

DESCRIPTION

CATALYST FOR CATALYTIC CRACKING OF HYDROCARBON, AND PROCESS FOR
PRODUCING SAME

5 TECHNICAL FIELD

[0001]

The present invention relates to a novel catalyst for catalytic cracking of hydrocarbons and a method for producing the same.

10 [0002]

More specifically, the present invention relates to a catalyst for catalytic cracking of hydrocarbons which has an excellent hydrothermal stability, a high capability to crack distillation residue (bottoms), and an excellent selectivity
15 (high liquid yield, with low gas and low coke yield), when used in the catalytic cracking of hydrocarbons, particularly, heavy oil hydrocarbons; and a method for producing the catalyst.

BACKGROUND ART

[0003]

20 Raw materials, which contain a high proportion of heavy hydrocarbons, such as heavy oil and heavy residual oil were used when gasoline is produced by catalytic cracking of hydrocarbons. In the catalytic cracking of heavy oil and heavy residual oil, a faujasite-type zeolite is often used as a catalyst.

Specifically, it is well known that a faujasite-type zeolite ion-exchanged with rare earth ions or an ultra-stable faujasite-type zeolite (sometimes written as USY zeolite) is used.
[0004]

5 Heavy oil contains heavy metals, such as nickel, vanadium and iron, which not only complicate the catalytic cracking of heavy oil, but also act as catalyst poisons, and also contains sulfur and nitrogen. Heavy metals adhere to the catalyst, and cause to increase the amount of dry gas (such as hydrogen, methane and
10 ethane) and coke generated, thereby reducing the yield of gasoline and the like. Further, in cases where the amount of coke generated is increased, it causes a temperature rise in the catalyst regenerator, and to decrease the crystallinity of the zeolite due to the water contained in the cokes, thereby resulting in a
15 reduction of the activity of the catalyst.

[0005]

In view of these problems, the present inventors have disclosed that a catalyst for catalytic cracking of hydrocarbons in which (1) alumina particles having a particle diameter of from
20 2 to 60 μm , and containing a metal component selected from one or more of alkali earth metals and rare earth metals and a phosphorus component; and (2) a crystalline aluminosilicate zeolite; are uniformly dispersed in (3) a porous inorganic oxide matrix, has a metal resistance, high activity and high selectivity,

and is capable of inhibiting the generation of hydrogen and coke
(Patent Document 1: JP 5-16908 B).

Further, the present inventors have disclosed that a
catalyst composition for fluid catalytic cracking of hydrocarbons
5 containing alumina, a crystalline aluminosilicate zeolite and an
inorganic oxide matrix other than alumina, each of the components
containing a phosphorus atom, has an excellent capability to crack
bottoms (bottom oil), generates a reduced amount of hydrogen and
coke, and increases the fractions of gasoline, kerosene and light
10 oil, when used in the catalytic cracking of heavy oil hydrocarbons
(Patent Document 2: JP 8-173816 A).

In addition, JP 2009-511245 A (Patent Document 3) discloses
that a hydrothermally stable, porous molecular sieve catalyst
obtained by evaporating moisture from a raw material mixture
15 containing (1) a molecular sieve having a -Si-OH-Al- skeleton
whose surface pores are modified by a specific phosphate; (2) a
water insoluble metal salt; and (3) a phosphoric acid compound;
has a high hydrothermal resistance and an improved gas olefin yield
and selectivity. It is also disclosed that the above mentioned
20 (2) water insoluble metal salt contains magnesia (MgO). In
Examples in Patent Document 3, HZSM-5 and ferrierite are used as
the molecular sieves, and MgO, Mg(OH)₂ and the like are used as
the water insoluble metal salts.

[0006]

The present inventors have also disclosed a method for producing a catalyst for catalytic cracking, in which minute spherical particles are formed by spray drying an aqueous slurry of a mixture comprising: air flow calcined alumina; a clay comprising as major components, silica and alumina; a silica-based inorganic oxide precursor; and a crystalline aluminosilicate; and the obtained minute spherical particles are washed such that the content of alkali metal oxides in terms of oxides is 1.0% by weight or less, followed by introduction of a rare earth(s). It is also disclosed that the thus obtained catalyst exhibits a high cracking activity and high gasoline selectivity, generates a reduced amount of coke and gas, and has a high hydrothermal resistance, when used in the catalytic cracking of heavy hydrocarbon oil containing a large amount of metals (Patent Document 4: JP 60-193543 A).

Further, the present inventors have proposed a catalyst for catalytic cracking of hydrocarbons in JP 11-246868 A (Patent Document 5) and in JP 2004-130193 A (Patent Document 6).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0007]

Patent Document 1: JP 5-16908 B

Patent Document 2: JP 8-173816 A

Patent Document 3: JP 2009-511245 A

Patent Document 4: JP 60-193543 A

Patent Document 5: JP 11-246868 A

Patent Document 6: JP 2004-130193 A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

5 [0008]

However, although the catalyst for catalytic cracking obtained by: spray drying the aqueous slurry of the above mentioned mixture to form minute spherical particles; washing the minute spherical particles; and then by introducing a rare earth(s);
10 exhibits a high cracking activity and high gasoline selectivity, there are problems that an effort to increase the amount of rare earth(s) introduced to the catalyst in order to further improve its activity have failed to significantly increase the introduced amount of rare earth(s), and that the improvement in the cracking
15 activity, gasoline selectivity and the like is small, thereby resulting in a reduction in the utilization efficiency of valuable rare earths and in economic efficiency.

[0009]

In the catalyst disclosed in Patent Document 1, although
20 the metal resistance, activity, selectivity and the like of the catalyst are improved, the improvement in the activity and the selectivity is attributed to the improvement in the metal resistance, and the improvement in the gasoline yield, selectivity and the like is insufficient (possibly due to the rare earth(s)

not being carried by the zeolite), leaving a room for further improvement.

[0010]

In the case of the catalyst disclosed in Patent Document
5 2, although the metal resistance, activity, selectivity and the
like are improved, the improvement in the activity and the
selectivity is also attributed to the improvement in the metal
resistance, due to the catalyst containing phosphorus. Thus, the
improvement in the gasoline yield, selectivity and the like is
10 insufficient, leaving a room for further improvement. Further,
a catalyst carrying a rare earth(s) is disclosed in Examples in
Patent Document 2, and in this catalyst, although an improvement
in the activity and the selectivity is observed, further
improvement in the metal resistance, activity, and selectivity
15 is required. In addition, there is a problem that, an effort to
increase the amount of rare earth(s) carried by the catalyst in
order to increase its activity and selectivity results in a
decrease in the utilization efficiency of the rare earth(s), as
with the catalyst disclosed in Patent Document 4 to be described
20 later.

[0011]

The catalyst disclosed in Patent Document 3 has a problem
that, although the hydrothermal resistance of the catalyst is
improved, the yield and the selectivity of gas olefin are increased

and the yield and the selectivity of gasoline are decreased.

[0012]

Further, conditions for introducing a rare earth(s) to the catalyst have been investigated in order to improve the utilization efficiency of the rare earth(s). However, there are problems that, in cases where the pH of the solution introduced the rare earth(s) to the catalyst which is disclosed in Patent Document 4 is not within the range of from 4.5 to 5.5, for example, 4 or less, the utilization efficiency of the rare earth(s) is decreased; and in cases where the pH is greater than 6, while the utilization efficiency of the rare earth(s) is improved, the improvement in the performance of the catalyst is insufficient, possibly due to generation of precipitation or double salts.

[0013]

On the other hand, although alkali earth metals are known to have effects similar to those provided by rare earths, the effects of alkali earth metals to improve the cracking activity, gasoline selectivity, hydrothermal resistance and the like are inferior to those of rare earths.

In addition, in the catalyst disclosed by the present inventors in Patent Document 5, a fibrillary pseudoboehmite alumina-type hydrated alumina treated with phosphate ions is used, but the gasoline yield, selectivity and the like of the catalyst are insufficient, as with the catalyst disclosed in Patent

Document 1, and there was a room for a further improvement. In the catalyst disclosed in Patent Document 6, a magnesium compound or the like was used as a metal scavenger. In this catalyst, while the metal resistance, activity, selectivity and the like are improved, the improvement in the activity and selectivity is also attributed to the improvement in the metal resistance, due to containing the metal scavenger. Thus, the improvement in the yield and the selectivity of gasoline are insufficient, leaving a room for further improvement. A catalyst carrying a rare earth(s) is disclosed in Examples in Patent Document 6, and in this catalyst, although the activity and selectivity are improved, a further improvement in the metal resistance, activity and selectivity is needed. In addition, as with the catalyst disclosed in Patent Document 4, this catalyst has a problem that an effort to increase the amount of rare earth(s) carried by the catalyst, in order to improve its activity and the selectivity, results in a decrease in the utilization efficiency of the rare earth(s).

MEANS FOR SOLVING THE PROBLEMS

[0014]

In view of the above problems, the present inventors have discovered, as a result of intensive studies, that it is possible to obtain a catalyst which has a high cracking activity and high gasoline selectivity, which generates a reduced amount of gas and

coke, and which is excellent in hydrothermal resistance, by:
forming minute spherical particles by spray drying; thoroughly
washing the minute spherical particles; and introducing magnesium,
and then phosphorus to the minute spherical particles; thereby
5 completing the present invention.

