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(54) Title: METHOD FOR PRODUCING AROMATIC HYDROCARBON AND/OR OLEFIN HAVING 4 OR LESS CARBON ATOMS AND APPARATUS FOR PRODUCING AROMATIC HYDROCARBON AND/OR OLEFIN HAVING 4 OR LESS CARBON ATOMS

(57) Abstract: A method for producing an aromatic hydrocarbon and/or an olefin having 4 or less carbon atoms comprises the following step; (1) passing a hydrocarbon through a first catalyst portion containing a solid acid catalyst (A) having an acid amount of 0.001 to 1 mmol/g, and then through a second catalyst portion containing a solid acid catalyst (B) having an acid amount of 90% or less of the acid amount of the solid acid catalyst (A); and (2) catalytically-cracking the hydrocarbon in the first catalyst portion and in the second catalyst portion at a reaction temperature of 600 C or higher.



DESCRIPTION

Title of Invention

METHOD FOR PRODUCING AROMATIC HYDROCARBON
AND/OR OLEFIN HAVING 4 OR LESS CARBON ATOMS AND
5 APPARATUS FOR PRODUCING AROMATIC HYDROCARBON
AND/OR OLEFIN HAVING 4 OR LESS CARBON ATOMS

Technical Field

[0001] The present invention relates to a method for producing an
aromatic hydrocarbon and/or an olefin having 4 or less carbon atoms
10 (hereinafter, sometimes designated as "light olefin").

Background Art

[0002] Light olefins such as ethylene, propylene and butene, and
aromatic hydrocarbons such as BTX (benzene, toluene and xylene) are
important chemical materials serving as raw materials for polymers and
15 various chemical materials. One production method therefor includes
a thermal cracking process of naphtha, but this process requires so high
temperature as 800°C or higher and consumes a great deal of energy
because of conducting thermal cracking which is an endothermic
reaction. In addition, although an increase in demand for and a failure
20 in supply of propylene among light olefins are anticipated, the ethylene
selectivity is high in such thermal cracking and it is difficult to respond
to an increase in production of propylene.

[0003] Thus, it is expected to realize catalytic cracking of naphtha by
using a catalyst. Such catalytic cracking enables a reaction at low
25 temperatures of about 600 to 700°C, thereby enabling energy saving,
and generally exerting a higher selectivity to propylene than the thermal

cracking. In addition, it is expected to control the selectivity of each product depending on the demand and supply balance and to enhance the selectivity of all valuable components, by controlling the catalyst.

[0004] With respect to the catalyst for catalytic cracking of naphtha, various studies have been previously conducted for solid acid catalysts focusing on zeolite. However, a problem is that the catalyst is coked and thus deactivated due to a sequential reaction of products. Another problem is that when zeolite is used as the catalyst, dealumination from a zeolite framework occurs to thereby deactivate zeolite due to water vapor generated during burning and removing a coke and due to steam coexisting during the reaction.

[0005] A method for suppressing such deactivation has been previously reported. For example, Japanese Patent Application Laid-Open No. 2010-42344 (Patent Literature 1) describes that with respect to the catalytic cracking by using zeolite which supports an alkali earth metal, a rare earth element and phosphorus, a reduction in activity is suppressed by using a catalyst prepared by supporting on the zeolite phosphorus and components other than phosphorus in separate steps than the case of using a catalyst prepared by supporting them at the same time.

[0006] Japanese Patent Application Laid-Open No. 2010-104878 (Patent Literature 2) describes that with respect to the catalytic cracking by using zeolite which supports an alkali earth metal, a rare earth element and phosphorus, a reduction in activity is suppressed by using a catalyst prepared by sequentially supporting on the zeolite an alkali earth metal, phosphorus and a rare earth element in this order or an

alkali earth metal, phosphorus, rare earth and phosphorus in this order, than the case of using a catalyst prepared by supporting them at the same time or in a different order from the above orders.

[0007] Japanese Patent Application Laid-Open No. 2010-104909 (Patent Literature 3) describes that with respect to the catalytic cracking by using zeolite which supports an alkali earth metal and phosphorus, a reduction in activity is suppressed by supporting on the zeolite by using a water-soluble salt containing the alkali earth metal and the phosphorus.

[0008] Japanese Patent Application Laid-Open No. 2010-202613 (Patent Literature 4) describes that with respect to the catalytic cracking of paraffins by using MCM-68, a reduction in activity is suppressed by dealuminizing MCM-68 having a low Si/Al ratio by a nitric acid treatment to make the Si/Al ratio higher, as compared with MCM-68 without being dealuminated.

[0009] All of these reports attempt to enhance performances by using only one catalyst for the reaction. In the catalytic cracking, the concentration of raw material hydrocarbon is higher at the earlier phase of the reaction, and the concentration of raw material hydrocarbon is lower at the later phase of the reaction and instead, the concentration of products such as light olefins, aromatics and light paraffins is higher. Therefore, since reactivity, coking, deactivation behavior and the like are different between the earlier phase and the later phase of the reaction, the catalysts suitable for the respective phases are estimated to be different from each other.

