

DESCRIPTION

Title of Invention: ADDITIVE FOR FLUID CATALYTIC CRACKING
CATALYST, AND METHOD FOR PRODUCING THE SAME

5

Technical Field

[0001]

The present invention relates to: an additive to be used
in fluid catalytic cracking (hereinafter, also referred to as
10 "FCC") together with a fluid catalytic cracking catalyst
(hereinafter, also referred to as "FCC catalyst") for
increasing the higher octane number of gasoline and
increasing the production of lower olefins; and a method for
producing the additive.

15

Background Art

[0002]

Fluid catalytic cracking apparatuses (hereinafter, also
referred to as "FCC apparatuses") in refineries are primarily
20 intended to produce a gasoline distillate by catalytically
cracking raw material hydrocarbon oil, and the gasoline is
desired to have a high octane number. Some refineries may be
required to generate a gasoline distillate by catalytically
cracking raw material hydrocarbon oil with an FCC apparatus,

and simultaneously to increase the production of lower olefins as petrochemical raw materials, in particular, propylene and butene.

[0003]

5 To meet the requirement, various methods have been proposed in which FCC is performed with addition of a composition containing pentasil-type zeolite such as ZSM-5-type zeolite (also referred to as an additive catalyst) to a catalyst for use in FCC.

10 [0004]

As such an additive, for example, Patent Literature 1 discloses a composition including pentasil-type zeolite and an inorganic oxide matrix and having many macropores with pore diameters of about 100 nm. Patent Literature 2
15 discloses a composition in the form of a particle including pentasil-type zeolite, a porous inorganic oxide, and phosphorus pentoxide, wherein the phosphorus pentoxide content in the surface part of the particle is higher than that in the center part of the particle. Patent Literature 3
20 discloses an additive for FCC catalysts as an additive capable of increasing the production of propylene and so on, the additive including a binder containing zeolite such as ZSM-5, a phosphate salts, clay, and silica. Moreover, Patent Literature 4 discloses an additive for FCC catalysts, the

additive including modified ZSM-5-type zeolite having specific properties, a filler, and a binder.

[0005]

Further, Patent Literature 5 discloses a catalyst with superior abrasion resistance, the catalyst containing a large amount of zeolite and also containing phosphorus and alumina, and this catalyst can be added to a catalyst and then used in FCC methods. Furthermore, Patent Literature 6 discloses an FCC catalyst including zeolite, kaolin, a phosphorus compound, a high-density nonreactive component, and optional reactive alumina, and this catalyst is also suitable as an additive for cracking processes using a molecular sieve component of large pore diameter.

Citation List

Patent Literature

[0006]

Patent Literature 1: JP-A 2005-270851

Patent Literature 2: JP-A 2007-244964

Patent Literature 3: JP-A 2014-527459

Patent Literature 4: WO 2017/82345

Patent Literature 5: JP-A 2002-537976

Patent Literature 6: JP-A 2007-534485

Summary of Invention

Technical Problem

[0007]

When raw material hydrocarbon oil to be catalytically
5 cracked is heavy hydrocarbon oil, in particular, residual oil
from atmospheric distillation, or residual oil from vacuum
distillation, the raw material hydrocarbon oil contains large
amounts of heavy metals such as vanadium and nickel.
Vanadium promotes dealumination from zeolite,
10 disadvantageously breaking the crystal structure to lower the
activity. Nickel causes generation of a large amount of coke
because of its high dehydrogenation activity. This coke
poisons active sites of FCC catalysts, and generates heat
when FCC catalysts are reactivated, promoting degradation of
15 zeolite.

[0008]

Conventional additives for FCC catalysts have had room
for further improvement in terms of obtaining lower olefins
such as propylene with high yields even when raw material
20 hydrocarbon oil to be catalytically cracked contains large
amounts of heavy metals.

[0009]

With considering such problems, an object of the present
invention is to provide: an additive for an FCC catalyst

(additive catalyst) that is used in FCC together with an FCC catalyst and can provide lower olefins such as propylene with high yields even when raw material hydrocarbon oil contains large amounts of heavy metals such as vanadium and nickel;
5 and a method for producing the additive.

Solution to Problem

[0010]

The summary of the present invention is as follows.

10 [1]

An additive for a fluid catalytic cracking catalyst, the additive comprising pentasil-type zeolite and an inorganic oxide matrix, wherein

the amount of the pentasil-type zeolite is 10 to 60% by
15 mass,

the additive contains 5 to 20% by mass of phosphorous in terms of mass of P_2O_5 , and

the inorganic oxide matrix contains an alumina component in such an amount that the amount of aluminum in terms of
20 Al_2O_3 is 2 to 20% by mass, relative to 100% by mass of the additive, and

the following formula (1) is satisfied:

$$0.02 \leq P(-25 \text{ ppm})/P(-30 \text{ ppm}) \leq 0.40 \dots (1)$$

wherein P(-25 ppm) and P(-30 ppm) are respectively a peak area ratio at -25 ppm and a peak area ratio at -30 ppm in ^{31}P -NMR measurement.

[0011]

5 [2]

A method for producing an additive for a fluid catalytic cracking catalyst, the method comprising:

spray-drying a slurry to obtain a powder; and

heating the powder at a temperature rising rate of

10 150°C/hour or higher, followed by heat-treating at 500 to 750°C, wherein the slurry includes:

pentasil-type zeolite;

a phosphorus-containing binder raw material;

at least one alumina component selected from the group

15 consisting of gibbsite and calcined products of gibbsite;

a filler consisting of an inorganic oxide differing from the alumina component; and

a dispersion medium, wherein

the amount of the pentasil-type zeolite is 10 to 60% by

20 mass,

the amount of the phosphorus-containing binder raw material is such an amount that the amount of phosphorous in terms of mass of P_2O_5 is 5 to 20% by mass, and

the amount of the alumina component is such an amount that the amount of aluminum in terms of mass of Al_2O_3 is 2 to 20% by mass,

all relative to 100% by mass of the solid content of the
5 slurry.

Advantageous Effects of Invention

[0012]

The additive for an FCC catalyst according to the
10 present invention can provide lower olefins such as propylene with high yields even when raw material hydrocarbon oil contains large amounts of heavy metals such as vanadium and nickel. The production method of the present invention enables production of an additive for an FCC catalyst that
15 can provide lower olefins such as propylene with high yields even when raw material hydrocarbon oil contains large amounts of heavy metals such as vanadium and nickel.

Description of Embodiments

20 [0013]

Hereinafter, the present invention will be described in more detail.