[0015]

As a result, it is possible to provide a catalyst for
catalytic cracking which has a high cracking activity and high
gasoline selectivity, which generates a reduced amount of gas and
10 coke, and which is excellent in hydrothermal resistance and in
economic efficiency.

[1] A catalyst for catalytic cracking of hydrocarbons
comprising a faujasite-type zeolite, a matrix component, a
phosphorus component and a magnesium component,

15 wherein the content of the faujasite-type zeolite (C_Z) in
terms of solid is within the range of from 10 to 50 % by weight;
the content of phosphorus (C_P) in terms of P_2O_5 is within the range
of from 0.1 to 10 % by weight; and the content of magnesium (C_M)
in terms of MgO is within the range of from 0.05 to 3% by weight.

20 [2] The catalyst for catalytic cracking of hydrocarbons
according to item [1], wherein the ratio (C_P) / (C_M) of the content
of phosphorus (C_P) to the content of magnesium (C_M) is within the
range of from 0.1 to 8.

[3] The catalyst for catalytic cracking of hydrocarbons

according to item [1] or [2], wherein the ratio (C_M) / (C_Z) of the content of magnesium (C_M) to the content of the faujasite-type zeolite (C_Z) is within the range of from 0.001 to 0.1.

[4] The catalyst for catalytic cracking of hydrocarbons

5 according to any one of items [1] to [3], further comprising a rare earth, wherein the content of the rare earth in terms of RE_2O_3 is within the range of from 0.1 to 2% by weight.

[5] The catalyst for catalytic cracking of hydrocarbons

according to any one of items [1] to [4], wherein the matrix
10 component contains alumina, and wherein the content of alumina in terms of Al_2O_3 is within the range of from 1 to 30% by weight.

[6] The catalyst for catalytic cracking of hydrocarbons

according to any one of items [1] to [5], wherein the faujasite-type zeolite is an ultra-stable zeolite (USY).

15 [7] A method for producing a catalyst for catalytic cracking of hydrocarbons, comprising the following steps (a) to (f):

(a) a step of spray drying a mixed slurry of a faujasite-type zeolite and a matrix-forming component in a hot air flow to form minute spherical particles;

20 (c) a step of subjecting the resultant to ion exchange with magnesium ions;

(e) a step of bringing the resultant into contact with phosphate ions; and

(f) a step of drying the resultant.

[8] The method for producing a catalyst for catalytic cracking of hydrocarbons according to item [7], wherein the pH at the step (c) of ion exchange with magnesium ions is within the range of from 3 to 8.

5 [9] The method for producing a catalyst for catalytic cracking of hydrocarbons according to item [7] or [8], wherein the pH at the step (e) of contact with phosphate ions is within the range of from 2 to 6.

[10] The method for producing a catalyst for catalytic cracking
10 of hydrocarbons according to any one of items [7] to [9], wherein the following step (d) is carried out before or after carrying out the step (c):

(d) the step of performing ion exchange with rare earth ions.

[11] The method for producing a catalyst for catalytic cracking
15 of hydrocarbons according to item [10], wherein the pH at the step (d) of ion exchange with rare earth (RE) ions is within the range of from 4 to 6.

[12] The method for producing a catalyst for catalytic cracking of hydrocarbons according to any one of items [7] to [11], wherein
20 the following step (b) is carried out after the step (a):

(b) the step of performing washing.

EFFECT OF THE INVENTION

[0016]

According to the present invention, it is possible to

provide a catalyst for catalytic cracking which has a high cracking activity and high gasoline selectivity, which generates a reduced amount of gas and coke, and which is excellent in hydrothermal resistance and in economic efficiency.

5 MODE FOR CARRYING OUT THE INVENTION

[0017]

First, the catalyst for catalytic cracking of hydrocarbons according to the present invention will be described below.

[0018]

10 Catalyst for catalytic cracking of hydrocarbons

The catalyst for catalytic cracking of hydrocarbons according to the present invention comprises a faujasite-type zeolite, a matrix component, phosphorus, and magnesium.

[0019]

15 Faujasite-type zeolite

The faujasite-type zeolite has a skeleton composed of SiO_2 and Al_2O_3 , and the molar ratio $(M_S) / (M_A)$ of the number of moles (M_S) of SiO_2 to the number of moles (M_A) of Al_2O_3 is preferably within the range of from 5 to 20, and more preferably, within the range
20 of from 6 to 15.

[0020]

A faujasite-type zeolite having the molar ratio $(M_S) / (M_A)$ within the above mentioned range has a high hydrothermal resistance, high activity, and high selectivity.

[0021]

If the molar ratio is too low, there are cases where the hydrothermal resistance (ratio of the activity maintained when subjected to regeneration treatment at a high temperature) of the zeolite may be insufficient, resulting in an insufficient activity, and also in an insufficient gasoline selectivity. In this case, the following situation is known to occur. In the process of fluid catalytic cracking, after the cracking reaction, carbonaceous substances deposited on the catalyst are removed by combustion in a regeneration tower to regenerate the catalyst. At this time, since heat due to the combustion causes the temperature rise, and hydrogen contained in the carbonaceous substances generates water, the catalyst results in being hydrothermally treated at a high temperature, thereby reducing the crystallinity of the zeolite.

15 [0022]

On the other hand, if the molar ratio (M_S) / (M_A) is too high, there are also cases where the activity of the zeolite becomes insufficient, possibly due to active spots being reduced, despite a high hydrothermal resistance.

20 [0023]

The content of the faujasite-type zeolite in the catalyst for catalytic cracking of hydrocarbons in terms of solid (mainly in terms of SiO_2 and Al_2O_3) is preferably within the range of from 10 to 50% by weight, and more preferably, within the range of from

15 to 40% by weight.

[0024]

If the content the faujasite-type zeolite in terms of solid is less than 10% by weight, the activity of the resulting catalyst
5 may be insufficient, due to the content of zeolite being too low.

[0025]

If the content of the faujasite-type zeolite in terms of solid is greater than 50% by weight, there are cases where the activity of the resulting catalyst may be too high to cause
10 over-cracking, thereby reducing the selectivity. Further, since the content of the matrix component, which is contained in the catalyst along with zeolite, is reduced, the abrasion resistance may be insufficient. As a result, when used as a fluid catalyst, the catalyst may be easily turned into powder and scattered around.
15 Although, an additional amount of catalyst can be supplemented in order to solve the above mentioned problem, it leads to another problem of economic efficiency.

[0026]

As the faujasite-type zeolite to be used in the present
20 invention, a NH_4Y zeolite, which is a NaY -type zeolite ion-exchanged with NH_4 ions, can be used. However, an ultra-stable zeolite (USY), which can be obtained by hydrothermally treating the NH_4Y zeolite, is preferred.

[0027]

The value of the lattice constant (a_0) of the ultra-stable zeolite is preferably within the range of from 24.40 to 24.60 Angstrom, more preferably, within the range of from 24.45 to 24.58 Angstrom. If the value of the lattice constant is within the range
5 as described above, the resulting catalyst has a very high selectivity.

[0028]

If the value of the lattice constant (a_0) of the ultra-stable zeolite is too small, there are cases where the resulting catalyst
10 has an insufficient activity and the selectivity, despite a high hydrothermal resistance and the metal resistance, depending on the content of the P component and the Mg component. If the value of the lattice constant (a_0) of the ultra-stable zeolite is too high, on the other hand, there are cases where a sufficient effect
15 of improving the hydrothermal resistance and the metal resistance cannot be obtained, depending on the content of the phosphorus component and the Mg component.

[0029]

In the present invention, the lattice constant is obtained
20 by measuring the spacing between the diffraction planes (553) and (642) of the ultra-stable zeolite, by X-ray diffraction analysis, using an anatase-type TiO_2 as a standard reference material.

[0030]

The above mentioned ultra-stable zeolite (USY) can be

produced by a conventionally known method. For example, Procedure A and Procedure B described in ZEOLITES AND CLAY MINERALS as Sorbents and Molecular Sieves, p 350 (1975), by R. M. Barrer, can be suitably used.

5 [0031]

Specifically, Procedure B describes that a zeolite whose lattice constant is decreased by 1 to 1.5% can be obtained as follows. A NaY zeolite is ion-exchanged with ammonium chloride to form $(\text{NH}_4)_{(0.75 \text{ to } 0.90)}\text{Na}_{(0.25 \text{ to } 0.10)}\text{-Y}$; the resultant is then washed,
10 subjected to heat treatment at a temperature of from 200 to 600°C, and subjected to ion exchange again to eliminate residual Na^+ so that the resultant is in a metastable state; and then the resultant is rapidly heated at a temperature of 600 to 800°C in a steam atmosphere; to obtain the ultra-stable zeolite.

15 [0032]

In the present invention, a zeolite obtained by further subjecting the resulting ultra-stable zeolite (USY) to acid treatment and the like can also be suitably used.