[0010] As the reaction using a plurality of catalysts, for example, US

Patent Application Publication No. 2010/0213101 A1 (Patent Literature 5) describes that a catalyst, in which a group VIII metal is supported on beta-zeolite having a small acid amount, is placed on the front stage, and a catalyst, in which a group VIII metal is supported on ZSM-5 having high Si, is placed on the rear stage. These catalysts are selected for the purpose of enhancing the selectivity for naphtha reforming at about 800 to about 1100°F (about 427 to about 593°C) to increase the octane number of an oil fraction to be generated.

Citation List

Patent Literature

[0011] [Patent Literature 1] Japanese Patent Application Laid-Open No. 2010-42344

[Patent Literature 2] Japanese Patent Application Laid-Open No. 2010-104878

[Patent Literature 3] Japanese Patent Application Laid-Open No. 2010-104909

[Patent Literature 4] Japanese Patent Application Laid-Open No. 2010-202613

[Patent Literature 5] US Patent Application Publication No. 2010/0213101 A1

Summary of Invention

[0012] However, the technique described in Patent Literature 5 does not suppose to suppress the deactivation of the catalyst due to coking in the catalytic cracking.

[0013] The present invention has been made under such circumstances, and an object thereof is to provide a method for producing an aromatic

hydrocarbon and/or a light olefin that can suppress the deactivation of the catalyst due to coking.

[0014] In order to solve the above problem, a certain aspect of the present invention is a method for producing an aromatic hydrocarbon and/or an olefin having 4 or less carbon atoms. This method includes passing a hydrocarbon through a first catalyst portion containing a solid acid catalyst (A) having an acid amount of 0.001 to 1 mmol/g, and then further through a second catalyst portion containing a solid acid catalyst (B) having an acid amount of 90% or less of the acid amount of the solid acid catalyst (A), and catalytically-cracking the hydrocarbon in the first catalyst portion and in the second catalyst portion at a reaction temperature of 600°C or higher.

[0015] Another aspect of the present invention is an apparatus for producing an aromatic hydrocarbon and/or an olefin having 4 or less carbon atoms. This apparatus is provided with a reaction portion having at least a first catalyst portion and a second catalyst portion. The first catalyst portion contains a solid acid catalyst (A) having an acid amount of 0.001 to 1 mmol/g, and the second catalyst portion is placed on the downstream side from the first catalyst portion and contains a solid acid catalyst (B) having an acid amount of 90% or less of the acid amount of the solid acid catalyst (A). The reaction portion is configured so as to be capable of catalytically-cracking the hydrocarbon supplied at a reaction temperature of 600°C or higher.

[0016] According to the present invention, it is possible to suppress the deactivation of the catalyst due to coking.

Description of Embodiments

[0017] Hereinafter, embodiments for performing the present invention will be described in detail. Configurations stated below are exemplifications and the scope of the present invention is not limited to these configurations.

5 [0018] The present inventors have intensively studied, and as a result, have found that a combination of solid acid catalysts which are different in terms of the acid amount allows a higher conversion to be maintained for a longer period than the case of using each catalyst singly, thereby leading to complete the present invention.

10 [0019] Specifically, the production method according to the present embodiment is a method for producing an aromatic hydrocarbon and/or a light olefin. This method includes passing a hydrocarbon through a first catalyst portion containing a solid acid catalyst having an acid amount of 0.001 to 1 mmol/g (hereinafter, sometimes designated as
15 "solid acid catalyst (A)"), and then further through a second catalyst portion containing a solid acid catalyst having an acid amount of 90% or less of the acid amount of the solid acid catalyst (A) (hereinafter, sometimes designated as "solid acid catalyst (B)"), and catalytically-cracking the hydrocarbon in the first catalyst portion and in
20 the second catalyst portion at a reaction temperature of 600°C or higher.

[0020] Herein, the first catalyst portion (solid acid catalyst (A)) is placed on the upstream side from the second catalyst portion (solid acid catalyst (B)). In other words, the second catalyst portion is placed on the downstream side from the first catalyst portion.

25 [0021] In the production method of the present embodiment, examples of the hydrocarbon suitable for raw materials include alkanes having 2

to 20 carbon atoms, olefins having 2 to 20 carbon atoms, aromatic hydrocarbons having 6 to 20 carbon atoms and naphthenes having 5 to 20 carbon atoms. The hydrocarbon is preferably hydrocarbons having 5 to 12 carbon atoms, and more preferably saturated hydrocarbons having 5 to 9 carbon atoms and/or aromatic hydrocarbons having 6 to 9 carbon atoms. Examples of the saturated hydrocarbon having 5 to 9 carbon atoms include pentane, hexane and heptane, and examples of the aromatic hydrocarbon having 6 to 9 carbon atoms include benzene, toluene and xylene. The hydrocarbon is preferably hydrocarbons containing a hydrocarbon having 5 to 12 carbon atoms at 80% by weight or more, and more preferably hydrocarbons containing a saturated hydrocarbon having 5 to 9 carbon atoms and/or a aromatic hydrocarbons having 6 to 9 carbon atoms at 80% by weight or more.