[Additive for FCC Catalyst]

The additive for an FCC catalyst according to the present invention is:

an additive for a fluid catalytic cracking catalyst, the additive containing pentasil-type zeolite and an inorganic
5 oxide matrix, wherein

the amount of the pentasil-type zeolite is 10 to 60% by mass,

the additive contains 5 to 20% by mass of phosphorous in terms of mass of P_2O_5 , and

10 the inorganic oxide matrix contains an alumina component in such an amount that the amount of aluminum in terms of Al_2O_3 is 2 to 20% by mass, relative to 100% by mass of the additive, and

the following formula (1) is satisfied:

15
$$0.02 \leq P(-25 \text{ ppm})/P(-30 \text{ ppm}) \leq 0.40 \dots (1)$$

wherein $P(-25 \text{ ppm})$ and $P(-30 \text{ ppm})$ are respectively a peak area ratio at -25 ppm and a peak area ratio at -30 ppm in ^{31}P -NMR measurement.

[0014]

20 The pentasil-type zeolite is dispersed in the inorganic oxide matrix.

Examples of the pentasil-type zeolite include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, and ZSM-48. ZSM-5 is particularly preferred because it has a solid acid

that has high acid strength and exhibits high shape selectivity to exerts a high effect of increasing the octane number of gasoline and yields of lower olefins.

[0015]

5 The amount of the pentasil-type zeolite in the additive for an FCC catalyst according to the present invention is 10% by mass or more, and more preferably 30% by mass or more in view of increasing yields of lower olefins such as propylene, and 60% by mass or less, and preferably 50% by mass or less
10 in view of preventing the decrease in the generation of lower olefins of interest due to overcracking and in view of retaining physical properties (e.g., formability or attrition resistance) applicable to actual use.

[0016]

15 The ratio between silica and aluminum contained in the pentasil-type zeolite in terms of the mass ratio of SiO_2 to Al_2O_3 (mass of SiO_2 /mass of Al_2O_3) is preferably 25 to 100.

[0017]

20 With the mass ratio being 25 or higher, the acid density on the pentasil-type zeolite is not excessively high, which prevents the overcracking of raw material hydrocarbon oil, thereby providing increased yields of lower olefins of interest. With the mass ratio being 100 or lower, the acid density on the pentasil-type zeolite is moderate, which

provides superior cracking activity for raw material hydrocarbon oil.

[0018]

The primary particle diameter of the pentasil-type zeolite is preferably 0.3 to 5 μm .

The primary particle diameter herein refers to median diameter (D50) measured with a method employed in Examples described later.

[0019]

The primary particle diameter of the pentasil-type zeolite is preferably 0.3 μm or larger, in view of preventing the decrease in yields of lower olefins due to the lowering of the hydrothermal resistance of the additive for an FCC catalyst and also preventing the lowering of ABD and deterioration of attrition due to the increase in voids among particles of the pentasil-type zeolite in the additive for an FCC catalyst.

[0020]

The primary particle diameter of the pentasil-type zeolite is preferably 5 μm or smaller, in view of preventing the lowering of catalyst activity due to the lowering of the dispersiveness of reaction fields given by a solid acid or pores of the zeolite in each particle of the additive for an FCC catalyst.

[0021]

The inorganic oxide matrix contains a binder to bond the components of the additive for an FCC catalyst, and this binder consists of an oxide containing phosphorus, and
5 preferably consists of an oxide containing phosphorus and aluminum.

[0022]

The amount of phosphorus in the additive for an FCC catalyst is 5% by mass or more and preferably 7% by mass or
10 more in terms of the amount of diphosphorus pentoxide (P_2O_5). The amount of phosphorus can be measured through ICP emission spectroscopy under conditions employed in Examples described later. With the amount of phosphorus in that range, the additive for an FCC catalyst is superior in attrition
15 resistance because of the high strength of the binder to bond together the pentasil-type zeolite, the alumina component, and the filler such as kaolin, and in addition, yields of lower olefins such as propylene in catalytic cracking of hydrocarbon oil can be increased because the hydrothermal
20 stability of the pentasil-type zeolite is retained. The amount of phosphorus according to the above conversion is 20% by mass or less and preferably 15% by mass or less. With the amount of phosphorus in this range, the pore volume of the additive for an FCC catalyst is not excessively small, which

allows reactants to diffuse in pores to increase yields of lower olefins such as propylene in catalytic cracking of hydrocarbon oil.

[0023]

5 The inorganic oxide matrix contains an alumina component. This alumina component is preferably obtained by subjecting at least one alumina component selected from the group consisting of gibbsite (one of aluminum hydroxides) and calcined products of gibbsite to heat treatment described
10 later.

[0024]

 The additive for an FCC catalyst according to the present invention contains the alumina component in the inorganic oxide matrix in such an amount that the amount of
15 aluminum in terms of Al_2O_3 is 2 to 20% by mass and preferably 2.5 to 15% by mass relative to 100% by mass of the additive. With the amount of the alumina component in that range, the decrease in the yield of propylene due to metal (heavy metals contained in raw material hydrocarbon oil, such as vanadium
20 and nickel) poisoning can be sufficiently suppressed in FCC, and catalyst physical properties (e.g., formability or attrition resistance) applicable to practical use can be retained.

[0025]

The inorganic oxide matrix may contain, as the binder, an optional binder other than the above-described oxide containing phosphorus and aluminum. Examples of the optional binder include inorganic oxides such as silica, silica-
5 magnesia, titania, zirconia, silica-zirconia, and calcium silicate.

The amount of the optional binder contained in the additive for an FCC catalyst according to the present invention is preferably 5 to 25% by mass and more preferably
10 10 to 15% by mass.

[0026]

The inorganic oxide matrix contains a filler consisting of an inorganic oxide that is commonly blended in additives for FCC catalysts. Examples of the filler include clay
15 minerals such as kaolin, bentonite, and halloysite, and kaolin is particularly preferred. The filler may be a heat-treated product of any of these clay minerals.

[0027]

The amount of the filler contained in the additive for
20 an FCC catalyst according to the present invention is an amount obtained by subtracting the total amount of the pentasil-type zeolite, the binder, and the alumina component from the amount of the additive for an FCC catalyst.

[0028]

The additive for an FCC catalyst according to the present invention satisfies the following formula (1):

$$0.02 \leq P(-25 \text{ ppm})/P(-30 \text{ ppm}) \leq 0.40 \dots (1)$$

In formula (1), $P(-25 \text{ ppm})$ and $P(-30 \text{ ppm})$ are
5 respectively a peak area ratio at -25 ppm and a peak area ratio at -30 ppm in ^{31}P -NMR measurement, and the details of them are as follows.