[0033]

20 Matrix component

The matrix component to be used in the present invention refers to a material(s) other than the above mentioned faujasite-type zeolite. As the matrix component, a conventionally known inorganic oxide(s) or an inorganic

compound(s), such as silica, alumina, silica alumina and aluminum phosphate, can be used. These also include a material referred to as a binder or filler.

[0034]

5 Specific examples of the matrix component which can be used include: conventionally known inorganic oxides and inorganic compounds derived from silica gel, silica sol, silica hydrosol, alumina gel, alumina sol, silica alumina gel, silica alumina sol, aluminum phosphate compounds and the like. Among these, silica
10 sol, silica hydrosol, alumina sol, silica alumina sol, aluminum phosphate compounds and the like can be suitably used, because they are capable of serving as a carrier (base material) or a binder of the faujasite-type zeolite, and allow for obtaining a catalyst for catalytic cracking of hydrocarbons which is excellent in
15 activity, abrasion resistance and the like, and which is also excellent in the cracking activity for distillation residue, metal resistance and the like.

[0035]

As alumina, air flow calcined alumina powder used in the
20 catalyst disclosed in JP 60-193543 A (Patent Document 4) can also be suitably used. Activated alumina can also be used. There are cases where activated alumina binds to a silica component, thereby contributing to the activity.

[0036]

The catalyst for catalytic cracking of hydrocarbons according to the present invention containing phosphorus and magnesium, preferably contains alumina. The content of alumina in terms of solid (Al_2O_3) is preferably within the range of from 1 to 30% by weight, and more preferably, within the range of from 2 to 20% by weight.

[0037]

If the matrix component contains alumina within the above mentioned range, it is possible to obtain a catalyst for catalytic cracking of hydrocarbons whose cracking activity and selectivity are significantly improved, and which is excellent in cracking activity for distillation residue and in metal resistance, when the magnesium component and phosphorus component to be described later are incorporated to the catalyst.

[0038]

Further, in the present invention, a conventionally known clay mineral, such as kaolin, metakaolin, hydrotalcite, montmorillonite or the like can be used as a filler. These clay minerals have no activity, and serve as an extender.

[0039]

The content of the matrix component in terms of solid in the catalyst for catalytic cracking of hydrocarbons is preferably within the range of from 50 to 90% by weight, and more preferably from 60 to 85% by weight.

[0040]

Too low a content of the matrix component in terms of solid results in too high a content of the faujasite-type zeolite. As a result, there are cases where the obtained catalyst has too low
5 a bulk density despite a high activity, or has an insufficient abrasion resistance, fluidity and the like. In such a case, the catalyst is not practical to be used as a catalyst for catalytic cracking of hydrocarbons, particularly, as a catalyst for fluid catalytic cracking of hydrocarbons.

10 [0041]

On the other hand, too high a content of the matrix component in terms of solid results in too low a content of the faujasite-type zeolite, which is a main active ingredient of the catalyst, and there are cases where the resulting catalyst has an insufficient
15 cracking activity.

[0042]

In the present invention, a magnesium component, a phosphorus component, and a rare earth component are used. By incorporating these components, a catalyst excellent in cracking
20 performance and gasoline selectivity can be obtained.

[0043]

Magnesium component

The catalyst for catalytic cracking of hydrocarbons according to the present invention contains a magnesium component,

as MgO, in an amount within the range of from 0.05 to 3% by weight, and more preferably, within the range of from 0.1 to 2.5% by weight. The magnesium component is usually contained in the catalyst in the form of ion, oxide or hydroxide. In the present invention,
5 a catalyst excellent in cracking performance and gasoline selectivity can be obtained, by incorporating a magnesium component.

[0044]

If the content of the magnesium component is too low, there
10 are cases where a sufficient effect of improving the hydrothermal resistance cannot be obtained, or where the cracking activity and the selectivity of the resulting catalyst for catalytic cracking of hydrocarbons are decreased, depending on the content of the phosphorus component to be described later. If the content of
15 the magnesium component is too high, on the other hand, while it depends on the type and the content of the faujasite-type zeolite used, there are cases where the magnesium component cannot be carried by the zeolite, and even if it could be carried, the efficiency of the zeolite to carry the magnesium component may
20 be significantly reduced. In addition, there are cases where the resulting catalyst has an insufficient cracking activity, gasoline selectivity, hydrothermal resistance and the like, depending on the content of the phosphorus component to be described later.

[0045]

Phosphorus component

The catalyst for catalytic cracking of hydrocarbons according to the present invention preferably contains a
5 phosphorus component, as P_2O_5 , within the range of from 0.1 to 10% by weight, and more preferably, within the range of from 0.2 to 5% by weight. By containing the phosphorus component, a catalyst excellent in cracking activity, hydrothermal resistance, and metal resistance can be obtained.

10 [0046]

The phosphorus component is contained in the form of phosphate ion or phosphorus oxide.

[0047]

If the content of the phosphorus component is too low, there
15 are cases where the resulting catalyst for catalytic cracking of hydrocarbons has an insufficient cracking activity, selectivity, cracking activity for distillation residue, metal resistance, hydrothermal resistance and the like, depending on the content of the above mentioned magnesium component.

20 [0048]

If the content of the phosphorus component is too high, there also are cases where the resulting catalyst for catalytic cracking of hydrocarbons has a reduced cracking activity, selectivity, cracking activity for distillation residue, metal resistance,

hydrothermal resistance and the like. The reason for this is not known. However, a conceivable explanation may be that an excessive amount of the phosphorus component causes to reduce the crystallinity of the faujasite-type zeolite, or to clog the micropores of the catalyst, or the like.

[0049]

Particularly, in the present invention, since the phosphorus component is incorporated in the catalyst in combination with the magnesium component, it is possible to improve the cracking activity, selectivity, cracking activity for distillation residue, metal resistance, hydrothermal resistance and the like of the resulting catalyst.

[0050]

If the content of the phosphorus component (C_p) in terms of P_2O_5 is greater than 10% by weight, there are cases where the cracking activity, selectivity, cracking activity for distillation residue, metal resistance, hydrothermal resistance and the like of the catalyst for catalytic cracking of hydrocarbons may be reduced, depending on the content of the faujasite-type zeolite, the content of alumina as the above mentioned matrix component, and the content of the above mentioned magnesium component.

[0051]

Further, it is preferred that phosphorus component be used

in an amount such that the ratio $(C_P) / (C_M)$ (the weight ratio, each in terms of oxide) of the content of the phosphorus component (C_P) to the content of the magnesium component (C_M) is within the range of from 0.1 to 8, and more preferably, within the range of
5 from 0.2 to 5.

[0052]

Rare earth component

The catalyst for catalytic cracking of hydrocarbons according to the present invention may also contain a rare earth
10 component. The content of the rare earth component in terms of RE_2O_3 is preferably within the range of from 0.1 to 2% by weight, and more preferably, within the range of from 0.2 to 1.5% by weight. By incorporating the rare earth component, it is possible to obtain a catalyst excellent in cracking activity, selectivity of gasoline
15 and the like.

[0053]

Examples of the rare earth component include rare earth metals such as lanthanum, cerium, and neodymium; and mixtures of these metals. Usually, mixed rare earths comprising as major
20 components lanthanum and cerium are used.

[0054]

If the content of the rare earth component in terms of RE_2O_3 in the catalyst for catalytic cracking of hydrocarbons is too low, the cracking activity, selectivity, hydrothermal resistance,

metal resistance and the like of the catalyst may be insufficient, depending on the content of the above mentioned magnesium component.

[0055]

5 If the content of the rare earth component in terms of RE_2O_3 in the catalyst for catalytic cracking of hydrocarbons is too high, on the other hand, it is difficult for the catalyst to carry the rare earth component, when the catalyst is produced by the method according to the present invention. Even if the rare earth
10 component could be carried by the catalyst, its content being too high is not preferred, because the effect of carrying the rare earth component, in other words, the effect of further improving the cracking activity, selectivity, hydrothermal resistance, metal resistance and the like cannot be obtained, and the
15 efficiency of the catalyst to carry the rare earth component is significantly reduced.

[0056]

The above described catalyst for catalytic cracking of hydrocarbons can be suitably used as a catalyst for fluid catalytic
20 cracking of hydrocarbons, and in this case, the average particle diameter of the catalyst is preferably within the range of from 40 to 100 μm , and more preferably within the range of from 50 to 80 μm .

[0057]

The catalyst for catalytic cracking of hydrocarbons according to the present invention can be produced by a method described below.

[0058]

5 Method for producing catalyst for catalytic cracking of hydrocarbons

The method for producing the catalyst for catalytic cracking of hydrocarbons according to the present invention includes the following steps (a) to (f):

- 10 (a) a step of spray drying a mixed slurry of a faujasite-type zeolite and a matrix-forming component in a hot air flow to form minute spherical particles;
- (c) a step of subjecting the resultant to ion exchange with magnesium ions;
- 15 (e) a step of bringing the resultant into contact with phosphate ions; and
- (f) a step of drying the resultant.