[0022] The examples of the hydrocarbon include heavy oils, light oils and naphtha, and the hydrocarbon is preferably naphtha. While naphtha is classified into light naphtha, heavy naphtha and full range naphtha depending on its boiling point, raw material naphtha may be any of them and is preferably light naphtha. Herein, light naphtha refers to one having a relatively low boiling point among naphtha, and heavy naphtha refers to one having a relatively high boiling point among naphtha.

[0023] With these raw materials, may be mixed an unreacted raw materials and a part of products in the catalytic cracking, which are recycled, or may be mixed hydrocarbons generated in other process.

These raw materials may be diluted with an inert gas such as nitrogen when being introduced into a reactor, but it is preferable not to use such

an inert gas in light of the cost of supplying an inert gas. To a reactor, may also be supplied hydrogen, but it is preferable not to supply hydrogen because a higher hydrogen concentration causes products to be hydrogenated to thereby lower the yield of an aromatic hydrocarbon and/or a light olefin. To these raw materials may also be entrained steam for the purposes of heat supply and coking suppression.

[0024] The reaction temperature of catalytic cracking of the hydrocarbon is 600°C or higher, preferably 600 to 900°C, more preferably 610 to 750°C, and still preferably 630 to 700°C. If the temperature is too low, the reaction does not progress sufficiently and the equilibrium between paraffins and olefins as products is shifted to the side of paraffins, and thus the yield of an aromatic hydrocarbon and/or a light olefin is lowered. On the other hand, if the temperature is too high, thermal cracking progresses to thereby lower the yield of an aromatic hydrocarbon and/or a light olefin, and also coking is increased to thereby speed up the deactivation of the catalyst.

[0025] While the solid acid catalysts include zeolite, silica alumina, sulfated zirconia and tungstated zirconia, it is preferable that at least one of the solid acid catalysts to be used in the catalyst layers be zeolite having an 8, 10 or 12-membered ring pore structure, and it is more preferable that at least two of the solid acid catalysts to be used in the catalyst layers be zeolites having an 8, 10 or 12-membered ring pore structure. Still preferably, at least two of the solid acid catalysts are zeolites having an 8 or 10-membered ring pore structure. It is to be noted that each of the above catalyst layers functions as the catalyst portion. Hereinafter, a catalyst layer as a form of the catalyst portion

will be described as an example, but the catalyst portion can take any of various forms.

[0026] It is preferable that the zeolite having an 8, 10 or 12-membered ring pore structure be at least one selected from MFI-type, MEL-type, MWW-type, TON-type, BEA-type, MSE-type, MOR-type, MTW-type and FAU-type zeolites, it is more preferable to be at least one selected from MFI-type, MSE-type and FAU-type zeolites, and most preferable is, in particular, MFI-type zeolite among them, which has high catalytic cracking activity and stability. ZSM-5 is one MFI-type zeolite.

[0027] One or more catalysts among the solid acid catalysts to be used may be modified by one or more components selected from alkali metals, alkali earth metals, rare earth metals, phosphorus, and transition metals such as group 4A, group 5A, group 6A, group 7A, group 8, group 1B and group 2B metals.

[0028] The acid amount of the catalyst is also referred to as "acidity" in the art, and is defined by a molar number of an acid per gram of the catalyst. The solid acid catalysts may be used in any form of a powder and a molded object. Hereinafter, the catalyst in the form of a molded object is designated as a molded catalyst. The molded catalyst may contain, as a binder and the like, one or more of clay minerals such as kaolin and bentonite and/or inorganic oxides such as silica, alumina and zirconia, in addition to the solid acid catalyst components.

[0029] The acid amounts of the solid acid catalysts can be measured by an ammonia temperature-programmed desorption method (hereinafter, ammonia TPD method). Herein, with respect to the molded catalyst, a catalyst, in which the acid amount obtained by measuring powders

formed by pulverizing the molded object by the ammonia TPD is smaller than the acid amount of the solid acid catalyst (A) used in any catalyst layer (catalyst portion) placed upstream, may be placed downstream, or a catalyst, in which the acid amount obtained by measuring the solid acid catalyst before being mixed with clay minerals, inorganic oxides and the like by the ammonia TPD is smaller than the acid amount of the solid acid catalyst (A) used in any catalyst layer (catalyst portion) placed upstream, may be placed downstream.

[0030] In the present embodiment, the acid amount of the solid acid catalyst (A) is 0.001 to 1 mmol/g, preferably 0.01 to 0.8 mmol/g, and more preferably 0.1 to 0.5 mmol/g. If the acid amount of the solid acid catalyst (A) is too large, the activity thereof is high, but the catalyst is easily deactivated due to coking, and on the other hand, if the acid amount is too small, a sufficient activity is not obtained.

[0031] In the present embodiment, the acid amount of the solid acid catalyst (B) is 90% or less, preferably 5 to 70%, and more preferably 20 to 60% of the acid amount of the solid acid catalyst (A). In the case of using three or more catalyst layers, the acid amounts of the solid acid catalysts used for any two catalyst layers can satisfy the above range.