[0029]

The additive for an FCC catalyst is homogeneously filled
10 into an NMR sample tube with a diameter of 3.2 mm for solids, and the sample tube is set in an NMR apparatus (magnetic field strength: 14.1 T (^1H resonance frequency: 600 MHz)) and rotated at 20 kHz at a magic angle (54.7°) to the external magnetic field. A peak of $\text{NH}_4\text{H}_2\text{PO}_4$ is regarded as 1 ppm as a
15 secondary reference for chemical shift. A single pulse method is used with setting the pulse flip angle to 90° and pulse repetition time to 11.5 seconds.

[0030]

An obtained spectrum is analyzed as follows. First,
20 baseline correction is performed for the spectrum. Next, five peaks at chemical shifts of approximately -6 ppm, -18 ppm, -25 ppm, -30 ppm, and -37 ppm are separated into Voigt functions. Integrated intensity is calculated for all of the functions, and the ratio between the integrated intensity of

the peak at a chemical shift of approximately -25 ppm (P(-25 ppm)) and the integrated intensity of the peak at a chemical shift of approximately -30 ppm (P(-30 ppm)) is calculated.

[0031]

5 The peak at a chemical shift of approximately -25 ppm is assigned to berlinite generated through reaction between gibbsite or a calcined product of gibbsite and a binder raw material containing a phosphorous component, and the peak at a chemical shift of approximately -30 ppm is assigned to
10 amorphous aluminum phosphate or the like.

[0032]

Formula (1) is an indicator of reactivity between the alumina component and a binder raw material containing a phosphorous component in producing an additive for an FCC
15 catalyst by using a production method described later, and a higher value of this indicates that the alumina component and the binder raw material containing a phosphorous component react to a higher degree.

[0033]

20 The value of $P(-25 \text{ ppm})/P(-30 \text{ ppm})$ is 0.02 to 0.40, preferably 0.02 to 0.35, more preferably 0.02 to 0.30, even more preferably 0.02 to 0.25, and particularly preferably 0.02 to 0.20. If the value of $P(-25 \text{ ppm})/P(-30 \text{ ppm})$ is

smaller than 0.02, the tolerance of the additive for an FCC catalyst to heavy metals may be lowered.

[0034]

The value of $P(-25 \text{ ppm})/P(-30 \text{ ppm})$ can be lowered, for example, by increasing the temperature rising rate in calcining in the method described later for producing an additive for an FCC catalyst, by using an alumina component with a large particle diameter, or by using an alumina component with a high sodium content.

10 [0035]

With the amount of phosphorous and that of the alumina component being in the above ranges and satisfaction of formula (1), it is expected that aluminum in the alumina component in the inorganic oxide matrix exerts a superior effect as a metal scavenger, and that, as a result, lower olefins such as propylene can be obtained with high yields through FCC even when raw material hydrocarbon oil contains large amounts of heavy metals such as vanadium and nickel.

[0036]

20 The pore volume of the additive for an FCC catalyst according to the present invention in terms of pores within the pore size range of 2 to 50 nm as measured by the BJH method is preferably 0.03 ml/g or larger, and the upper limit value may be, for example, 0.08 ml/g.

[0037]

With the pore volume being within the range, lower olefins such as propylene can be obtained with high yields through FCC even when raw material hydrocarbon oil contains
5 large amounts of heavy metals such as vanadium and nickel.

[0038]

The additive for an FCC catalyst according to the present invention preferably satisfies the following formula (A):

10
$$\text{Al}(9 \text{ ppm})/\text{Al}(\text{T}) \geq 0.10 \dots (\text{A})$$

In formula (A), Al(9 ppm) and Al(T) are respectively a peak area ratio at approximately 9 ppm and the total of all peak areas in the range of -30 ppm to 80 ppm in ^{27}Al -NMR measurement, and the details of them are as follows.

15 [0039]

The additive for an FCC catalyst is homogeneously filled into an NMR sample tube for solids with a diameter of 3.2 mm, and the sample tube is set in an NMR apparatus (magnetic field strength: 14.1 T (^1H resonance frequency: 600 MHz)) and
20 rotated at 20 kHz at a magic angle (54.7°) to the external magnetic field. A peak of 1 mol/L $\text{Al}(\text{NO}_3)_3$ aqueous solution is regarded as 0 ppm as a reference for chemical shift. A single pulse method is used with setting the pulse flip angle to 10° and pulse repetition time to 0.1 seconds.

[0040]

An obtained spectrum is analyzed as follows. First, baseline correction is performed for the spectrum. Next, seven peaks at chemical shifts of approximately -9 ppm, approximately 0 ppm, approximately 9 ppm, approximately 27 ppm, approximately 40 ppm, approximately 55 ppm, and approximately 60 ppm are separated into Voigt functions. Integrated intensity is calculated for all of the functions, and the ratio between the integrated intensity of the peak at a chemical shift of approximately 9 ppm (Al(9 ppm)) and the sum total of integrated intensity for all the functions (Al(T)) is calculated.

[0041]

The peak at a chemical shift of approximately 9 ppm is assigned to six-coordinated Al. This peak is derived from an alumina component such as gibbsite, for example, added in a production method described later. As the addition of an alumina component is more, or as a binder raw material containing phosphorus and an alumina component contained in a catalyst react to a lower degree in a production method described later, the peak area increases and thus formula (A) gives a higher value.

[0042]

The additive for an FCC catalyst according to the present invention typically has the shape of a microspherical particle. The additive for an FCC catalyst when used is mixed with an FCC catalyst that is used in FCC apparatuses and contains faujasite-type zeolite for the purpose of generation of gasoline, and hence the size of each particle of the additive for an FCC catalyst is preferably comparable to or larger than those of common FCC catalysts.

[0043]

The mean particle diameter of the microspherical particle as measured through a laser diffraction/scattering method under conditions employed in Examples described later is preferably 40 to 140 μm and more preferably 60 to 120 μm .