Step (a)

A mixed slurry of a faujasite-type zeolite and a
20 matrix-forming component is spray dried in a hot air flow to form minute spherical particles.

[0059]

As the faujasite-type zeolite, the above mentioned faujasite-type zeolite is used. Among these, an ultra-stable

zeolite can be suitably used. As the matrix-forming component, the above mentioned matrix component, or one which turns into the matrix component after being incorporated into the catalyst, such as silica gel, silica sol, alumina gel, alumina sol, silica alumina gel, silica alumina sol, an aluminum phosphate compound or the like can be suitably used.

[0060]

The mixed slurry may contain the above mentioned extender.

[0061]

The concentration of the mixed slurry is not particularly limited, as long as a catalyst for catalytic cracking having a desired average particle diameter, particle size distribution, abrasion resistance and the like can be obtained. Generally, it is preferred that the concentration of the mixed slurry be within the range of from 10 to 50% by weight, and more preferably, within the range of from 20 to 40% by weight. If the concentration is within the above mentioned range, the spray drying can be performed easily, and the particle size and the particle size distribution can be adjusted to desired values.

[0062]

If the concentration of the mixed slurry is too low, the economic efficiency may be reduced, because the slurry contains large amount of water that evaporates during the spray drying, and thus requires a large amount of thermal energy. In addition,

there are cases where a catalyst having a desired average particle diameter and particle size distribution cannot be obtained, or where the bulk density is decreased to result in an insufficient fluidity. If the concentration of the slurry is too high, on the other hand, the viscosity of the mixed slurry may be too high, resulting in a difficulty to perform the spray drying, or a failure to obtain a catalyst having a desired average particle diameter and particle size distribution.

[0063]

The method of spray drying is not particularly limited as long as a catalyst for catalytic cracking having a desired average particle diameter, particle size distribution, abrasion resistance and the like can be obtained, and a conventionally known method can be used. For example, a conventionally known method such as a rotating disk method, pressure nozzle method, two-fluid nozzle method or the like can be used.

In general, the inlet temperature of the hot air used in the spray drying is preferably within the range of from 250 to 500°C, and the outlet temperature is preferably within the range of from 150 to 250°C.

[0064]

In the present invention, in general, the average particle diameter of the minute spherical particles is preferably within the range of from 40 to 100 μm , and more preferably within the

range of from 50 to 80 μm . The particle size is evaluated based on the measurement by the dry-type micromesh sieve method, and the value at 50% by weight is determined as the average particle diameter.

5 [0065]

In the present invention, it is preferred that the following step (b) be carried out after the above mentioned step (a).

[0066]

Step (b)

10 Then, the minute spherical particles are washed.

[0067]

Washing is carried out in order to remove catalyst poisons such as alkali metals, Cl^- , SO_4^{2-} and the like which may be included in the above mentioned faujasite-type zeolite or the

15 matrix-forming component. It is preferred that these catalyst poisons are reduced as much as possible. In general, the content of the alkali metals in terms of alkali metal oxides is preferably 1% by weight or less, and more preferably, 0.5% by weight or less. In general, the content of anions such as Cl^- , SO_4^{2-} and the like

20 is preferably 2% by weight or less, and more preferably 1% by weight or less.

[0068]

Usually, the minute spherical particles can be washed with splashing water, preferably hot water. However, an aqueous

solution of ammonium salts, such as ammonium sulphate, ammonium chloride and the like; hot aqueous ammonia; or the like can also be used to wash the minute spherical particles.

[0069]

5 Step (c)

Then, magnesium is introduced into the minute spherical particles by subjecting the particles to ion exchange with magnesium ions.

[0070]

10 The ion exchange with magnesium ions can be carried out, for example, by bringing the washed minute spherical particles into contact with an aqueous magnesium compound solution, or preferably, by dispersing the washed minute spherical particles in the aqueous magnesium compound solution.

15 [0071]

Examples of the magnesium compound include magnesium chloride, magnesium nitrate, magnesium sulfate and the like. The magnesium compound is used in an amount such that the content of magnesium (C_M) in terms of MgO in the resulting catalyst for
20 catalytic cracking of hydrocarbons is within the range of from 0.05 to 3% by weight, and more preferably within the range of from 0.1 to 2.5% by weight.

[0072]

In addition, it is preferred that the magnesium compound

be used in an amount such that the ratio $(C_M) / (C_Z)$ of the content of magnesium (C_M) to the content (C_Z) of the faujasite-type zeolite in the resulting catalyst for catalytic cracking of hydrocarbons is within the range of from 0.001 to 0.1, and more preferably within
5 the range of from 0.002 to 0.08.

[0073]

If the above mentioned ratio $(C_M) / (C_Z)$ is too low, there are cases where the effect of improving the hydrothermal stability, cracking activity, selectivity and the like of the catalyst for
10 catalytic cracking of hydrocarbons is insufficient. If the ratio $(C_M) / (C_Z)$ is too high, on the other hand, it may be difficult for the faujasite-type zeolite to carry magnesium, and, even if magnesium could be carried, the hydrothermal stability, cracking activity, selectivity and the like of the catalyst for catalytic
15 cracking of hydrocarbons may not be improved, and the catalyst may have an insufficient hydrothermal stability, depending on the content of the phosphorus component.

[0074]

The pH of a dispersion liquid obtained by dissolving the
20 minute spherical particles in the aqueous magnesium compound solution is preferably within the range of from 3 to 8, and more preferably, within the range of from 4 to 7.5. Usually, aqueous ammonia is used in order to increase the pH of the dispersion liquid, and an aqueous solution of an acid, such as sulfuric acid,

hydrochloric acid or nitric acid, is used in order to reduce the pH.

[0075]

If the pH of the dispersion liquid obtained by dissolving
5 the minute spherical particles in the aqueous magnesium compound
solution is too low, there are cases where the crystallinity of
the faujasite-type zeolite contained in the particles may be
reduced, depending on the type of faujasite-type zeolite used,
resulting in an insufficient cracking activity. In addition,
10 when alumina is contained as the matrix-forming component, there
are cases where the alumina is dissolved out of the minute
spherical particles, and the effect of using alumina, the effect
of improving the capacity to carry the phosphorus component, and
the effect of carrying the phosphorus component cannot be obtained
15 sufficiently.

[0076]

If the pH of the dispersion liquid obtained by dissolving
the minute spherical particles in the aqueous magnesium compound
solution is too high, on the other hand, there are cases where
20 the amount of the magnesium component carried by the minute
spherical particles may be insufficient, or where the effect of
further reducing the alkali metal (Na_2O) may not be obtained. In
addition, in cases where silica sol, which is a type of matrix
component, is used, the abrasion resistance of the resulting

catalyst for catalytic cracking of hydrocarbons may be insufficient. The following step (d) can be carried out before or after performing the above mentioned step (c).

[0077]

5 Step (d)

Next, a rare earth(s) is introduced into the minute spherical particles by subjecting the particles to ion exchange with rare earth ions.

[0078]

10 It is preferred that minute spherical particles be washed by splashing water or hot water before being subjected to the ion exchange with rare earth ions, in order to eliminate anions included in the magnesium compound, and in cases where excessive magnesium ions exist, to eliminate residual magnesium ions.

15 [0079]

The ion exchange with rare earth ions can be carried out, for example, by bringing the magnesium ion-exchanged minute spherical particles into contact with an aqueous solution of a rare earth compound, or preferably by dispersing the magnesium
20 ion-exchanged minute spherical particles into the aqueous solution of the rare earth compound.

[0080]

Examples of the rare earth compound include lanthanum chloride, cerium chloride, lanthanum nitrate, cerium nitrate,

lanthanum sulfate, cerium sulfate and the like; and water-soluble compounds of mixed rare earths comprising lanthanum and cerium as major components, and the like.

[0081]

5 It is preferred that the rare earth compound be used in an amount such that the content (C_M) of the rare earth(s) in terms of RE_2O_3 in the resulting catalyst for catalytic cracking of hydrocarbons is within the range of from 0.1 to 2% by weight, and more preferably, within the range of from 0.2 to 1.5% by weight.

10 [0082]

 The pH of a dispersion liquid used when carrying out the ion exchange with rare earth (RE) ions is preferably within the range of from 4 to 6, and more preferably, within the range of from 4.5 to 5.5. If the pH of the dispersion liquid used when
15 carrying out the ion exchange with rare earth ions is less than 4, there are cases where the ion exchange with rare earth ions cannot be sufficiently achieved, or where the magnesium ions which are already carried by the minute spherical particles are desorbed therefrom.

20 [0083]

 If the pH of the dispersion liquid used when carrying out the ion exchange with rare earth ions is greater than 6, there are cases where the rare earth ions are converted into hydroxides, and deposit on the catalyst without being ion-exchanged with

zeolite, resulting in a failure to provide the effect of improving the cracking activity, selectivity, hydrothermal resistance, metal resistance and the like. After being subjected to the ion exchange with rare earth ions, it is preferred that the minute spherical particles be washed by splashing water or hot water to remove anions contained in the rare earth compound.

[0084]

Step (e)

Then, phosphorus is introduced into the minute spherical particles by bringing the particles into contact with phosphate ions.