[0032] In the present embodiment, two or more catalyst layers may be formed by packing the solid acid catalysts which are different in terms of the acid amount into the respective separate reactors, and placing the two or more reactors each thus packed with the catalyst in series. In this case, one reactor packed with the catalyst constitutes one catalyst layer. Herein, it is preferable to form two or more catalyst layers in one reactor by packing the solid acid catalysts which are different in

terms of the acid amount into one reactor, in light of costs of facilities and operations.

[0033] In the case of packing the solid acid catalysts which are different in terms of the acid amount into the respective separate reactors, and using the two or more reactors each thus packed with the catalyst, the type of each of the reactors may be any of a fixed bed, a moving bed and a fluidized bed, or may be a combination of different types of the reactors. In light of costs of facilities and operations, it is to be noted that it is preferable that there be no facilities between a plurality of the reactors, for separating the components of the raw materials and the products. Herein, the "fixed-bed" flow type reactor, so-called "fixed bed reactor" is, for example, a type of a reactor which holds a granular catalyst by any member, which can be realized at low costs. For the member that holds a granular catalyst, for example, a combination of quartz wool and quartz sand, a network bed, or the like is used. In addition, the "fluidized bed" type reactor, so-called "fixed bed reactor", is a reactor configured so that gas explodes like bubbles in a powdery catalyst.

[0034] In the case of packing the solid acid catalysts which are different in terms of the acid amount into one reactor to form two or more catalyst layers in the reactor, it is preferable to use a fixed-bed reactor. While the solid acid catalysts which are different in terms of the acid amount are packed into the reactor in series, the stages of the solid acid catalysts which are different in terms of the acid amount may be directly in contact with each other, or may be apart from each other via an inert layer or a layer of a catalyst other than the solid acid catalysts which are

different in terms of the acid amount, interposed therebetween. In the case of using three or more solid acid catalysts, the mutual positions of at least two thereof may be so that the solid acid catalyst having a larger acid amount is present at the upstream and the solid acid catalyst having a smaller acid amount is present at the downstream, and the position(s) of the remaining catalyst(s) is(are) not particularly limited. Herein, it is preferable that the solid acid catalyst having a larger acid amount be separated into a plurality of stages depending on its type sequentially from the upstream side and packed into the reactor. The reactor according to the present embodiment is packed with the solid acid catalyst having a relatively large acid amount at the upstream side, and packed with the solid acid catalyst having a relatively low acid amount at the downstream side.

[0035] With respect to the weight of the solid acid catalyst (A) and the weight of the solid acid catalyst (B), it is preferable that the weight of the solid acid catalyst (B) be 1/100 to 100 times the weight of the solid acid catalyst (A), and it is more preferable to be 1/10 to 10 times the weight of the solid acid catalyst (A). In the case of using three or more solid acid catalysts, the weight of any one solid acid catalyst corresponding to the solid acid catalyst (B) may be within the above range relative to the weight of any one solid acid catalyst corresponding to the solid acid catalyst (A).

[0036] For the catalyst layers to be used, two or more catalyst layers may be used, but it is preferable to use 2 to 5 catalyst layers, and it is most preferable to use 2 to 3 catalyst layers, in light of the effects on cost of catalyst production and time and effort of packing.

[0037] With respect to the combination of the solid acid catalyst (A) and the solid acid catalyst (B), the solid acid catalysts having different systems such as zeolite and silica alumina may be combined, and a combination of the same systems which are different in terms of the acid amount, such as a combination of zeolites which are different in the acid amount is more preferable from the operability. In the case of using zeolite, zeolites which are different in terms of the structure such as MFI and FAU may be combined, but at least two of the solid acid catalysts are preferably MFI-type zeolites which are the same in terms of the crystal structure, and it is more preferable that all the solid acid catalysts be MFI-type zeolite.

[0038] The acid amount can be controlled by various factors such as raw materials, compositions, preparation methods, preparation conditions, post-treatments and metal supporting, and a method for obtaining the solid acid catalysts which are different in terms of the acid amount is not particularly limited. In the case of zeolite, the acid amount can be easily controlled by methods such as a method of changing a Si/Al₂ molar ratio, a method of conducting a water vapor treatment, a method of conducting an acid treatment, a method of conducting an alkali treatment and a method of changing an ion exchange rate. The change in Si/Al₂ molar ratio is preferable in terms of no need for a post-treatment of zeolite. In post-treatments such as a water vapor treatment, an acid treatment and an alkali treatment, zeolites which are different in terms of the acid amount can be prepared from one zeolite, and thus there is an advantage that zeolites differing in acid amount are less expensively available than the case of purchasing a

plurality of zeolites. Among these post-treatment, a water vapor treatment is preferable because a waste liquid is only water unlike the cases of an acid treatment and an alkali treatment and such a treatment is thus easier and does not involve a reduction in catalyst amount.