[0044]

[Method for Producing Additive for FCC Catalyst]

The method for producing an additive for an FCC catalyst according to the present invention includes:

spray-drying a slurry to obtain a powder; and

heating the powder at a temperature rising rate of

150°C/hour or higher, followed by heat-treating at 500 to 750°C, wherein the slurry includes:

pentasil-type zeolite;

a phosphorus-containing binder raw material;

at least one alumina component selected from the group consisting of gibbsite and calcined products of gibbsite;

a filler consisting of an inorganic oxide differing from the alumina component; and

5 a dispersion medium, wherein

the amount of the pentasil-type zeolite is 10 to 60% by mass,

the amount of the phosphorus-containing binder raw material is such an amount that the amount of phosphorous in terms of mass of P_2O_5 is 5 to 20% by mass, and

10 the amount of the alumina component is such an amount that the amount of aluminum in terms of mass of Al_2O_3 is 2 to 20% by mass,

all relative to 100% by mass the solid content of the slurry (i.e., the components other than the dispersion medium).

[0045]

The specific aspect and preferred aspect of the pentasil-type zeolite is as described above.

20 The amount of the pentasil-type zeolite is 10% by mass or more and preferably 30% by mass or more relative to 100% by mass of total amount of the components of the slurry other than the dispersion medium, in view of obtaining an additive for an FCC catalyst that provides high yields of lower

olefins such as propylene, and 60% by mass or less and preferably 50% by mass or less relative to 100% by mass of total amount of the components of the slurry other than the dispersion medium, in view of obtaining an additive for an FCC catalyst that prevents the decrease in the generation of lower olefins of interest due to overcracking of raw material hydrocarbon oil.

[0046]

The phosphorus-containing binder raw material is preferably a compound that generates phosphate ions (PO_4^{3-}) through heating (e.g., at 500 to 750°C). The phosphorus-containing binder raw material is preferably a compound containing phosphorus, aluminum, and oxygen. Examples of such compounds include aluminum dihydrogen phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$), aluminum hydrogen phosphate ($\text{Al}_2(\text{HPO}_4)_3$), and aluminum phosphate (AlPO_4), and aluminum dihydrogen phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$) is preferred because of high hardening and binding properties or high reactivity with zeolite. One of those compounds may be used singly, or two or more thereof may be used in combination. The phosphorus-containing binder raw material preferably contains aluminum dihydrogen phosphate as a primary component (a component that accounts for 70% by mass or more).

[0047]

As the phosphorus-containing binder raw material, an aqueous solution thereof may be used. Examples of commercially available products of the aqueous solution include aluminum dihydrogen phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$) aqueous solutions (brand: 50L, 100L, ACIDPHOS 120M, manufactured by Taki Chemical Co., Ltd.).

[0048]

The phosphorus-containing binder raw material is used in such an amount that, the amount of phosphorus is 5 to 20% by mass and preferably 6 to 15% by mass in terms of diphosphorus pentoxide (P_2O_5) relative to 100% by mass of the total amount of the components of the slurry other than the dispersion medium. With the amount of phosphorus being in the range, specifically, 5% by mass or more, an additive for an FCC catalyst can be produced that is superior in attrition resistance and can provide lower olefins such as propylene with high yields in catalytic cracking of hydrocarbon oil.

[0049]

The slurry may contain an optional binder other than the binder raw material, and the specific aspect thereof is as described above.

When at least one alumina component selected from the group consisting of gibbsite and calcined products of gibbsite is added, an additive for an FCC catalyst to be

obtained has higher hydrothermal resistance and higher tolerance to metals and gives higher yields of lower olefins even when much deposit of vanadium, nickel, and so on is generated than those obtained, for example, when boehmite, an alumina monohydrate, is added. By inference, the reason is as follows: the alumina component such as that of gibbsite type has low reactivity with phosphorus sources, moreover mesopores derived from the alumina component can be generated in a catalyst, and more reaction fields that trap heavy metals such as vanadium and nickel can be imparted.

[0050]

Examples of the calcined product of gibbsite include calcined products containing χ -alumina, and a product obtained by heating gibbsite at a temperature rising rate of 150°C (preferably 180°C)/hour or higher, and subjecting the resultant to heat treatment at 500 to 750°C (preferably at 550 to 700°C) preferably for 0.2 to 5.0 hours (more preferably for 0.5 to 2.0 hours).

[0051]

The alumina component is used in such an amount that the amount of aluminum in terms of Al_2O_3 is 2 to 20% by mass and preferably 2.5 to 15% by mass, relative to 100% by mass of the total amount of the components of the slurry other than the dispersion medium. With the amount of the alumina

component being in the range, the decrease in yields of lower olefins such as propylene due to metal poisoning can be sufficiently suppressed in FCC, and catalyst physical properties (e.g., formability or attrition resistance) applicable to practical use can be retained.

[0052]

The mean particle diameter of the alumina component as measured through a method employed in Examples described later is preferably 2 to 50 μm and more preferably 5 to 30 μm . With the mean particle diameter being in the range, particles of the alumina component can be sufficiently diffused in an additive for an FCC catalyst, further, side reaction between the alumina component and the phosphorus-containing binder raw material can be suppressed, and more reaction fields that trap metal components such as vanadium and nickel can be formed. If the mean particle diameter is excessively larger than that range, on the other hand, properties required for practical use (e.g., formability or attrition resistance) may be impaired.

[0053]

Examples of commercially available products of the gibbsite include "C-303", "C-301N", and "CL-303" (manufactured by Sumitomo Chemical Co., Ltd.); and "B-316" (brand name, manufactured by ALMORIX LTD.). Examples of

commercially available products of the calcined product of gibbsite include "AP-22" manufactured by POLOCEL.

[0054]

The specific aspect and preferred aspect of the filler
5 consisting of an inorganic oxide are as described above.

The amount of the filler is an amount obtained by subtracting the total amount of the pentasil-type zeolite, the binder raw material containing phosphorus and aluminum, and the optional binder raw material from the total amount of
10 the components of the slurry other than the dispersion medium.

Water is preferred as the dispersion medium.

[0055]

In the production method of the present invention, first, the pentasil-type zeolite, the phosphorus-containing binder
15 raw material, the gibbsite-type aluminum hydroxide, the filler, and the dispersion medium, and the optional binder raw material, as necessary, are mixed together to prepare a slurry. Conventionally known methods can be applied in preparation of the slurry. The solid content concentration
20 of the slurry is preferably about 25 to 50% by mass in view of spray-drying operations.

[0056]

Next, the slurry is spray-dried to obtain a powder, and this powder is heated at a temperature rising rate of

150°C/hour or higher, preferably of 180°C/hour or higher. If the temperature rising rate is lower than the lower limit value, the reaction between the alumina component and the phosphorus-containing binder raw material excessively

5 proceeds, and yields of lower olefins such as propylene may decrease through heavy metal poisoning of an additive for an FCC catalyst. The upper limit of the temperature rising rate varies among heating apparatuses, and, for example, may be 800°C/hour.

