

CATALYTIC COMPOSITION FOR FLUIDIZED CATALYTIC CRACKING OF HYDROCARBONS AND METHOD FOR PRODUCING THE SAME

TECHNICAL FIELD

[0001]

The present invention relates to a composition for fluidized catalytic cracking of hydrocarbons, the composition increasing an octane number in gasoline or light olefins produced by contacting the hydrocarbons to a catalyst for fluidized catalytic cracking (sometimes referred to as FCC catalyst hereinafter) in a fluidized catalytic cracking unit (sometimes referred to as an FCC unit hereinafter) for hydrocarbons, and a method of producing the same. More specifically, the present invention relates to a catalyst for fluidized catalytic cracking of hydrocarbons having a form of spherical fine particles and comprising phosphorus components, pentacyl-type zeolite, and an inorganic oxide matrix, the catalyst characterized in that a content of phosphorus in a surface portion of the spherical fine particle is higher than that in the central portion thereof, and a method of producing the same.

BACKGROUND ART

[0002]

A main purpose of an FCC unit in a refinery is to crack hydrocarbons as a feed catalytically and produce a gasoline fraction, and the gasoline should have a high octane number. In some refineries, it is required to produce light olefins, especially propylene and butene which are used as raw materials in the petrochemical industry simultaneously when hydrocarbons as a feed are catalytically cracked in the FCC unit.

Conventionally, as an FCC catalyst used in production of gasoline by catalytically cracking hydrocarbons in the FCC unit, a catalyst based on faujasite-type zeolite has been

widely used. While the catalyst based on the faujasite-type zeolite, has higher activity in cracking hydrocarbons than an amorphous catalyst, but an octane number of gasoline produced by using the faujasite-type zeolite based catalyst is low and also a content of olefin in the gasoline is low, which is disadvantageous.

[0003]

To increase an octane number of or a content of light olefins in gasoline produced with an FCC unit, there has been employed a method of catalytically cracking hydrocarbons by mixing an FCC catalyst containing pentacyl-type zeolite such as ZSM-5 (sometime referred to as additive catalyst hereinafter) to the FCC catalyst based on faujasite-type zeolite, and there have been proposed various types of additive catalysts and a method of producing the catalysts.

[0004]

For instance, Japanese Patent 05064743 A (Patent document 1) describes a method of preparing an FCC catalyst with high attrition resistance and capable of increasing an octane number of gasoline produced by using the catalyst, and in the method, zeolite is added in a water-based slurry containing a phosphate and with pH in the range from 2 to 6 and further a matrix precursor is added to the mixture to obtain a homogeneous slurry, and then the slurry is spray-dried to form catalyst particles. The patent document 1 also discloses the pentacyl-type zeolite such as ZSM-5 and ZSM-11 as the zeolite available in the method.

[0005]

Japanese Patent 2004143373 A (Patent document 2) describes a method of producing olefins, and in the method, when olefins are produced by catalytically cracking a hydrocarbon feed, pentacyl-type zeolite containing a rare earth element and also containing manganese and/or zirconium as a catalyst. The patent document 2 also discloses that the catalyst contains phosphorus by 0.1 to 5% by weight.

[0006]

Japanese Patent 2005270851 A (Patent document 3) describes a catalytic composition for increasing an octane number in gasoline or light olefins, the composition comprising pentacyl-type zeolite and an inorganic oxide matrix, and in the catalytic composition, the total pore volume is 0.30 ml/g or more, the average pore diameter is in the range from 100 ± 20 nm, and a percentage of the pore volume in the pore diameter range of 100 ± 20 nm is 50% or more against the total pore volume.

[0007]

In the conventional catalytic compositions as described above, for increasing an octane number of or a content of light olefins in gasoline, it is required to make higher a content of pentacyl-type zeolite in the catalyst particles. However, the pentacyl-type zeolite is expensive, and in addition, when the content is made higher, the attrition resistance of the catalyst particles becomes disadvantageously lower.

