaction tube (inner diameter: 7 mm) made of InconelTM was filled with 0.36 g of each of the catalysts of Examples 4, 5 and Comparative Example 3. n-hexane was introduced at a rate of $SV = 20 \text{ h}^{-1}$ under the conditions in which the reaction peak temperature of a catalyst layer was 650[degree] and the reaction pressure was atmospheric pressure, thereby performing a conversion reaction into ethylene and propylene. At the time, a dilution gas was not used. Analyses were performed in the same way as in Example 1. The obtained results are shown in Table 2.

[0071] Reactions and analyses were performed by using each of the catalysts of Examples 6, 7 and Comparative Example 4 and in the same way as in Example 4. The obtained results are shown in Table 2.

[0072] In the catalyst of each Example, having a peak apex in the 50-54 ppm region of a spectrum within the 46-62 ppm range of a chemical shift obtained by ²⁷Al-MAS NMR measurement, a reduction amount in the conversion rate of the substrate is smaller than that in the catalyst of each Comparative Example, having a peak apex outside the 50-54 ppm region, and accordingly it has been confirmed that the degradation of the former catalyst is suppressed.

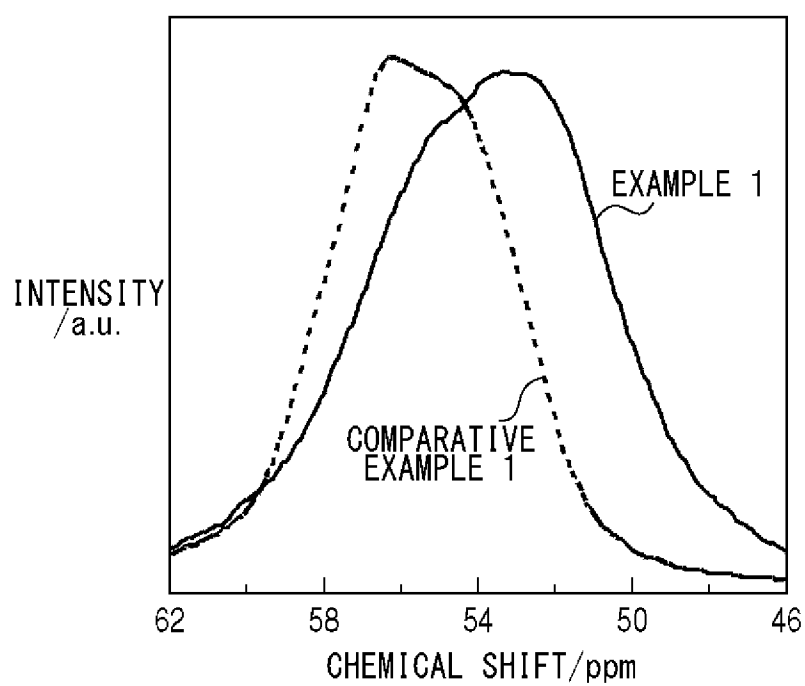
Industrial Applicability

[0073] The present invention can be applied to a technical field in which an unsaturated hydrocarbon is produced by performing catalytic cracking using naphtha as a raw material.