10 [0057]

Subsequently, heat treatment is performed at a temperature of 500 to 750°C, preferably of 550 to 700°C, preferably for 0.2 to 5.0 hours, more preferably for 0.5 to 2.0 hours, to obtain an additive for an FCC catalyst.

15 [0058]

Conditions for spray-drying are, for example, as follows.

Spray inlet temperature: 200 to 450°C

Outlet temperature: 110 to 350°C

The powder obtained through spray-drying may be allowed
20 to cool to normal temperature (e.g., 0 to 40°C), then classified to adjust the mean particle diameter, for example, to 40 to 140 µm, preferably to 60 to 120 µm, and subjected to heat treatment.

[0059]

Heat treatment of the spray-dried powder under the above conditions can suppress the reaction between the alumina component and phosphorus-containing binder raw material added, and the resulting additive for an FCC catalyst is inferred to possess many reaction fields that trap heavy metals such as vanadium and nickel formed on the surface of the alumina component, and to exhibit high metal tolerance.

[0060]

The heat treatment is preferably performed in a water vapor atmosphere to allow the phosphorus-containing binder raw material to more diffuse, promote modification of acid sites of zeolite, and further suppress the clogging of pores of zeolite caused by polyphosphoric acid.

[0061]

[Method of Using Additive for FCC Catalyst]

The additive for an FCC catalyst according to the present invention (also referred to as "additive catalyst") when used is mixed with an FCC catalyst containing faujasite-type zeolite in fluid catalytic cracking of hydrocarbon oil with an FCC apparatus.

[0062]

Common FCC catalysts used for FCC apparatuses can be used as the FCC catalyst containing faujasite-type zeolite. Examples of such FCC catalysts include commercially available

FCC catalysts such as DCT, ACZ, and CVZ (each is a trademark or registered trademark of a product manufactured by JGC Catalysts and Chemicals Ltd.).

[0063]

5 The amount of the additive for an FCC catalyst is preferably 0.1% by mass or more and more preferably 1% by mass or more relative to 100% by mass of the total amount of the additive for an FCC catalyst and the FCC catalyst, in view of obtaining lower olefins such as propylene with high
10 yields through FCC even when raw material hydrocarbon oil contains large amounts of heavy metals, and the additive for an FCC catalyst is used typically in an amount of 30% by mass or less in view of cracking activity of raw material hydrocarbon oil; however, the additive for an FCC catalyst
15 may be added in an amount of up to 60% by mass in, for example, a novel process to increase the production of light olefins.

[0064]

 In fluid catalytic cracking processes for hydrocarbon
20 oil for which the additive for an FCC catalyst according to the present invention is used, conditions for fluid catalytic cracking of hydrocarbon oil in common FCC apparatuses can be employed, except that the additive for an FCC catalyst

according to the present invention is used as an additive for FCC catalysts.

Examples

5 [0065]

Hereinafter, the present invention will be more specifically described with reference to Examples; however, the present invention is by no means limited to these Examples.

10 [Example 1]

ZSM-5-type zeolite produced according to Examples 1 in patent literature JP-A 2011-213525 was suspended in pure water, and pulverized with a bead mill to a mean particle diameter of 2.5 μm to prepare a slurry with a ZSM-5-type
15 zeolite concentration of 25% by mass (hereinafter, also referred to as "pulverized ZSM-5 slurry"). Weighed was 2,400 g of the pulverized ZSM-5 slurry (the amount was such an amount that the mass of ZSM-5-type zeolite was 40% by mass (600 g) based on the mass of the target product (the additive
20 for a catalyst, the same applies hereinafter) (1,500 g)), and 15% ammonium aqueous solution was added thereto until the pH of the pulverized ZSM-5 slurry reached 9.0. 651.0 g of kaolin (the amount was such an amount that the mass after dehydration was 36.5% by mass (547.5 g) based on the mass of

the target product) was mixed therewith, and with the resultant, 225.2 g of gibbsite (gibbsite-type aluminum hydroxide) ("C-303" manufactured by Sumitomo Chemical Co., Ltd., median diameter: 5.3 μm) (the amount was such an amount
5 that the mass of aluminum in terms of Al_2O_3 was 10.0% by mass (150 g) based on the mass of the target product) was mixed. Dispersion treatment was performed for the slurry by using a homogenizer. To the resulting slurry, an aqueous solution containing aluminum dihydrogen phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$) that
10 contained 8.5% by mass of aluminum in terms of Al_2O_3 and 33.5% by mass of phosphorus in terms of P_2O_5 ("100L" manufactured by Taki Chemical Co., Ltd.) was added in an amount of 482.1 g (which was such an amount that the mass of phosphorus in terms of P_2O_5 was 10.8% by mass (162 g) based on the mass of
15 the target product), and to the resultant, 527.3 g of pure water was added so that the concentration of the slurry (in terms of the concentration of the target product) reached approximately 35% by mass to obtain a slurry with a concentration of approximately 35% by mass (hereinafter, also
20 referred to as "mixed slurry"). This mixed slurry was spray-dried (spray inlet temperature: 250 to 260°C, outlet temperature: 150°C), and the resulting particles were allowed to cool to about 25°C, and then classified through a sieve with a mesh size of 212 μm to prepare microspherical

particles with a mean particle diameter of 84 μm . 150 g of the microspherical particles were placed in a calcination container (capacity: 6.2 L), and with use of a small rotary furnace, the temperature thereof was elevated to 600°C at a temperature rising rate of 300°C/hour, followed by calcination at 600°C for 30 minutes to obtain additive A for an FCC catalyst. To keep the inside of the container in a 100% steam atmosphere, water was introduced thereinto at a rate of 1.0 g/min from the time at which the temperature of the inside of the calcination container reached 150°C until the retention at 600°C was terminated. The physical properties and so on of additive A for an FCC catalyst are shown in Table 1.

[0066]

[Example 2]

The same operations as in Example 1 were performed to obtain additive B for an FCC catalyst, except that the amounts of the kaolin, gibbsite-type aluminum hydroxide, and aluminum dihydrogen phosphate aqueous solution were respectively changed to 740.2 g (which was such an amount that the mass after dehydration was 41.5% by mass based on the mass of the target product (1,500 g)), 112.6 g (which was such an amount that the mass of aluminum in terms of Al_2O_3 was 5% by mass based on the mass of the target product), and

446.4 g (which was such an amount that the mass of phosphorus in terms of P_2O_5 was 10.0% by mass based on the mass of the target product). The physical properties and so on of additive B for an FCC catalyst are shown in Table 1.