[0085]

Examples of the phosphoric acid compound used to introduce phosphate ions into the minute spherical particles include:

orthophosphoric acid, triammonium orthophosphate, diammonium hydrogen orthophosphate, diammonium hydrogen orthophosphate, pyrophosphoric acid, ammonium pyrophosphate, diammonium dihydrogen pyrophosphate and the like.

[0086]

Among these, orthophosphoric acid and pyrophosphoric acid can be efficiency introduced, and the resulting catalyst for catalytic cracking of hydrocarbons is excellent in cracking activity, selectivity, cracking activity for distillation residue, metal resistance, hydrothermal resistance and the like.

[0087]

Introduction of phosphorus can be carried out by adding the above mentioned phosphoric acid compound to a dispersion liquid of the minute spherical particles into which magnesium, and rare
5 earth(s) as necessary, have been introduced. It is preferred that the phosphoric acid compound be used in an amount such that the content (C_P) of phosphoric acid in terms of P_2O_5 in the resulting catalyst for catalytic cracking of hydrocarbons is within the range of from 0.1 to 10% by weight, and more preferably, within
10 the range of from 0.2 to 8% by weight.

[0088]

If the content of phosphoric acid (C_P) in terms of P_2O_5 is less than 0.1% by weight, there are cases where the effect of improving the cracking activity, selectivity, cracking activity
15 for distillation residue, metal resistance, and hydrothermal resistance of the resulting catalyst for catalytic cracking of hydrocarbons may not be sufficiently obtained.

[0089]

If the content of phosphoric acid (C_P) in terms of P_2O_5 is
20 greater than 10% by weight, there are cases where the cracking activity, selectivity, activity for cracking residual oil, metal resistance, hydrothermal resistance and the like of the resulting catalyst for catalytic cracking of hydrocarbons may be reduced, depending on the content of the faujasite-type zeolite, the

content of alumina as the matrix component, and the content of the magnesium component. Further, it is preferred that the phosphoric acid compound be used in an amount such that the ratio $(C_P) / (C_M)$ of the content of the phosphoric acid (C_P) to the content of the magnesium component (C_M) be within the range of from 0.1 to 8, and more preferably, within the range of from 0.2 to 5.

[0090]

If the ratio $(C_P) / (C_M)$ is not within the above mentioned range, the effect of incorporating the phosphoric acid in combination with the magnesium component, in other words, the effect of improving the cracking activity, selectivity, cracking activity for distillation residue, metal resistance, hydrothermal resistance and the like may not be sufficiently obtained.

[0091]

The pH of the dispersion liquid of the minute spherical particles, which is used when bringing these particles into contact with phosphate ions, is not particularly limited, as long as the above mentioned specified amount of phosphoric acid can be introduced, and it varies depending on the type of the phosphoric acid compound used. However, in general, the pH of the dispersion liquid is preferably within the range of from 2 to 6, and more preferably, within the range of from 3 to 5.

[0092]

If the pH of the dispersion liquid of the minute spherical particles, which is used when introducing phosphorus into these particles, is too low, the dispersion liquid is strongly acidic, and there is a possibility that the crystallinity of the zeolite
5 contained in the minute spherical particles may be reduced, resulting in a decrease in the cracking activity and selectivity of the resulting catalyst. If the pH of the dispersion liquid is too high, on the other hand, the dispersibility of the phosphorus component is reduced, and the effect of improving the
10 hydrothermal resistance may be insufficient.

[0093]

Step (f)

Next, the dispersion liquid of the minute spherical particles is filtered to separate the minute spherical particles,
15 and the separated particles are dried.

[0094]

The method for drying the minute spherical particles is not particularly limited, as long as water contained in the particles can be reduced to the range of from 8 to 15% by weight, in general,
20 and a conventionally known drying method can be used.

[0095]

For example, in cases where a large amount of minute spherical particles are produced, industrially, a rotary dryer (rotary kiln) can be suitably used.

[0096]

In the catalyst for catalytic cracking of hydrocarbons thus obtained, the content of the faujasite-type zeolite (C_z) in terms of solid is within the range of from 10 to 50% by weight; the content
5 of phosphorus (C_p) in terms of P_2O_5 is within the range of from 0.1 to 10% by weight; and the content of magnesium (C_M) in terms of MgO is within the range of from 0.05 to 3% by weight.

[0097]

Further, in cases where the catalyst for catalytic cracking
10 of hydrocarbons is a catalyst for fluid catalytic cracking, the average particle diameter of the catalyst is within the range of from 40 to 80 μm . The particle size of the catalyst can be controlled by adjusting the average particle diameter of the minute spherical particles to a predetermined range when preparing
15 them in step (a), for example, by adjusting the viscosity of the dispersion liquid, the nozzle system, and the amount of the dispersion liquid sprayed, as appropriate.

EXAMPLES

[0098]

20 The present invention will now be described with reference to Examples. It should be noted, however, that the present invention is in no way limited by the following Examples.

[0099]

[Example 1]

Preparation of faujasite-type zeolite (1)

A quantity of 1 kg of NaY zeolite (the molar ratio: $\text{SiO}_2 / \text{Al}_2\text{O}_3 = 5.2$, lattice constant = 24.66 Angstrom; manufactured by JGC C&C) was dispersed in 10 kg of pure water, and the temperature
5 of the resultant was elevated to 60°C. Then 2 molar equivalent of ammonium sulphate relative to the amount of the NaY zeolite was added to the resultant, followed by ion exchange for 1 hour. The resultant was then filtered, thoroughly washed with hot water, and dried at 130°C for 10 hours, to prepare ammonium ion-exchanged
10 zeolite powder (1). At this time, in the obtained ammonium ion-exchanged zeolite powder (1), NH_4 ion-exchange ratio was 65%, and the ratio of residual Na ions was 35% (this is referred to as $\text{NH}_{4(65)}\text{Na}_{(35)}\text{Y}$).

Next, the resulting ammonium ion-exchanged zeolite powder
15 was baked at 500°C for 4 hours to obtain $\text{H}_{(65)}\text{Na}_{(35)}\text{Y}$ powder, which was then dispersed again in 5 kg of aqueous ammonium sulphate solution having a concentration of 40% by weight, and the temperature of the obtained dispersion liquid was elevated to 60°C, and the pH of the dispersion liquid was adjusted to 4.5, followed
20 by ion exchange for 8 hours. Then the resultant was thoroughly washed by splashing hot water and dried at 150°C for 10 hours to prepare ammonium ion-exchanged zeolite powder (2). At this time, in the obtained ammonium ion-exchanged zeolite powder (2), the NH_4 ion-exchange ratio was 90%, and the ratio of residual Na ions

was 10% (this is referred to as $\text{NH}_{4(90)}\text{Na}_{(10)}\text{Y}$).

The resulting ammonium ion-exchanged zeolite powder (2) was filled in a stainless container, and subjected to heat treatment at a temperature of 700°C for 1 hour, in a saturated water vapor atmosphere, using a rotary steaming apparatus, to prepare faujasite-type zeolite (1), as an ultra-stable zeolite.

[0100]

The molar ratio: $\text{SiO}_2 / \text{Al}_2\text{O}_3$, the Na_2O content, the lattice constant, and the specific surface area of the resulting faujasite-type zeolite (1) were measured, and the results are shown in the Table.

[0101]

Preparation of catalyst (1) for catalytic cracking of hydrocarbons

A commercially available water glass #3 and sulfuric acid were rapidly stirred and mixed, to prepare silica hydrosol having a concentration of 12.5% by weight in terms of SiO_2 . To 4,000 g of the above mentioned silica hydrosol, 1,125 g (dry basis) of kaolin, 125 g (dry basis) of activated alumina, and 750 g (dry basis) of faujasite-type zeolite (1) were added, to prepare mixed slurry (1) having a solids concentration of 30%.

[0102]

Then, mixed slurry (1) having a solids concentration of 30% was sprayed into a hot air flow having an inlet temperature of 250°C , to prepare minute spherical particles (1). At this time,

the average particle diameter of the minute spherical particles (1) was 65 μm , and the outlet temperature of the hot air flow was 150°C. (step (a))

A quantity of 2,000 g, in dry weight, of the resulting minute spherical particles (1) were suspended in 10 kg of hot water, which amounted to 5 times the amount of the minute spherical particles (1), followed by addition of 203 g of ammonium sulphate, which was an equimolar amount as alumina in faujasite-type zeolite (1) contained in the minute spherical particles (1). The resultant was then dehydrated and washed with splashing water. (step (b))

The washed minute spherical particles (1) were suspended in 10 kg of hot water, and 200 g of aqueous magnesium chloride solution having a concentration of 10% by weight in terms of MgO was added to the resultant, followed by ion exchange at 60°C for 30 minutes. At this time, aqueous ammonia having a concentration of 15% by weight was added to adjust the pH of the resultant to 5.5. The resultant was then dehydrated and washed with splashing water. (step (c))

Then the thus obtained magnesium ion-exchanged minute spherical particles (1) were then suspended in 10 kg of hot water, and followed by addition of 14.1 g of aqueous H_3PO_4 solution having a concentration of 85% by weight in terms of P_2O_5 . The pH of the resultant at this time was adjusted to 4. The resultant was then dehydrated and washed with splashing water. (step (e))

The washed minute spherical particles (1) carrying the magnesium component and the phosphorus component were dried at 150°C using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (1) for catalytic cracking of hydrocarbons. (step (f)) The MgO content, the P₂O₅ content and the average particle diameter of the resulting catalyst (1) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. Further, the catalytic performance of the catalyst (1) for catalytic cracking of hydrocarbons was evaluated according to the following conditions, and results are shown in the Table.