5 [0039] Both of the solid acid catalyst (A) and the solid acid catalyst (B) may contain zeolite represented by the formula $xM_2O \cdot yAl_2O_3 \cdot zSiO_2 \cdot nH_2O$. The molar ratio z/y of Si to Al_2 in the zeolite (A1) contained in the solid acid catalyst (A) may be different from the molar ratio z/y of Si to Al_2 in the zeolite (B1) contained in the
10 solid acid catalyst (B). By changing the Si/ Al_2 molar ratio of zeolite in this way, it is possible to control the acid amount. Herein, in general, as the Si/ Al_2 molar ratio is larger, the acid amount decreases. The Si/ Al_2 molar ratio can be modulated by changing the composition of the raw materials, and zeolites which are different in terms of the Si/ Al_2
15 molar ratio can be easily purchased.

[0040] The water vapor treatment means a method for treating zeolite with water vapor or water vapor diluted with an inert gas such as nitrogen at a temperature of usually 400 to 900°C, preferably 500 to 700°C, in the gas phase, this method making it possible to partially
20 remove aluminum in the zeolite framework to thereby make the acid amount smaller. At least one of the zeolite (A1) of the solid acid catalyst (A) and the zeolite (B1) of the solid acid catalyst (B) may be one which has an acid amount modulated by having been treated with water vapor.

25 [0041] The acid treatment means a method for treating zeolite with an acid such as hydrochloric acid, nitric acid or sulfuric acid at 30 to 100°C,

this method making it possible to partially remove aluminum in the zeolite framework to thereby make the acid amount smaller.

In one aspect of the embodiment, the above-described method is performed in a reaction apparatus including the first catalyst portion and the second catalyst portion, and the selectivity defined as the ratio of the total number of carbon atoms contained in olefins having 4 or less carbon atoms, benzene, toluene and xylene discharged from the reaction apparatus in a unit time to the total number of carbon atoms contained in the hydrocarbon supplied to the reaction apparatus in the unit time is 55% or more. In this embodiment, the first catalyst portion and the second catalyst portion may be located either within the same reactor or within different reactors.

[0042] The alkali treatment means a method for treating zeolite with an aqueous alkali solution such as an aqueous sodium hydroxide solution or an aqueous potassium hydroxide solution, this method making it possible to elute silicon in the zeolite framework to thereby make the acid amount larger.

EXAMPLES

[0043] Hereinafter, Examples of the present embodiment will be illustrated, but the present invention is not limited thereto.

[0044] (1) Measurement of Acid Amount

An acid amount of each catalyst was measured by the ammonia TPD method. Measurement was conducted by using BELCAT manufactured by BEL Japan, Inc. A powder sample was packed into a quartz cell, and the temperature thereof was raised to 500°C under a He flow and held for 1 hour, and the sample was cooled to 100°C.

Subsequently, 5% by volume of NH_3/He was supplied thereto at 100°C for 30 minutes to allow ammonia to be adsorbed, and thereafter He purge was conducted for 15 minutes. Thereafter, the temperature was raised to 700°C at a rate of $10^\circ\text{C}/\text{min}$ and held for 20 minutes to quantitatively measure ammonia desorbed. By analyzing zeolite, peaks at low temperatures of 200 to 300°C and peaks at high temperature of not less than 300°C are apparent, and the peaks at high temperatures are derived from acids and thus peak separation was conducted between 200°C and 300°C to thereby calculate the acid amount.

[0045] (2) Water Vapor Treatment

Zeolite was set in a water vapor treatment apparatus, the temperature thereof was raised to 600°C at a rate of $5^\circ\text{C}/\text{min}$ in a nitrogen stream, and thereafter 20% by volume of water vapor/nitrogen was supplied thereto to conduct a water vapor treatment. After a treatment for a predetermined period, stream was switched to nitrogen to cool the zeolite.

[0046] (3) Reaction Test

By using as a hydrocarbon raw material n-hexane and using a fixed-bed reactor, catalytic cracking was conducted. As the catalyst, one whose particle size was regulated to a particle size of 250 to $500\ \mu\text{m}$ was used. A granular catalyst was held by using quartz wool and quartz sand. The catalyst was packed into an Inconel reaction tube so that the total amount was 0.36 g. The upper and the lower of a catalyst layer were held by quartz wool, and the more upper and the more lower thereof was packed with quartz sand in order to make the retention time of gas

in the reaction tube shorter. In the case where a plurality of catalysts were separated into two stages and packed thereinto, quartz wool and the like were not packed therebetween and the catalyst layer at the upper stage was directly packed onto the catalyst layer at the lower stage. A thermocouple was set so as to be located at the center of the catalyst layer to measure the temperature of the catalyst layer. Gas was supplied from the upper portion of the reaction tube and extracted from the lower portion thereof. The temperature of the reaction tube was raised to a predetermined temperature at a rate of 5°C/min under atmospheric pressure in a nitrogen stream. Thereafter, the supply of nitrogen was stopped, and n-hexane was supplied at a rate of 7.2 g/h. In addition to n-hexane, neither diluted gas nor water vapor was supplied during the reaction. Since the temperature of the catalyst layer was rapidly lowered by endotherm caused by catalytic cracking immediately after starting the reaction, the temperature of an electric furnace was modulated so that the temperature of the catalyst layer was a predetermined temperature. After a reaction for a predetermined period, the supply of n-hexane was stopped, followed by cooling in a nitrogen stream. Analysis was conducted by gas chromatography to calculate the conversion (%) from the result. The selectivity of ethylene, propylene, butenes and BTX was calculated. The present embodiment relates to an effect of simultaneously satisfying a high activity and suppression of a reduction in activity in the method for producing an aromatic hydrocarbon and/or a light olefin, and such an effect is higher in the method that exhibits a high total selectivity of ethylene, propylene, butenes and BTX, a high initial conversion, and a

high conversion also after the lapse of a predetermined period from the start of reaction.