5 [0067]

[Example 3]

The same operations as in Example 1 were performed to obtain additive C for an FCC catalyst, except that the type of the gibbsite-type aluminum hydroxide was changed to "C-
10 301N" (median diameter: 2.5 μm) manufactured by Sumitomo Chemical Co., Ltd. The physical properties and so on of additive C for an FCC catalyst are shown in Table 1.

[0068]

[Example 4]

15 The same operations as in Example 1 were performed to obtain additive D for an FCC catalyst, except that the type of the gibbsite-type aluminum hydroxide was changed to "B-316" (median diameter: 17.4 μm) manufactured by ALMORIX LTD. The physical properties and so on of additive D for an FCC
20 catalyst are shown in Table 1.

[0069]

[Example 5]

The same operations as in Example 1 were performed to obtain additive E for an FCC catalyst, except that the type

of the gibbsite-type aluminum hydroxide was changed to "CL-303" (median diameter: 5.6 μm , Na_2O content: 0.19% by weight) manufactured by Sumitomo Chemical Co., Ltd. The physical properties and so on of additive E for an FCC catalyst are shown in Table 1.

[0070]

[Example 6]

The same operations as in Example 1 were performed to obtain additive F for an FCC catalyst, except that the type of the aluminum hydroxide was changed to a calcined product of gibbsite (crystal phase: χ -alumina) ("AP-22" manufactured by POROCEL). The physical properties and so on of additive F for an FCC catalyst are shown in Table 1.

[0071]

[Example 7]

The same operations as in Example 1 were performed to obtain additive G for an FCC catalyst, except that the amount of the pulverized ZSM-5 slurry was changed to 1,800 g (which was such an amount that the mass of ZSM-5-type zeolite was 30.0% by mass (450 g) based on the mass of the target product (1,500 g)); that the amounts of the kaolin and aluminum dihydrogen phosphate aqueous solution were respectively changed to 891.7 g (which was such an amount that the mass after dehydration was 50.0% by mass based on the mass of the

target product (1,500 g)) and 358.2 g (which was such an amount that the mass of phosphorus in terms of P_2O_5 was 8.0% by mass based on the mass of the target product); and that the amount of pure water to be added for concentration adjustment for the mixed slurry was changed to 1010.6 g. The physical properties and so on of additive G for an FCC catalyst are shown in Table 1.

[0072]

[Example 8]

The same operations as in Example 1 were performed to obtain additive H for an FCC catalyst, except that the amount of the pulverized ZSM-5 slurry was changed to 3,000 g (which was such an amount that the mass of ZSM-5-type zeolite was 50% by mass (750 g) based on the mass of the target product (1,500 g)); and that the amounts of the kaolin and aluminum dihydrogen phosphate aqueous solution were respectively changed to 413.8 g (which was such an amount that the mass after dehydration was 23.2% by mass based on the mass of the target product (1,500 g)) and 604.5 g (which was such an amount that the mass of phosphorus in terms of P_2O_5 was 13.5% by mass based on the mass of the target product). The physical properties and so on of additive H for an FCC catalyst are shown in Table 1.

[0073]

[Example 9]

The same operations as in Example 1 were performed to obtain additive I for an FCC catalyst, except that the amounts of the kaolin and gibbsite-type aluminum hydroxide were respectively changed to 561.8 g (which was such an amount that the mass after dehydration was 31.5% by mass based on the mass of the target product (1,500 g)) and 337.8 g (which was such an amount that the mass of aluminum in terms of Al_2O_3 was 15.0% by mass based on the mass of the target product). The physical properties and so on of additive I for an FCC catalyst are shown in Table 1.

[0074]

[Comparative Example 1]

The same operations as in Example 1 were performed to obtain additive J for an FCC catalyst, except that the temperature rising rate was changed to 100°C/hour. The physical properties and so on of additive J for an FCC catalyst are shown in Table 1.

[0075]

[Comparative Example 2]

The same operations as in Example 1 were performed to obtain additive K for an FCC catalyst, except that the gibbsite-type aluminum hydroxide was not used; and that the amounts of the kaolin and aluminum dihydrogen phosphate

aqueous solution were respectively changed to 847.2 g (which was such an amount that the mass after dehydration was 47.5% by mass based on the mass of the target product (1,500 g)) and 446.4 g (which was such an amount that the mass of phosphorus in terms of P_2O_5 was 10.0% by mass based on the mass of the target product). The physical properties and so on of additive K for an FCC catalyst are shown in Table 1.

[0076]

[Comparative Example 3]

The same operations as in Example 1 were performed to obtain additive L for an FCC catalyst, except that 90.4 g (which was such an amount that the mass of aluminum in terms of Al_2O_3 was 5% by mass based on the mass of the target product (1,500 g)) of 83.0% by mass of boehmite-type aluminum hydroxide ("CATAPAL 200" manufactured by Sasol Limited) was used in place of the gibbsite-type aluminum hydroxide; and that the amounts of the kaolin and aluminum dihydrogenphosphate aqueous solution were respectively changed to 758.0 g (which was such an amount that the mass was 42.5% by mass based on the mass of the target product) and 446.4 g (which was such an amount that the mass was 12.5% by mass based on the mass of the target product). The physical properties and so on of additive L for an FCC catalyst are shown in Table 1.

[0077]

[Comparative Example 4]

Additive K for an FCC catalyst was prepared in accordance with the description of the preparation method for sample B in Example 1 in Japanese Translation of PCT International Application Publication No. 2002-537976. Specifically, 800 g (by dry weight) of ZSM-5, 830 g (by dry weight) of kaolin, 130 g (in terms of Al_2O_3 , by dry weight) of CATAPAL B (manufactured by Sasol Limited), 390 g of 85% H_3PO_4 aqueous solution, and pure water were mixed together to obtain a mixed slurry with a solid content concentration of 45%. The mixed slurry was thoroughly stirred, and spray-dried under the same conditions as in Example 1 to prepare microspherical particles. The resulting microspherical particles were left to stand, and the temperature was increased to 530°C at a temperature rising rate of 300°C/hour, followed by calcination at 530°C for 2 hours to obtain additive M for an FCC catalyst. The physical properties and so on of additive M for an FCC catalyst are shown in Table 1.

[0078]

[Measurement Methods and Evaluation Methods]

The measurement methods and evaluation methods in Examples and so on are as follows.