[0103]

Performance test

First, the catalyst (1) for catalytic cracking of hydrocarbons was pseudo-equilibrated according to the following conditions, and the cracking performance thereof was evaluated.

[0104]

Pseudo-equilibration

The catalyst (1) for catalytic cracking of hydrocarbons was baked at 600°C for 1 hour, and then allowed to absorb a solution of nickel naphthenate and vanadium naphthenate in benzene such that the concentrations of the nickel and vanadium were 2,000 ppm and 4,000 ppm, respectively. Then the catalyst was dried at 110°C, followed by baking at 600°C for 1.5 hours. The resultant was then

subjected to steam treatment at 780°C for 6 hours, and baked again at 600°C for 1 hour to complete pseudo-equilibration.

[0105]

Cracking performance

5 A cracking reactor (ACE-MAT, model R +; manufactured by Kayser Technology Inc.) was used.

[0106]

Raw material oil: desulfurized atmospheric residue (DSAR)

Ratio of the catalyst / raw material (C/O): 5

10 Reaction temperature: 520°C

Space velocity: 8 hr⁻¹

Boiling range of gasoline: C₅ to 216°C

Boiling range of light cycle oil (LCO): 216°C to 343°C

Boiling range of heavy cycle oil (HCO): 343°C or more

15 Conversion ratio (% by weight) = 100 - (LCO + HCO % by weight)
(% by weight)

Hydrothermal resistance

The same procedure as described above was repeated to carry out the pseudo-equilibration and the evaluation of the cracking
20 performance, except that the pseudo-equilibration was performed at a temperature of 800°C. The conversion ratio (2) at this time is shown in the Table. Further, the ratio: conversion ratio (2) / conversion ratio (1) of the conversion ratio (2) at this time to the conversion ratio (1) as measured above, is shown in the

Table, as the hydrothermal resistance. The higher the ratio is, the higher the hydrothermal resistance is.

[0107]

[Example 2]

5 Preparation of catalyst (2) for catalytic cracking of hydrocarbons

The same procedure as in Example 1 was carried out except that, in step (c), 24 g of aqueous magnesium chloride solution having a concentration of 10% by weight in terms of MgO was added, to prepare catalyst (2) for catalytic cracking of hydrocarbons.

10 [0108]

The MgO content, the P_2O_5 content, and the average particle diameter of the resulting catalyst (2) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. Further, the catalytic performance and the hydrothermal

15 resistance of the catalyst (2) for catalytic cracking of hydrocarbons were evaluated, and the results are shown in the Table.

[0109]

[Example 3]

20 Preparation of catalyst (3) for catalytic cracking of hydrocarbons

The same procedure as in Example 1 was carried out except that, in step (c), 400 g of aqueous magnesium chloride solution having a concentration of 10% by weight in terms of MgO was added, to prepare catalyst (3) for catalytic cracking of hydrocarbons.

[0110]

The MgO content, the P_2O_5 content, and the average particle diameter of the resulting catalyst (3) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table.

5 Further, the catalytic performance and the hydrothermal resistance of the catalyst (3) for catalytic cracking of hydrocarbons were evaluated, and the results are shown in the Table.

[0111]

10 [Example 4]

Preparation of catalyst (4) for catalytic cracking of hydrocarbons

The same procedure as in Example 1 was carried out except that, in step (e), 6.8 g of aqueous H_3PO_4 solution having a concentration of 85% by weight in terms of P_2O_5 was added, to prepare
15 catalyst (4) for catalytic cracking of hydrocarbons.

[0112]

The MgO content, the P_2O_5 content, and the average particle diameter of the resulting catalyst (4) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table.

20 Further, the catalytic performance and the hydrothermal resistance of the catalyst (4) for catalytic cracking of hydrocarbons were evaluated, and the results are shown in the Table.

[0113]

[Example 5]

Preparation of catalyst (5) for catalytic cracking of hydrocarbons

The same procedure as in Example 1 was carried out except that, in step (e), 162.4 g of aqueous H_3PO_4 solution having a
5 concentration of 85% by weight in terms of P_2O_5 was added, to prepare catalyst (5) for catalytic cracking of hydrocarbons.

[0114]

The MgO content, the P_2O_5 content, and the average particle diameter of the resulting catalyst (5) for catalytic cracking of
10 hydrocarbons were measured, and the results are shown in the Table. Further, the catalytic performance and the hydrothermal resistance of the catalyst (5) for catalytic cracking of hydrocarbons were evaluated, and the results are shown in the Table.

15 [0115]

[Example 6]

Preparation of catalyst (6) for catalytic cracking of hydrocarbons

A commercially available water glass #3 and sulfuric acid were rapidly stirred and mixed, to prepare silica hydrosol having
20 a concentration of 12.5% by weight in terms of SiO_2 . To 4,000 g of the above mentioned silica hydrosol, 1,375 g (dry basis) of kaolin, 125 g (dry basis) of activated alumina, and 500 g (dry basis) of faujasite-type zeolite (1) were added, to prepare mixed slurry (2) having a solids concentration of 30%.

[0116]

Then, mixed slurry (2) having a solids concentration of 30% was sprayed into a hot air flow having an inlet temperature of 250°C, to prepare minute spherical particles (2). At this time,
5 the average particle diameter of the minute spherical particles (2) was 65 μm , and the outlet temperature of the hot air flow was 150°C. (step (a))

A quantity of 2,000 g, in dry weight, of the resulting minute spherical particles (2) were suspended in 10 kg of hot water, which
10 amounted to 5 times the amount of the minute spherical particles (2), followed by addition of 135 g of ammonium sulphate, which was an equimolar amount as alumina in faujasite-type zeolite (1) contained in the minute spherical particles (1). The resultant was then dehydrated and washed with splashing water. (step (b))

15 The washed minute spherical particles (2) were suspended in 10 kg of hot water, and 200 g of aqueous magnesium chloride solution having a concentration of 10% by weight in terms of MgO was added to the resultant, followed by ion exchange at 60°C for 30 minutes. At this time, aqueous ammonia having a concentration
20 of 15% by weight was added to adjust the pH of the resultant to 5.5. The resultant was then dehydrated and washed with splashing water. (step (c))

Then the thus obtained magnesium ion-exchanged minute spherical particles (2) were then suspended in 10 kg of hot water,

and followed by addition of 14.1 g of aqueous H_3PO_4 solution having a concentration of 85% by weight in terms of P_2O_5 . The pH of the resultant at this time was adjusted to 4. The resultant was then dehydrated and washed with splashing water. (step (e))

5 The washed minute spherical particles (2) carrying the magnesium component and the phosphorus component were dried at 150°C using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (6) for catalytic cracking of hydrocarbons. (step (f)) The MgO content, the P_2O_5 content,
10 and the average particle diameter of the resulting catalyst (6) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. Further, the catalytic performance and the hydrothermal resistance of the catalyst (6) for catalytic cracking of hydrocarbons were evaluated, and the
15 results are shown in the Table.

[0117]

[Example 7]

Preparation of catalyst (7) for catalytic cracking of hydrocarbons

20 A commercially available water glass #3 and sulfuric acid were rapidly stirred and mixed, to prepare silica hydrosol having a concentration of 12.5% by weight in terms of SiO_2 . To 4,000 g of the above mentioned silica hydrosol, 875 g (dry basis) of kaolin, 125 g (dry basis) of activated alumina, and 1,000 g (dry basis) of faujasite-type zeolite (1) were added, to prepare mixed slurry

(3) having a solids concentration of 30%.

[0118]

Then, mixed slurry (3) having a solids concentration of 30% was sprayed into a hot air flow having an inlet temperature of 250°C, to prepare minute spherical particles (3). At this time, the average particle diameter of the minute spherical particles (3) was 65 μm , and the outlet temperature of the hot air flow was 150°C. (step (a))

A quantity of 2,000 g, in dry weight, of the resulting minute spherical particles (3) were suspended in 10 kg of hot water, which amounted to 5 times the amount of the minute spherical particles (3), followed by addition of 271 g of ammonium sulphate, which was an equimolar amount as alumina in faujasite-type zeolite (1) contained in the minute spherical particles (1). The resultant was then dehydrated and washed with splashing water. (step (b))

The washed minute spherical particles (3) were suspended in 10 kg of hot water, and 200 g of aqueous magnesium chloride solution having a concentration of 10% by weight in terms of MgO was added to the resultant, followed by ion exchange at 60°C for 30 minutes. At this time, aqueous ammonia having a concentration of 15% by weight was added to adjust the pH of the resultant to 5.5. The resultant was then dehydrated and washed with splashing water. (step (c))

Then the thus obtained magnesium ion-exchanged minute

spherical particles (3) were then suspended in 10 kg of hot water, and followed by addition of 14.1 g of aqueous H_3PO_4 solution having a concentration of 85% by weight in terms of P_2O_5 . The pH of the resultant at this time was adjusted to 4. The resultant was then
5 dehydrated and washed with splashing water. (step (e))

The washed minute spherical particles (3) carrying the magnesium component and the phosphorus component were dried at 150°C using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (7) for catalytic cracking
10 of hydrocarbons. (step (f))

The MgO content, the P_2O_5 content, and the average particle diameter of the resulting catalyst (7) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. Further, the catalytic performance and the hydrothermal
15 resistance of the catalyst (7) for catalytic cracking of hydrocarbons were evaluated, and the results are shown in the Table.