DISCLOSURE OF THE INVENTION

[0008]

An object of the present invention is to provide, for solving the problems described above, an FCC catalytic composition (additive catalyst) having high attrition resistance and showing excellent effect in increasing an octane number in gasoline of and a content of light olefins even when a content of pentacyl-type zeolite in the catalyst particles is low, and a method of producing the FCC composition.

[0009]

The present inventors made strenuous efforts for solving the problems described above, and found the fact that the problems can be solved by making higher a content of phosphorus in a surface portion of spherical fine particles constituting an additive catalyst than that in the central portion. The present invention is based on the finding.

The inventors also found that, when a primary phosphate is used as a raw material for the phosphorus component, a content of the phosphorus component in a surface portion of the spherical fine particle is higher than that in the central portion.

[0010]

The present invention provides, in a first aspect, a catalytic composition for fluidized catalytic cracking of hydrocarbons having a form of spherical fine particles and comprising phosphorus pentoxide (P_2O_5) by 5 to 20% by weight, pentacyl-type zeolite by 10 to 50% by weight, and a porous inorganic oxide by 30 to 85% by weight, in the spherical fine particles, a content of P_2O_5 in a surface portion is by 1.05 times or more higher than that in the central portion.

[0011]

The present invention provides, in a second aspect thereof, a method of producing the catalytic composition for fluidized catalytic cracking of hydrocarbons, and the method comprises the steps of:

(1) mixing the following (i) to (iii) components:

(i) an aqueous solution of primary phosphate as P_2O_5 by 5 to 20% by weight;

(ii) pentacyl-type zeolite by 10 to 50% by weight; and

(iii) a precursor for a porous inorganic oxide including inorganic oxides other than P_2O_5 in the primary phosphate by 30 to 85% by weight, and

(2) spray-drying the obtained slurry to produce spherical fine particles.

[0012]

The present invention provides, in a third aspect thereof, a method of producing the catalytic composition for fluidized catalytic cracking of hydrocarbons, and in the method, the primary phosphate is at least one selected from the group consisting of aluminum primary phosphate, magnesium primary phosphate, calcium primary phosphate, zinc primary phosphate, and manganese primary phosphate.

[0013]

The FCC catalytic composition (additive catalyst) according to the present invention contains pentacyl-type zeolite in the catalyst particles, and is excellent in the attrition resistance. Furthermore the FCC catalytic composition can effectively increase an octane number in gasoline or a content of light olefins even when a content of the pentacyl-type zeolite is low.

With the production method according to the present invention, the FCC catalytic composition according to the present invention can easily and economically be produced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

FIG. 1 shows a cross-sectional image of a catalyst A photographed with an electron probe microanalyzer (WDS) and an element distribution chart obtained by linearly analyzing a linear portion of a central portion of the image; and

FIG. 2 is a cross-sectional image of a catalyst B photographed with an electron probe microanalyzer (WDS) and an element distribution chart obtained by linearly analyzing a linear portion of a central portion of the image.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0015]

Catalytic Composition for Fluidized Catalytic Cracking of Hydrocarbons

In the FCC catalytic composition according to the present invention, a content of the phosphorus component is in the range from 5 to 20% by weight as P_2O_5 . When a content of the phosphorus component is less than 5% by weight as P_2O_5 , a binding force of the catalytic composition becomes weaker and the attrition resistance becomes lower. Furthermore, the effect provided by adding a phosphorus component, namely the effect of

maintaining the hydrothermal stability of ZSM-5 provided by adding the phosphorus component can not be obtained, and therefore the desired effect of increasing the octane number or a content of light olefins cannot be obtained.

When a content of P_2O_5 as the phosphorus component is more than 20% by weight, a pore volume of the catalyst becomes smaller with diffusion of reactants in the catalytic pore suppressed, and the desired effect of increasing an octane number and a content of light olefins can not be obtained.

A desirable content of the phosphorus component is in the range from 7 to 15% by weight when calculated as that of P_2O_5 .