[0047] [Example 1]

The upper stage of the catalyst layer was packed with 0.18 g of H-ZSM-5 (catalyst A) having a Si/Al₂ molar ratio of 80 and an acid amount of 0.424 mmol/g, and the lower stage of the catalyst layer was packed with 0.18 g of H-ZSM-5 (catalyst B) having a Si/Al₂ molar ratio of 500 and an acid amount of 0.091 mmol/g. The ratio of the acid amount of the catalyst at the lower stage to the acid amount of the catalyst at the upper stage (catalyst B/catalyst A) was 21%. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 1.

[0048] [Comparative Example 1]

The upper stage of the catalyst layer was packed with 0.18 g of the catalyst B, and the lower stage of the catalyst layer was packed with 0.18 g of the catalyst A. The ratio of the acid amount of the catalyst at the lower stage to the acid amount of the catalyst at the upper stage (catalyst A/catalyst B) was 466%. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 1.

[0049] [Comparative Example 2]

The catalyst layer was packed with 0.36 g of a catalyst in which the catalyst A and the catalyst B whose particle sizes were regulated were mixed in a weight ratio of 1:1. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 1.

[0050] [Comparative Example 3]

The catalyst layer was packed with 0.36 g of only the catalyst A. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 1.

[0051] [Comparative Example 4]

5 The catalyst layer was packed with 0.36 g of only the catalyst B. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 1.

[0052] [Comparative Example 5]

10 The same operation as in Example 1 was conducted except that the reaction temperature was 550°C. The reaction results are shown in Table 1.

[0053] [Comparative Example 6]

15 The same operation as in Example 1 was conducted except that the reaction temperature was 500°C. The reaction results are shown in Table 1.

[0054] [Example 2]

20 The catalyst A was treated with water vapor for 6 hours to obtain H-ZSM-5 (catalyst C) having an acid amount of 0.087 mmol/g. The upper stage of the catalyst layer was packed with 0.18 g of H-ZSM-5 (catalyst D) having a Si/Al₂ molar ratio of 150 and an acid amount of 0.234 mmol/g, and the lower stage of the catalyst layer was packed with 0.18 g of the catalyst C. The ratio of the acid amount of the catalyst at the lower stage to the acid amount of the catalyst at the upper stage (catalyst C/catalyst D) was 37%. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 2.

25

[0055] [Comparative Example 7]

The upper stage of the catalyst layer was packed with 0.18 g of the catalyst C, and lower stage of the catalyst layer was packed with 0.18 g of the catalyst D. The ratio of the acid amount of the catalyst at the lower stage to the acid amount of the catalyst at the upper stage (catalyst D/catalyst C) was 269%. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 2.

[0056] [Comparative Example 8]

The catalyst layer was packed with 0.36 g of a catalyst in which the catalyst C and the catalyst D whose particle sizes were regulated were mixed in a weight ratio of 1:1. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 2.

[0057] [Example 3]

H-ZSM-5 (catalyst E) different from the catalyst A, having a Si/Al₂ molar ratio of 80 and an acid amount of 0.175 mmol/g, was treated with water vapor for 1 hour to obtain H-ZSM-5 (catalyst F) having a Si/Al₂ molar ratio of 80 and an acid amount of 0.110 mmol/g. The catalyst E was treated with water vapor for 4 hours to obtain H-ZSM-5 (catalyst G) having a Si/Al₂ molar ratio of 80 and an acid amount of 0.064 mmol/g. The upper stage of the catalyst layer was packed with 0.18 g of the catalyst F, and the lower stage of the catalyst layer was packed with 0.18 g of the catalyst G. The ratio of the acid amount of the catalyst at the lower stage to the acid amount of the catalyst at the upper stage (catalyst G/catalyst F) was 58%. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 3.

[0058] [Comparative Example 9]

The upper stage of the catalyst layer was packed with 0.18 g of the catalyst G, and the lower stage of the catalyst layer was packed with 0.18 g of the catalyst F. The ratio of the acid amount of the catalyst at the lower stage to the acid amount of the catalyst at the upper stage (catalyst F/catalyst G) was 172%. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 3.

[0059] [Comparative Example 10]

The catalyst layer was packed with 0.36 g of only the catalyst F. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 3.

[0060] [Comparative Example 11]

The catalyst layer was packed with 0.36 g of only the catalyst G. With respect to this, the reaction test was conducted at 650°C. The reaction results are shown in Table 3.