[0119]

[Example 8]

20 Preparation of catalyst (8) for catalytic cracking of hydrocarbons

The same procedure as in Example 1 was carried out to prepare magnesium ion-exchanged minute spherical particles (1). (step (c))

The magnesium ion-exchanged minute spherical particles (1)

were suspended in 10 kg of hot water, and 100 g of aqueous rare earth chloride solution having a concentration of 20% by weight in terms of RE_2O_3 was added, followed by ion exchange at 60°C for 30 minutes. At this time, aqueous ammonia having a concentration of 15% by weight was added to adjust the pH of the resultant to 5.5. The resultant was then dehydrated and washed with splashing water. (step (d))

Then the thus obtained rare earth ion-exchanged minute spherical particles (1) were suspended in 10 kg of hot water, followed by addition of 14.1 g of aqueous H_3PO_4 solution having a concentration of 85% by weight in terms of P_2O_5 . The pH of the resultant at this time was adjusted to 4. The resultant was then dehydrated and washed with splashing water (step (e)).

The washed minute spherical particles (1) carrying the magnesium component, the rare earth component and the phosphorus component were dried at 150°C using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (8) for catalytic cracking of hydrocarbons. (step (f))

The content of MgO , RE_2O_3 and P_2O_5 , and the average particle diameter of the resulting catalyst (8) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. Further, the catalytic performance and the hydrothermal resistance of the catalyst (8) for catalytic cracking of hydrocarbons were evaluated, and the results are shown in the

Table.

[0120]

[Example 9]

Preparation faujasite-type zeolite (2)

5 The ammonium ion-exchanged zeolite powder (2), which were prepared in the same manner as in Example 1, was filled in a stainless container, and subjected to heat treatment at a temperature of 760°C for 1 hour, in a saturated water vapor atmosphere, using a rotary steaming apparatus, to prepare
10 faujasite-type zeolite (2), as an ultra-stable zeolite.

[0121]

 The molar ratio: $\text{SiO}_2 / \text{Al}_2\text{O}_3$, the Na_2O content, the lattice constant, and the specific surface area of the resulting faujasite-type zeolite (2) were measured, and the results are
15 shown in the Table.

[0122]

Preparation of catalyst (9) for catalytic cracking of hydrocarbons

 The same procedure as in Example 1 was carried out, except that faujasite-type zeolite (2) was used instead of faujasite-type
20 zeolite (1), to prepare catalyst (9) for catalytic cracking of hydrocarbons.

[0123]

 The MgO content, the P_2O_5 content, and the average particle diameter of the resulting catalyst (9) for catalytic cracking of

hydrocarbons were measured, and the results are shown in the Table. In addition, the catalytic performance and the hydrothermal resistance of the catalyst (9) for catalytic cracking of hydrocarbons were evaluated and the results are shown in the Table.

5 [0124]

[Comparative Example 1]

Preparation of catalyst (R1) for catalytic cracking of hydrocarbons

The same procedure as in Example 1 was carried out, up to
10 step (c), to prepare magnesium ion-exchanged minute spherical particles (R1). Then the washed minute spherical particles (R1) carrying the magnesium component were dried at 150°C using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (R1) for catalytic cracking of hydrocarbons.

15 [0125]

The MgO content, and the average particle diameter of the resulting catalyst (R1) for catalytic cracking of hydrocarbons were measured and the results are shown in the Table. In addition, the catalytic performance and the hydrothermal resistance of the
20 catalyst (R1) for catalytic cracking of hydrocarbons were evaluated and the results are shown in the Table.

[0126]

[Comparative Example 2]

Preparation of catalyst (R2) for catalytic cracking of

hydrocarbons

The same procedure as in Example 1 was carried out, up to step (b), to prepare washed minute spherical particles (R2). Then the washed minute spherical particles (R2) were suspended in 10 kg of hot water, followed by addition of 14.1 g of aqueous H_3PO_4 solution having a concentration of 85% by weight in terms of P_2O_5 . At this time, the pH of the resultant was adjusted to 4. The resultant was then dehydrated and washed with splashing water.

[0127]

The washed minute spherical particles (R2) carrying the phosphorus component were dried at 150°C using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (R2) for catalytic cracking of hydrocarbons.

[0128]

The P_2O_5 content and the average particle diameter of the resulting catalyst (R2) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. In addition, the catalytic performance and the hydrothermal resistance of the catalyst (R2) for catalytic cracking of hydrocarbons were evaluated and the results are shown in the Table.

[0129]

[Comparative Example 3]

Preparation of catalyst (R3) for catalytic cracking of
hydrocarbons

The same procedure as in Example 1 was carried out, up to step (b), to prepare washed minute spherical particles (R3). Then the washed minute spherical particles (R3) were suspended in 10 kg of hot water, and 100 g of aqueous rare earth chloride solution having a concentration of 20% by weight in terms of RE_2O_3 was added to the resultant, followed by ion exchange at 60°C for 30 minute. At this time, aqueous ammonia having a concentration of 15% by weight was added to adjust the pH of the resultant to 5.5. The resultant was then dehydrated and washed with splashing water.

10 [0130]

The washed minute spherical particles (R3) carrying the rare earth component were dried at 150°C using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (R3) for catalytic cracking of hydrocarbons.

15 [0131]

The RE_2O_3 content and the average particle diameter of the resulting catalyst (R3) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. In addition, the catalytic performance and the hydrothermal resistance of the resulting catalyst (R3) for catalytic cracking of hydrocarbons were evaluated and the results are shown in the Table.

[0132]

[Comparative Example 4]

Preparation of catalyst (R4) for catalytic cracking of

hydrocarbons

The same procedure as in Comparative Example 3 was carried out, except that 400 g of aqueous rare earth chloride solution having a concentration of 20% by weight in terms of RE_2O_3 was added, followed by ion exchange at 60°C for 30 minute. At this time, aqueous ammonia having a concentration of 15% by weight was added to adjust the pH of the resultant to 5.5. The resultant was then dehydrated and washed with splashing water.

[0133]

The washed minute spherical particles (R4) carrying the rare earth component were dried at 150°C for 2 hours, using a drier, such that the water content of the particles was 10% by weight, to prepare catalyst (R4) for catalytic cracking of hydrocarbons.

[0134]

The RE_2O_3 content and the average particle diameter of the resulting catalyst (R4) for catalytic cracking of hydrocarbons were measured, and the results are shown in the Table. The utilization efficiency of the rare earth(s) at this time was as low as 60%.

[0135]

In addition, the catalytic performance and the hydrothermal resistance of the catalyst (R4) for catalytic cracking of hydrocarbons were evaluated and the results are shown in the Table.

[0136]

[Comparative Example 5]

Preparation of catalyst (R5) for catalytic cracking of
hydrocarbons

5 The same procedure as in Example 1 was carried out, up to
step (b), to prepare washed minute spherical particles (R5). Then
the washed minute spherical particles (R5) were dried at 150°C
for 2 hours, using a drier, to prepare catalyst (R5) for catalytic
cracking of hydrocarbons.

[0137]

10 The average particle diameter of the resulting catalyst (R5)
for catalytic cracking of hydrocarbons was measured, and the
results are shown in the Table. In addition, the catalytic
performance and the hydrothermal resistance of the catalyst (R5)
for catalytic cracking of hydrocarbons were evaluated and the
15 results are shown in the Table.