[0016]

In the FCC catalytic composition according to the present invention, a content of pentacyl-type zeolite is in the range from 10 to 50% by weight. When a content of pentacyl-type zeolite is less than 10% by weight, the desired effect of increasing an octane number and a content of light olefins may not be obtained. When a quantity of the catalytic composition is increased for achieving the effect of increasing the octane number and the content of light olefins, cracking activity of the FCC catalyst is degraded because a quantity of the FCC catalyst used for catalytic cracking of hydrocarbons becomes smaller.

When the content of pentacyl-type zeolite is higher than 50% by weight, the effect of increasing the octane number and the content of light olefins is the same as that provided when the content of the zeolite is 40% by weight, and therefore it is not economical. The content of the pentacyl-type zeolite is preferably in the range from 10 to 40% by weight.

[0017]

The pentacyl-type zeolite available for the purpose of the present invention includes, but not limited to, ZSM-5, ZSM-11, ZMS-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38 and ZSM-38. ZSM-5 containing a solid acid with strong acidity and showing the high shape-selectivity is especially advantageous, since the composition provides the remarkable

effect of increasing the octane number in gasoline and a content of light olefins.

[0018]

The FCC catalytic composition according to the present invention contains components other than the phosphorus component (P_2O_5) and pentacyl-type zeolite in the range from 30 to 85% by weight as porous inorganic oxides. When an amount of the porous inorganic oxides is less than 30% by weight, attrition resistance of the catalytic composition is generally degraded.

When a content of the porous inorganic oxide is more than 85% by weight, sometimes the effect of increasing the octane number and the content of light olefins can not be provided since the content of pentacyl-type zeolite is reduced. The content of the porous inorganic oxide is preferably in the range from 40 to 75% by weight.

[0019]

As the porous inorganic oxide available for the purpose of the present invention, it is possible to use porous inorganic oxides which are generally used in the FCC catalyst containing faujasite-type zeolite used for production of gasoline, and the oxides include, for instance, refractory oxides such as silica, alumina, silica-alumina, silica-magnesia, alumina-boria, titania, zirconia, silica-zirconia, calcium silicate and calcium aluminate, and clay minerals such as kaolin, bentonite and haloisite. Especially, the porous inorganic oxide comprising of the clay mineral such as kaolin is preferable.

[0020]

The FCC catalytic composition according to the present invention has a shape like a spherical fine particle. It is preferable that an average particle diameter of the spherical fine particles is in the range from 60 to 90 μm . It is also preferable that a size of the spherical fine particle is about the same as or larger than that of a conventional FCC catalyst, because the FCC catalytic composition is used by mixing with the FCC catalyst containing faujasite-type zeolite for production of gasoline used in the FCC unit.

The FCC catalytic composition according to the present invention is used as an additive catalyst, and is used at a blending ratio of 20% by weight or below against a weight of the FCC catalyst, and therefore fluidity of the catalyst is little affected even when the particle diameter is large.

[0021]

The FCC catalytic composition according to the present invention is characterized in that a content of the phosphorus component in a surface portion of the spherical fine particle is 1.05 times or more higher than that in a central portion of the spherical fine particle.

The FCC catalytic composition according to the present invention can enhance attrition resistance of the spherical fine particle because the content of P_2O_5 in the surface portion of the spherical fine particle is 1.05 times or more higher than that in the central portion of the spherical fine particle. Furthermore the effect of increasing the octane number and the content of light olefins can be provided by keeping the content of a phosphorus component of the spherical fine particle in the optimal range.

[0022]

When a ratio of the content of P_2O_5 in the surface portion of the spherical fine particle to that in the central portion of the spherical fine particle (hereinafter, referred to as "Surface P/Central P") is smaller than 1.05, a content of a phosphorus component has to be increased for obtaining desired attrition resistance of the spherical fine particle, and it is difficult to achieve the effect of increasing the octane number and the content of light olefins.

Surface P/Central P in a range from 1.05 to 1.2 is preferable in the FCC catalytic composition according to the present invention.