(Methods for Measuring Element Contents)

In mass spectrometry for elements, chemical analysis was performed by using an atomic absorption photometer for Na, and an inductively coupled plasma spectrometer for elements other than Na. Specifically, sulfuric acid and hydrofluoric acid were added to zeolite (ZSM-5) or a catalyst; the resultant was heated for evaporation to dryness; the dried product was dissolved in concentrated hydrochloric acid; the resultant was diluted with water to a concentration of 10 to 100 ppm by mass to prepare a solution; and the solution was analyzed by using an atomic absorption photometer (Z-2310) manufactured by Hitachi High-Tech Science Corporation and an inductively coupled plasma spectrometer (ICPS-8100) manufactured by Shimadzu Corporation. The wavelengths were as follows. Na: 589.6 nm, Al: 396.2 nm, Si: 251.6 nm, P: 178.3 nm.

[0079]

(²⁷Al-MAS NMR Measurement and ³¹P-MAS NMR Measurement)

An additive for an FCC catalyst was homogeneously filled into an NMR sample tube for solids with a diameter of 3.2 mm. The resulting sample tube was set in an NMR apparatus (VNMR-600 manufactured by Agilent Technologies, magnetic field strength: 14.1 T (¹H resonance frequency: 600 MHz)), and rotated at a high speed of 20 kHz at a magic angle (54.7°) to the external magnetic field.

[0080]

In ^{27}Al measurement, a peak of 1 mol/L $\text{Al}(\text{NO}_3)_3$ aqueous solution was regarded as 0 ppm as a reference for chemical shift. A single pulse method was used with setting the pulse
5 flip angle to 10° and pulse repetition time to 0.1 s.

[0081]

In ^{31}P measurement, a peak of $\text{NH}_4\text{H}_2\text{PO}_4$ was used and regarded as 1 ppm as a secondary reference for chemical shift. A single pulse method was used with setting the pulse flip
10 angle to 90° and pulse repetition time to 11.5 s.

[0082]

The spectra obtained were analyzed by using Origin. First, baseline correction was performed for the spectra. Next, peaks were separated into Voigt functions. In ^{27}Al -MAS
15 NMR, seven peaks at chemical shifts of approximately -9 ppm, approximately 0 ppm, approximately 9 ppm, approximately 27 ppm, approximately 40 ppm, approximately 55 ppm, and approximately 60 ppm were separated into functions. Integrated intensity was calculated for all of the functions,
20 and the ratio of each peak to the sum total of areas was calculated to determine the area ratio of each peak. Among them, the area ratio at approximately 9 ppm assigned to six-coordinated Al derived from aluminum hydroxide, boehmite alumina, and so on added was calculated.

[0083]

In ^{31}P -MAS NMR, five peaks at chemical shifts of approximately -6 ppm, -18 ppm, -25 ppm, -30 ppm, and -37 ppm were separated into functions, and the area ratio of each peak was determined in the same manner. The ratio between the area ratio at -25 ppm assigned to berlinite generated through reaction between aluminum hydroxide and a phosphorus component and the area ratio at -30 ppm assigned to amorphous aluminum phosphate or the like was calculated.

10 [0084]

(Mean Particle Diameter of Zeolite and Aluminum Hydroxide)

Measurement of grain size distribution of samples was performed by using a laser diffraction/scattering particle size distribution analyzer (LA-950V2) manufactured by HORIBA, Ltd. Specifically, each sample was put into a solvent (water) so that the light transmittance fell within the range of 70 to 95%, and measurement was performed under conditions as follows. Circulation rate: 5.0 L/min, ultrasonic irradiation: 1 minute, number of repetitions: 15. Median diameter (D50) was employed as the mean particle diameter. The measurement was performed assuming that the refractive index of zeolite and that of aluminum hydroxide were respectively 1.46 and 1.66.

[0085]

(Mean Particle Diameter of Additive for FCC Catalyst)

Measurement of grain size distribution of samples was performed by using a laser diffraction/scattering particle size distribution analyzer (LA-300) manufactured by HORIBA, Ltd. Specifically, each sample was put into a solvent (water) so that the light transmittance fell within the range of 70 to 95%, and measurement was performed under conditions as follows. Circulation rate: 2.8 L/min, ultrasonic irradiation: 3 minutes, number of repetitions: 30. Median diameter (D50) was employed as the mean particle diameter.

[0086]

(Specific Surface Area and Pore Volume of Additive for FCC Catalyst)

Measurement of specific surface area (SA) and pore volume for pores with pore diameters of 50 nm or smaller was performed by using a BELSORP-mini Ver 2.5.6 manufactured by MicrotracBEL Corp. Specifically, a sample obtained by pre-treating a catalyst at 500°C for 1 hour was used, and measurement was performed with nitrogen as a gas to be adsorbed. Specific surface area (SA) of each additive for an FCC catalyst was calculated by using the BET method, pore volume of each additive for an FCC catalyst in terms of micropores with pore diameters of 2 nm or smaller was calculated by using the MP method, and volume of mesopores

with pore diameters of 2 to 50 nm was calculated by using the BJH method.

[0087]

(Amount of Ammonia Adsorption)

5 Amounts of ammonia adsorption were measured by using a
BELCAT Version 2.5.5 manufactured by MicrotracBEL Corp. with
a temperature-programmed desorption (TPD) method.
Specifically, each additive for an FCC catalyst was subjected
to pseudo-equilibration treatment (Ni/V = 2000 ppm/4000 ppm,
10 100% steaming at 810°C for 12 hours) for activity evaluation,
and the resultants were pre-treated at 500°C for 1 hour for
use. In a TPD apparatus, 0.2 g of each pre-treated sample
was heat-treated at 500°C under helium flow for 1 hour, and
then cooled to 100°C. Each sample was allowed to adsorb
15 ammonia at 100°C for 30 minutes, and degassed at the same
temperature under helium flow for 30 minutes. Thereafter,
the amount of ammonia desorption during increasing the
temperature from 100°C to 500°C at 10°C/min was detected with
a TCD, and the amount of ammonia adsorption was calculated
20 from the amount of desorption.

[0088]

(Catalyst Performance)

Additives A to J for an FCC catalyst produced in
Examples and so on were subjected to catalyst evaluation test

by using ACE-MAT (Advanced Cracking Evaluation - Micro Activity Test) with the same raw material oil under the same reaction conditions. Before performing the catalyst evaluation test, each catalyst was allowed to support Ni/V =
5 2000 ppm/4000 ppm by using Mitchell's method and pre-treated at 810°C under a steam atmosphere at 100°C for 12 hours.