[0061] [Table 1]

	Catalyst (upper)	Catalyst (lower)	Reaction temperature °C	Reaction time 1h		Reaction time 13h	
				Conversion %	Selectivity C-mol%	Conversion %	Selectivity C-mol%
Example 1	A	B	650	95.6	60.2	80.2	62.3
Comparative Example 1	B	A	650	86.2	61.7	55.6	66.3
Comparative Example 2	A+B		650	95.8	61.2	51.0	62.8
Comparative Example 3	A		650	96.5	61.3	72.1	64.0
Comparative Example 4	B		650	76.7	64.3	73.3	65.3
Comparative Example 5	A	B	550	71.7	44.5	68.1	45.6
Comparative Example 6	A	B	500	53.4	36.5	49.0	37.5

* Selectivity: selectivity of an olefin having 2 to 4 carbon atoms and BTX

[0062] [Table 2]

	Catalyst (upper)	Catalyst (lower)	Reaction temperature °C	Reaction time 1h		Reaction time 17h		Reaction time 35h	
				Conve rsion %	Selectivity C-mol%	Conv ersion %	Selectivity C-mol%	Conv ersion %	Selectivity C-mol%
Example 2	D	C	650	92.6	66.3	90.5	67.3	76.1	67.9
Comparative Example 7	C	D	650	97.3	69.1	74.1	70.1	44.8	68.3
Comparative Example 8	C+D		650	96.2	66.5	82.9	67.9	49.8	69.6

* Selectivity: selectivity of an olefin having 2 to 4 carbon atoms and BTX

[0063] [Table 3]

	Catalyst (upper)	Catalyst (lower)	Reaction temperature °C	Reaction time 1h		Reaction time 21h		Reaction time 35h	
				Conve rsion %	Selectivity C-mol%	Conve rsion %	Selectivity C-mol%	Conv ersion %	Selectivity C-mol%
Example 3	F	G	650	95.5	68.8	84.4	70.4	60.8	71.1
Comparative Example 9	G	F	650	99.5	68.7	66.8	70.9	46.0	69.3
Comparative Example 10	F		650	99.3	67.8	82.7	70.5	55.2	71.0
Comparative Example 11	G		650	88.8	68.5	79.0	70.0	56.9	70.8

* Selectivity: selectivity of an olefin having 2 to 4 carbon atoms and BTX

5 [0064] Comparisons of Example 1 with Comparative Examples 1 to 4,
Example 2 with Comparative Examples 7 and 8, and Example 3 with
Comparative Examples 9 to 11 revealed that the catalyst having a larger
acid amount was placed upstream and the catalyst having a smaller acid
amount than the former catalyst was placed downstream to thereby
10 allow a high activity to be maintained for a longer period than the case
of a placement different from the above placements or the use of any
catalyst singly.

15 [0065] Specifically, the configuration in Comparative Example 1, in
which the catalyst A having a larger acid amount was placed
downstream and the catalyst B having a smaller acid amount than the
former catalyst was placed on the upstream, is compared with the
configuration in Example 1 to thereby find out that the conversion is

low from the earlier phase. In addition, the configuration in Comparative Example 2, in which the catalyst A having a larger acid amount and the catalyst B having a smaller acid amount were mixed, is compared with the configuration in Example 1 to thereby find out that while the conversion at the earlier phase (reaction time: 1 hour) is high, the conversion at a reaction time of 13 hours is rapidly lowered. In addition, Example 1 is compared with Comparative Examples 5 and 6 to thereby find out that when the reaction temperature is lower than 600°C, a reduction in activity is suppressed, but the conversion is low from the earlier phase and the total selectivity of ethylene, propylene, butenes and BTX is remarkably lower than the case where the reaction temperature is 600°C or higher.

[0066] Specifically, the production method according to Examples is configured so that a selectivity defined as a ratio of a total number (molar number) of carbon atoms of olefins having 4 or less carbon atoms, benzene, toluene and xylene generated in a unit time to a total number of carbon atoms in the hydrocarbon supplied in the unit time is 55% or more. It may be preferably configured so that the selectivity is 60% or more. The production method may also be configured so that a selectivity defined as a ratio of a total number (molar number) of carbon atoms of olefins having 4 or less to the total number of carbon atoms in the hydrocarbon supplied is 30% or more.

Thus, according to the production method of the present embodiment, it is possible to suppress the deactivation due to coking and to stably maintain a high catalyst activity for a longer period as compared with the case of using one catalyst.

[0067] It is to be noted that another production method according to Examples can also be considered as a method for producing an aromatic hydrocarbon and/or a light olefin, including passing a hydrocarbon through a first catalyst portion containing a first zeolite having an acid amount of 0.001 to 1 mmol/g and a 10-membered ring pore structure, and then further through a second catalyst portion containing a second zeolite having an acid amount of 90% or less of the acid amount of the first zeolite and a 10-membered ring pore structure, and catalytically-cracking the hydrocarbon.

[0068] It is also possible to consider the present embodiment as a production apparatus. In this case, an apparatus for producing an aromatic hydrocarbon and/or a light olefin according to the present embodiment is provided with a reactor having at least a first catalyst portion and a second catalyst portion. The first catalyst portion contains a solid acid catalyst (A) having an acid amount of 0.001 to 1 mmol/g, and the second catalyst portion is placed on the downstream side from the first catalyst portion and contains a solid acid catalyst (B) having an acid amount of 90% or less of the acid amount of the solid acid catalyst (A). The reaction portion is configured so as to be capable of catalytically-cracking the hydrocarbon supplied at a reaction temperature of 600°C or higher.