[0138]

[Table 1-1]

	Mixed slurry											
	Faujasite-type zeolite						Matrix-forming component					
	Type	SiO ₂ /Al ₂ O ₃	Lattice constant	Specific surface area	Na ₂ O content	Concentration	Binder		Filler (1)		Filler (2)	
		Molar ratio	Angstrom	m ² /g	% by weight	% by weight	Type	Concentration % by weight	Type	Concentration % by weight	Type	Concentration % by weight
Example 1	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Example 2	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Example 3	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Example 4	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Example 5	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Example 6	USY	5.1	24.56	650	4	6	silica hydrosol	6	kaolin	16.5	activated alumina	1.5
Example 7	USY	5.1	24.56	650	4	12	silica hydrosol	6	kaolin	10.5	activated alumina	1.5
Example 8	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Example 9	USY	5.3	24.45	700	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Comparative Example 1	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Comparative Example 2	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Comparative Example 3	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Comparative Example 4	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5
Comparative Example 5	USY	5.1	24.56	650	4	9	silica hydrosol	6	kaolin	13.5	activated alumina	1.5

[0139]

[Table 1-2]

	Production of catalyst for catalytic cracking of hydrocarbons										
	Spray drying		Step (c)			Step (d)			Step (e)		
	Inlet temperature °C	Outlet temperature °C	Magnesium compound		pH	Rare earth compound		pH	Phosphorus compound		pH
			type	Amount used % by weight		type	Amount used % by weight		type	Amount used % by weight	
Example 1	250	150	MgCl ₂	1.00	5.5	-	-	-	H ₃ PO ₄	0.4	4
Example 2	250	150	MgCl ₂	0.12	5.5	-	-	-	H ₃ PO ₄	0.4	4
Example 3	250	150	MgCl ₂	2.00	5.5	-	-	-	H ₃ PO ₄	0.4	4
Example 4	250	150	MgCl ₂	1.00	5.5	-	-	-	H ₃ PO ₄	0.2	4
Example 5	250	150	MgCl ₂	1.00	5.5	-	-	-	H ₃ PO ₄	5	4
Example 6	250	150	MgCl ₂	1.00	5.5	-	-	-	H ₃ PO ₄	0.4	4
Example 7	250	150	MgCl ₂	1.00	5.5	-	-	-	H ₃ PO ₄	0.4	4
Example 8	250	150	MgCl ₂	1.00	5.5	RECl ₃	1	5.5	H ₃ PO ₄	0.4	4
Example 9	250	150	MgCl ₂	1.00	5.5	-	-	-	H ₃ PO ₄	0.4	4
Comparative Example 1	250	150	MgCl ₂	1.00	5.5	-	-	-	-	-	-
Comparative Example 2	250	150	-	-	-	-	-	-	H ₃ PO ₄	14.1	4
Comparative Example 3	250	150	-	-	-	RECl ₃	1	5.5	-	-	-
Comparative Example 4	250	150	-	-	-	RECl ₃	4	5.5	-	-	-
Comparative Example 5	250	150	-	-	-	-	-	-	-	-	-

[0140]

[Table 1-3]

	Catalyst for catalytic cracking of hydrocarbons											
	Faujasite-type zeolite	Matrix component			MgO		RE ₂ O ₃		P ₂ O ₅	C _M /C _Z	C _P /C _M	Average particle diameter
		Binder	Filler (1)	Filler (2)								
	Content % by weight	Content % by weight	Content % by weight	Content % by weight	Content % by weight	Ratio of MgO carried %	Content % by weight	Ratio of RE ₂ O ₃ carried %	Content % by weight	Weight ratio	Weight ratio	μm
Example 1	29.6	19.8	44.5	4.9	0.8	80%	-	-	0.4	0.027	0.50	65
Example 2	29.8	19.9	44.8	5.0	0.12	100%	-	-	0.4	0.004	3.33	65
Example 3	29.5	19.6	44.2	4.9	1.4	70%	-	-	0.4	0.048	0.03	65
Example 4	29.7	19.8	44.6	5.0	0.8	80%	-	-	0.2	0.027	0.25	65
Example 5	28.6	19.1	42.9	4.8	0.8	80%	-	-	3.8	0.028	4.8	65
Example 6	19.8	19.8	54.3	4.9	0.8	80%	-	-	0.4	0.040	0.50	65
Example 7	39.5	19.8	34.6	4.9	0.8	80%	-	-	0.4	0.020	0.50	65
Example 8	29.4	19.6	44.1	4.9	0.8	80%	0.9	90%	0.4	0.027	0.50	65
Example 9	29.6	19.8	44.5	4.9	0.8	80%	-	-	0.4	0.033	0.40	65
Comparative Example 1	29.8	19.8	44.6	5.0	0.8	80%	-	-	-	0.027	-	65
Comparative Example 2	29.9	19.9	44.8	5.0	-	-	-	-	0.4	-	-	65
Comparative Example 3	29.7	19.8	44.6	5.0	-	-	0.9	90%	-	-	-	65
Comparative Example 4	29.3	19.5	43.9	4.9	-	-	2.4	60%	-	-	-	65
Comparative Example 5	30	20	45	5	-	-	-	-	-	-	-	65

[0141]

[Table 1-4]

	Activity							
	Conversion ratio (1) wt%	H ₂ wt%	Gasoline wt%	LCO wt%	HCO wt%	Coke wt%	Conversion ratio (2) wt%	Hydrothermal resistance / metal resistance
								Conversion ratio (2) / (1)
Example 1	68.5	0.7	45.4	17.5	14.0	7.0	61.3	0.89
Example 2	66.9	0.7	43.6	18.1	15.0	6.6	59.1	0.88
Example 3	69.3	0.7	46.2	17.6	13.1	7.3	62.4	0.90
Example 4	66.5	0.7	43.0	18.3	15.2	6.5	58.9	0.89
Example 5	67.2	0.7	44.1	18.1	14.7	6.6	59.7	0.89
Example 6	64.3	0.7	42.0	19.0	16.7	6.0	56.2	0.87
Example 7	72.4	0.7	46.2	15.3	12.3	7.6	65.4	0.90
Example 8	68.4	0.7	45.8	17.8	13.8	7.2	62.7	0.92
Example 9	68.2	0.7	45.5	17.8	14.0	6.8	62.6	0.92
Comparative Example 1	67.1	0.6	43.8	18.3	14.6	6.4	56.8	0.85
Comparative Example 2	66.7	0.7	42.7	18.1	15.2	6.7	58.4	0.88
Comparative Example 3	67.0	0.6	43.5	18.4	14.6	6.4	59.0	0.88
Comparative Example 4	68.7	0.7	45.2	17.4	13.9	7.1	61.0	0.89
Comparative Example 5	65.2	0.7	41.6	19.3	15.5	6.5	53.1	0.81

[0142]

In can be seen from the Tables shown above that, when the catalysts obtained in Examples are compared with those obtained in Comparative Examples, those obtained in Examples have a higher conversion ratio, and a better hydrothermal resistance and metal resistance, in general.

CLAIMS

1. A catalyst for catalytic cracking of hydrocarbons comprising a faujasite-type zeolite, a matrix component, a phosphorus component and a magnesium component,

5 wherein the content of the faujasite-type zeolite (C_z) in terms of solid is within the range of from 10 to 50 % by weight; the content of phosphorus (C_p) in terms of P_2O_5 is within the range of from 0.1 to 10 % by weight; and the content of magnesium (C_M) in terms of MgO is within the range of from 0.05 to 3% by weight.

10 2. The catalyst for catalytic cracking of hydrocarbons according to claim 1, wherein the ratio (C_p) / (C_M) of said content of phosphorus (C_p) to said content of magnesium (C_M) is within the range of from 0.1 to 8.

15 3. The catalyst for catalytic cracking of hydrocarbons according to claim 1 or 2, wherein the ratio (C_M) / (C_z) of said content of magnesium (C_M) to said content of the faujasite-type zeolite (C_z) is within the range of from 0.001 to 0.1.

20 4. The catalyst for catalytic cracking of hydrocarbons according to any one of claims 1 to 3, further comprising a rare earth, wherein the content of said rare earth in terms of RE_2O_3 is within the range of from 0.1 to 2% by weight.

5. The catalyst for catalytic cracking of hydrocarbons according to any one of claims 1 to 4, wherein said matrix component contains alumina, and wherein the content of alumina in terms of Al_2O_3 is within the range of from 1 to 30% by weight.

6. The catalyst for catalytic cracking of hydrocarbons according to any one of claims 1 to 5, wherein said faujasite-type zeolite is an ultra-stable zeolite (USY).

10

7. A method for producing a catalyst for catalytic cracking of hydrocarbons, comprising the following steps (a) to (f):

(a) a step of spray drying a mixed slurry of a faujasite-type zeolite and a matrix-forming component in a hot air flow to form minute spherical particles;

(c) a step of subjecting the resultant to ion exchange with magnesium ions;

(e) a step of bringing the resultant into contact with phosphate ions; and

(f) a step of drying the resultant.

20

8. The method for producing a catalyst for catalytic cracking of hydrocarbons according to claim 7, wherein the pH at the step (c) of ion exchange with magnesium ions is within the range of

from 3 to 8.

9. The method for producing a catalyst for catalytic cracking of hydrocarbons according to claim 7 or 8, wherein the pH at the
5 step (e) of contact with phosphate ions is within the range of from 2 to 6.

10. The method for producing a catalyst for catalytic cracking of hydrocarbons according to any one of claims 7 to 9, wherein
10 the following step (d) is carried out before or after carrying out said step (c):

(d) the step of performing ion exchange with rare earth ions.

11. The method for producing a catalyst for catalytic cracking
15 of hydrocarbons according to claim 10, wherein the pH at the step (d) of ion exchange with rare earth (RE) ions is within the range of from 4 to 6.

12. The method for producing a catalyst for catalytic cracking
20 of hydrocarbons according to any one of claims 7 to 11, wherein the following step (b) is carried out after said step (a):

(b) the step of performing washing.