[0089]

Each pre-treated additive for an FCC catalyst was blended with an equilibrated FCC catalyst to prepare a mixed
10 catalyst so that the amount of the additive for an FCC catalyst in the mixed catalyst reached a constant amount of 2.4% by weight, and the mixed catalyst was evaluated (measured for the yield (% by mass) of propylene) by using an ACE-MAT activity tester.

15 The reaction conditions were as follows.

- Reaction temperature: 510°C
- Raw material oil: oil of 100% by mass of desulfurized vacuum gas oil (DSVGO)
- WHSV: 8 h⁻¹
- 20 - Catalyst/oil ratio: 5% by mass/% by mass

The evaluation results are shown in Table 1.

[0090]

Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Additive for FCC catalyst (target product)		A	B	C	D	E	F	G	H	I	J	K	L	M
Proportion of raw material based on mass of target product (% by mass)														
Phosphorus-containing binder (mass of phosphorus in terms of mass of P ₂ O ₅)														
100L		10.8	10.0	10.8	10.8	10.8	10.8	8.0	13.5	10.8	10.8	10.0	10.0	12.0
85% H ₃ PO ₄ Aqueous solution		40.0	40.0	40.0	40.0	40.0	40.0	30.0	50.0	40.0	40.0	40.0	40.0	40.0
ZSM-5		36.5	41.5	36.5	36.5	36.5	36.5	50.0	23.2	31.5	36.5	48.5	42.5	41.5
Kaolin (in terms of mass after dehydration)														
Alumina component (mass of aluminum in terms of mass of Al ₂ O ₃)														
Gibbsite or calcined product thereof														
C-303		10.0	5.0					10.0	10.0	15.0	10.0			
C-301N				10.0										
B316					10.0									
CL-303						10.0								
AP-22 (γ -alumina)							10.0							
Boehmite													5.0	
CATAPAL 200														6.5
CATAPAL B														
Physical properties and so on of alumina component	Median diameter	5.3	5.3	2.5	17.4	5.6	9.4	5.3	5.3	5.3	5.3	-	0.2	36.0
	LOI (loss on ignition)	33.4	33.4	33.4	34.1	33.4	11.3	33.4	33.4	33.4	33.4	-	17.0	25.9
	Na ₂ O content	0.17	0.17	0.26	0.41	0.09	0.32	0.17	0.17	0.17	0.17	-	0.00	0.00
Calcination conditions	Calcination temperature	600	600	600	600	600	600	600	600	600	600	600	600	530
	Retention time at calcination temperature	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	2
	Temperature rising rate	300	300	300	300	300	300	300	300	300	100	300	300	300
Physical properties and so on of additive for FCC catalyst														
Composition	LOI (loss on ignition)	1.0	0.7	0.8	0.6	0.5	0.7	1.0	1.0	1.1	1.1	0.7	0.8	0.6
	Na ₂ O	0.14	0.12	0.12	0.14	0.11	0.12	0.14	0.14	0.14	0.14	0.12	0.11	0.10
	Al ₂ O ₃	30.3	25.9	30.2	31.4	30.7	31.0	32.5	22.6	34.7	30.3	24.4	26.9	26.2
	P ₂ O ₅	10.7	10.3	10.7	10.8	10.8	10.7	8.1	13.5	10.7	10.7	9.8	10.4	13.3
Physical properties	Specific surface area	127	121	122	128	129	114	96	155	137	141	110	136	109
	Mean particle diameter	77	73	76	74	90	78	78	75	77	77	80	79	77
	ABD (bulk density)	0.68	0.70	0.69	0.73	0.74	0.72	0.72	0.66	0.70	0.72	0.72	0.70	0.73
	Pore volume (pore diameter <2 nm)	0.066	0.064	0.067	0.069	0.071	0.060	0.060	0.072	0.068	0.071	0.060	0.067	0.054
	Pore volume (pore diameter 2-50 nm)	0.049	0.035	0.041	0.048	0.045	0.031	0.035	0.052	0.052	0.049	0.023	0.026	0.023
	Al (9 ppm)/Al (1)	0.35	0.21	0.35	0.39	0.37	0.36	0.40	0.32	0.48	0.30	0.00	0.15	0.19
	P (-25 ppm)/P (-30 ppm)	0.15	0.09	0.33	0.08	0.27	0.07	0.12	0.17	0.21	0.46	0.00	0.00	0.00
	Amount of ammonia adsorption 100-500°C (Ni/V=2000/4000 810-13 hr)	76	72	61	82	63	72	60	88	79	54	40	32	57
Activity	C3=(Ni/V=2000/4000 810-13 hr)	6.1	6.0	5.8	6.4	5.8	6.0	5.8	6.5	6.2	5.5	5.7	5.2	5.6

CLAIMS

[Claim 1]

An additive for a fluid catalytic cracking catalyst, the additive comprising pentasil-type zeolite and an inorganic oxide matrix, wherein

the amount of the pentasil-type zeolite is 10 to 60% by mass,

the additive contains 5 to 20% by mass of phosphorous in terms of mass of P_2O_5 , and

the inorganic oxide matrix contains an alumina component in such an amount that the amount of aluminum in terms of Al_2O_3 is 2 to 20% by mass, relative to 100% by mass of the additive, and

the following formula (1) is satisfied:

$$0.02 \leq P(-25 \text{ ppm})/P(-30 \text{ ppm}) \leq 0.40 \dots (1)$$

wherein $P(-25 \text{ ppm})$ and $P(-30 \text{ ppm})$ are respectively a peak area ratio at -25 ppm and a peak area ratio at -30 ppm in ^{31}P -NMR measurement.

[Claim 2]

A method for producing an additive for a fluid catalytic cracking catalyst, the method comprising:

spray-drying a slurry to obtain a powder; and

heating the powder at a temperature rising rate of 150°C or higher/hour, followed by heat-treating at 500 to 750°C, wherein the slurry comprises:

pentasil-type zeolite;

a phosphorus-containing binder raw material;

at least one alumina component selected from the group consisting of gibbsite and calcined products of gibbsite;

a filler consisting of an inorganic oxide differing from the alumina component; and

a dispersion medium, wherein

the amount of the pentasil-type zeolite is 10 to 60% by mass,

the amount of the phosphorus-containing binder raw material is such an amount that the amount of phosphorous in terms of mass of P_2O_5 is 5 to 20% by mass, and

the amount of the alumina component is such an amount that the amount of aluminum in terms of mass of Al_2O_3 is 2 to 20% by mass,

all relative to 100% by mass of a solid content of the slurry.