[0069] Although the present invention has been described in the foregoing with reference to the above embodiment and each Example, the present invention is not limited to the above embodiment and Examples, and appropriate combinations and substitutions of the configurations of the above embodiment and each Example are

contemplated to be encompassed in the present invention. It is also possible to appropriately change the combinations and the treatment orders in the embodiment and each Example and to add various design modifications to the embodiment and each Example based on the knowledge of one person skilled in the art, and the embodiment to which such modifications are added can also be encompassed in the scope of the present invention.

CLAIMS

[Claim 1]

A method for producing an aromatic hydrocarbon and/or an olefin having 4 or less carbon atoms, comprising:

5 passing a hydrocarbon through a first catalyst portion containing a solid acid catalyst (A) having an acid amount of 0.001 to 1 mmol/g, and then through a second catalyst portion containing a solid acid catalyst (B) having an acid amount of 90% or less of the acid amount of the solid acid catalyst (A); and

10 catalytically-cracking the hydrocarbon in the first catalyst portion and in the second catalyst portion at a reaction temperature of 600°C or higher.

[Claim 2]

The method according to claim 1, wherein the solid acid catalyst (A) and the solid acid catalyst (B) are zeolites that are the same as each other in structure.

[Claim 3]

The method according to claim 2, wherein both of zeolite (A1) of the solid acid catalyst (A) and zeolite (B1) of the solid acid catalyst (B) are represented by a formula

20 $xM_2O \cdot yAl_2O_3 \cdot zSiO_2 \cdot nH_2O$, and the molar ratio z/y of Si to Al_2 in the zeolite (A1) is different from the molar ratio z/y of Si to Al_2 in the zeolite (B1).

[Claim 4]

The method according to claim 2 or 3, wherein at least one of the zeolite

25 (A1) of the solid acid catalyst (A) and the zeolite (B1) of the solid acid catalyst (B) has an acid amount modulated by having been treated with

water vapor.

[Claim 5]

The method according to any one of claims 1 to 4, wherein the method is performed in a reaction apparatus including the first catalyst portion and the second catalyst portion, and the selectivity defined as the ratio of the total number of carbon atoms contained in olefins having 4 or less carbon atoms, benzene, toluene and xylene discharged from the reaction apparatus in a unit time to the total number of carbon atoms contained in the hydrocarbon supplied to the reaction apparatus in the unit time is 55% or more.

[Claim 6]

The method according to any one of claims 1 to 5, wherein the hydrocarbon comprises a saturated hydrocarbon having 5 to 9 carbon atoms and/or an aromatic hydrocarbon having 6 to 9 carbon atoms.

[Claim 7]

The method according to any one of claims 1 to 5, wherein the hydrocarbon comprises naphtha.

[Claim 8]

The method according to any one of claims 1 to 7, wherein at least one of the solid acid catalyst (A) and the solid acid catalyst (B) is zeolite having an 8, 10 or 12-membered ring pore structure.

[Claim 9]

The method according to any one of claims 1 to 8, wherein at least one of the solid acid catalyst (A) and the solid acid catalyst (B) is MFI-type zeolite.

[Claim 10]

The method according to any one of claims 1 to 9, wherein the method is performed in a fixed bed reactor, and the reactor has a plurality of stages differing in the types of the catalysts packed therein, and the solid acid catalyst (B) is packed in a stage located on a downstream side from a stage packed with the solid acid catalyst (A).

[Claim 11]

An apparatus for producing an aromatic hydrocarbon and/or an olefin having 4 or less carbon atoms, the apparatus comprising a reaction portion having at least a first catalyst portion and a second catalyst portion, wherein

the first catalyst portion contains a solid acid catalyst (A) having an acid amount of 0.001 to 1 mmol/g;

the second catalyst portion is placed on a downstream side from the first catalyst portion and contains a solid acid catalyst (B) having an acid amount of 90% or less of the acid amount of the solid acid catalyst (A); and

the reaction portion is configured so as to be capable of catalytically cracking a hydrocarbon supplied thereto at a reaction temperature of 600°C or higher.

[Claim 12]

The apparatus according to claim 11, wherein both of the solid acid catalyst (A) and the solid acid catalyst (B) are zeolites having an 8 or 10-membered ring pore structure.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G11/05
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

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

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

EPO-Internal, WPI Data, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 3 847 793 A (SCHWARTZ A ET AL) 12 November 1974 (1974-11-12) claims 1-3,8 column 4, lines 23-40	1-12
A	US 4 591 425 A (KOVACH STEPHEN M [US] ET AL) 27 May 1986 (1986-05-27) claim 1; figure 1	1,11
A	US 2001/042700 A1 (SWAN GEORGE A [US] ET AL) 22 November 2001 (2001-11-22) claim 1 page 3, paragraph 26-29	1,11



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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