[0023]

The "surface portion" of the spherical fine particle in the present invention is

defined as a portion separated from the spherical fine particle by attrition when the spherical fine particle is filled into a cylindrical catalytic tube and flowed in the tube by air for 20 hours, and the remaining portion is defined as the "central portion" of the spherical fine particle. It is to be noted that an amount of the surface portion should not exceed that of the central portion. A spherical fine particle, in which the surface portion separated from the spherical fine particle due to attrition exceeds the remaining amount of the spherical fine particle, is not preferable as the FCC catalyst because the attrition resistance is not sufficient.

In the present invention, the "surface portion" and the "central portion" are not defined based on a center and a diameter of the spherical fine particle, because concentrations of phosphorus in the surface portion and in the central portion can not directly be analyzed.

[0024]

In the examples of the present invention, contents of P_2O_5 in the surface portion and in the central portion of the spherical fine particle are obtained as described below.

As a pre-treatment for the FCC catalytic composition according to the present invention, a spherical fine particles are prepared as a test sample by calcinating the FCC catalytic composition for 2 hours at 600 °C and then removing fine powder having the size of 40 μm or below with a sieve. Then, the spherical fine particles are measured according to a system and a method described in "Method for Measuring Attrition Resistance for Catalyst, by Yoshiaki Ohishi, Shokubai Kasei Gihou, vol. 13, No. 1, 65-66 pp (1996)".

[0025]

Namely, 45 grams of the test sample is mixed with 5 grams of water, and the mixture is filled in a cylindrical catalytic tube constituting a catalyst attrition measurement device, and then fine powder (F) of a surface portion of the sample pulverized by attrition is collected by blowing air into the catalytic tube at a rate of 0.104 m/sec and flowing the sample in the catalytic tube for 20 hours.

The obtained fine powder (F) is considered as that from the surface portion of the spherical fine particle and the remaining spherical fine particles in the catalytic tube (B) are considered as the central portion of the sample spherical fine particles.

[0026]

A content of P_2O_5 in the surface portion and a content of P_2O_5 in the central portion are obtained by measuring contents of P_2O_5 in the fine powder (F) and the spherical fine particles (B). Further, a depth of the surface portion can be obtained by measuring differences between an average particle diameter of the test sample and that of the spherical fine particles (B).

In the FCC catalytic composition according to the present invention, a ratio of a content of P_2O_5 in the fine powder (F) to that in the spherical fine particle (B) is 1.05 times or more.

[0027]

Method for Producing the Catalytic Composition for Fluidized Catalytic Cracking of Hydrocarbons

The catalytic composition for FCC according to the present invention is produced as described below. Spherical fine particles as the FCC catalytic composition are prepared by spray-drying a slurry obtained by mixing an aqueous solution of P_2O_5 as primary phosphate (sometimes referred to as dihydrogen phosphate) by 5 to 20% by weight, pentacyl-type zeolite by 10 to 50% by weight, and a precursor for porous inorganic oxides including those other than P_2O_5 in the primary phosphate by 30 to 85% by weight.

[0028]

In the production method according to the present invention, it is important to use a dihydrogen phosphate as a source material of a phosphorus component. A spherical fine particle having a content of phosphorus in the surface of the spherical fine particle higher than that in the central portion cannot be obtained from phosphorus compounds such as

phosphoric acid and ammonium phosphate other than dihydrogen phosphates.

It is preferable to use aluminum dihydrogen phosphate, magnesium dihydrogen phosphate, calcium dihydrogen phosphate, zinc dihydrogen phosphate and manganese dihydrogen phosphate as the dihydrogen phosphates. Aluminum dihydrogen phosphate is especially preferable.

[0029]

In the method of production according to the present invention, a slurry is prepared by mixing an aqueous solution of the dihydrogen phosphate, pentacyl-type zeolite and the precursor of the porous inorganic oxide. The slurry preferably has an oxide content in the range from 25 to 50 % by weight, because the concentration in the range is suited for spray-drying. Then, the prepared mixed slurry is spray-dried, the resultant spherical fine particles are washed and dried, and then the FCC catalytic composition according to the present invention is obtained by calcination, if necessary.

[0030]

The FCC catalytic composition according to the present invention (additive catalyst) is used by mixing with an FCC catalyst containing faujasite-type zeolite by 0.1 to 10% by weight in the mixed catalyst in fluidized catalytic cracking of hydrocarbons with an FCC unit.