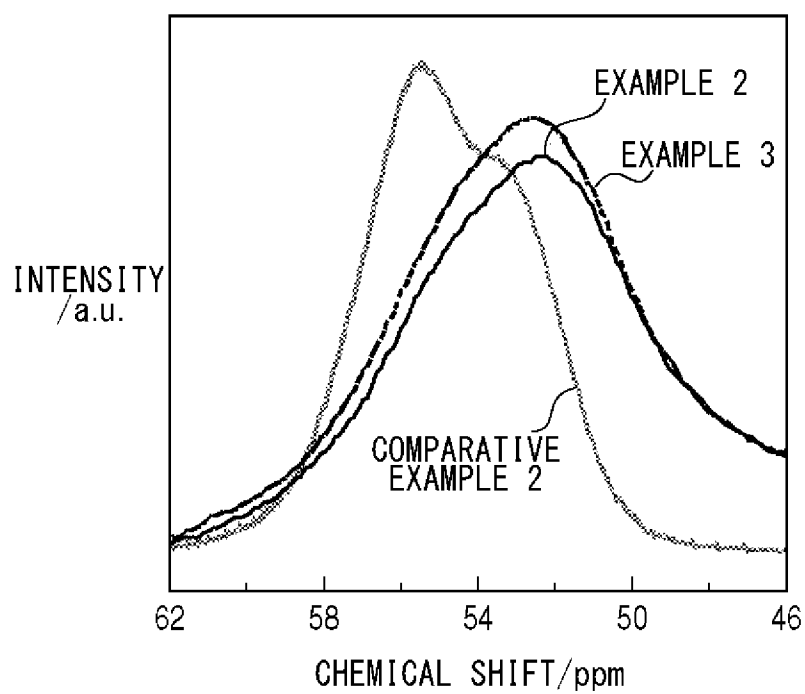
Claims

- [Claim 1] A catalyst for producing an unsaturated hydrocarbon by catalytic cracking of naphtha, the catalyst comprising:
crystalline aluminosilicate that has a peak apex in the 50-54 ppm region of a spectrum within the 46-62 ppm range of a chemical shift obtained by ^{27}Al -MAS NMR measurement.
- [Claim 2] The catalyst for producing an unsaturated hydrocarbon according to claim 1, wherein
the crystalline aluminosilicate has a 10-membered or 12-membered ring structure.
- [Claim 3] The catalyst for producing an unsaturated hydrocarbon according to claim 1 or claim 2, wherein
the crystalline aluminosilicate is MFI-type zeolite or BEA-type zeolite.
- [Claim 4] A method of producing the catalyst for producing an unsaturated hydrocarbon of any one of claims 1 to 3, the method comprising:
exposing crystalline aluminosilicate, which is a raw material, to an inert gas at a high-temperature of 400 to 1000[degree].
- [Claim 5] A method of producing the catalyst for producing an unsaturated hydrocarbon of any one of claims 1 to 3, the method comprising:
impregnating crystalline aluminosilicate, which is a raw material, with an alkaline solution.
- [Claim 6] A method of producing the catalyst for producing an unsaturated hydrocarbon of any one of claims 1 to 3, the method comprising:
exposing crystalline aluminosilicate, which is a raw material, to water vapor at a high-temperature of 500 to 900[degree].
- [Claim 7] A method of producing the catalyst for producing an unsaturated hydrocarbon of any one of claims 1 to 3, the method comprising:
impregnating crystalline aluminosilicate, which is a raw material, with an acidic aqueous solution.
- [Claim 8] A method of producing an unsaturated hydrocarbon, wherein
naphtha is catalytically cracked by using the catalyst for producing an unsaturated hydrocarbon of any one of claims 1 to 3.

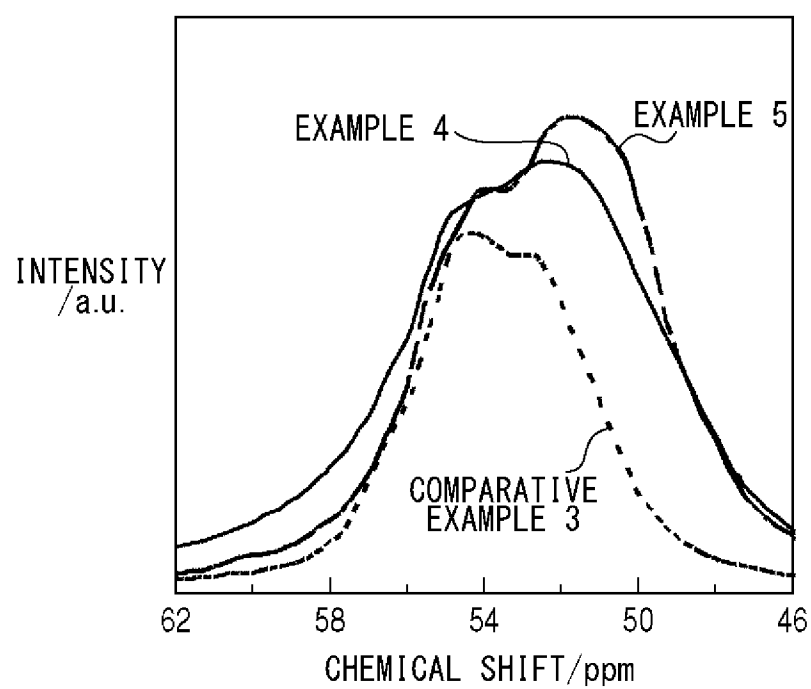
[Fig. 1]



[Fig. 2]



[Fig. 3]



[Fig. 4]