As the FCC catalyst containing faujasite-type zeolite, a conventional FCC catalyst may be used in an FCC unit. Such FCC catalysts include, for instance, FCC catalysts procurable from the market such as HMR, STW, DCT, ACZ, CVZ (all these catalysts are trademarks or registered trademarks owned by Catalysts & Chemicals Industries Co., Ltd.).

[0031]

When an amount of the FCC catalytic composition according to the present invention (additive catalyst) mixed in the FCC catalyst containing the faujasite-type zeolite is less than 0.1% by weight in the mixed catalyst, the desired effect of increasing an octane

number and a content of light olefins may not be achieved. In addition, when the amount of the FCC catalytic composition according to the present invention (additive catalyst) mixed in the FCC catalyst is more than 10% by weight in the mixed catalyst, an amount of the FCC catalyst containing faujasite-type zeolite becomes smaller, and it is not desirable because the catalytic cracking activity of hydrocarbons is degraded. The amount of the FCC catalytic composition mixing with the FCC catalyst containing faujasite-type zeolite is preferably in the range from 1 to 5% by weight.

[0032]

Conditions of fluidized catalytic cracking of hydrocarbons for the conventional FCC unit may be employed in a process for fluidized catalytic cracking of hydrocarbons using the FCC catalytic composition according to the present invention.

EXAMPLES

[Example 1]

[0033]

1786 grams (25% by weight in the final catalytic composition) of slurry containing ZSM-5 zeolite (830 NHA: Produced by Tosoh Corporation) by 28% by weight is mixed with 1395 grams of kaolin (60% by weight in the final catalytic composition), followed by adding 723 grams of an aqueous solution of aluminum dihydrogen phosphate $[\text{Al}(\text{H}_2\text{PO}_4)_3]$ (Produced by Yoneyama Chemical Co., Ltd.) containing 8.7% by weight of Al_2O_3 and 32.8% by weight of P_2O_5 (15% by weight in the final catalytic composition). Furthermore, 1096 grams of pure water is added in the mixture to obtain a mixed slurry with the concentration of 40% by weight. This mixed slurry is spray-dried to obtain spherical fine particles, and the spherical fine particles are calcinated for 2 hours at 600 °C to prepare Catalyst A.

[0034]

Table 1 shows properties of the Catalyst A including the composition, contents of P_2O_5 in a surface portion and a central portion of catalyst particle, Surface P/Central P, and an average particle diameter of each sample measured before and after the attrition test.

Fig. 1 shows an image of a cross section of Catalyst A taken with an electron probe microanalysis system (WDS), and a distribution chart prepared by linearly analyzing a linear portion of a central portion of the image.

[Comparative Example 1]

[0035]

Catalyst B is prepared by the same method as that employed in Example 1 except the point that a phosphoric acid solution with the concentration of 85% by weight is added in place of the solution of aluminum dihydrogen phosphate $[Al (H_2PO_4)_3]$, so that the concentration in the final catalytic composition is 15% by weight. Properties of Catalyst B are shown in Table 1.

Fig. 2 shows an image of a cross section of Catalyst B taken with an electron probe microanalysis system (WDS), and a distribution chart of elements prepared by linearly analyzing a linear portion of a central portion of the image.

[Comparative Example 2]

[0036]

Catalyst C is prepared using the same method as that employed in Example 1 except the point that a solution of aluminum dihydrogen phosphate $[Al (H_2PO_4)_3]$ is added so that the total concentration of Al_2O_3 and P_2O_5 in the final catalytic composition is 5% by weight and kaolin is used as balance. Properties of Catalyst C are shown in Table 1.

[Example 2]

[0037]

Catalyst D is prepared using the same method as that employed in Example 1 except the point that a solution of aluminum dihydrogen phosphate $[Al (H_2PO_4)_3]$ is added

so that the total concentration of Al_2O_3 and P_2O_5 in the final catalytic composition is 10% by weight and kaolin is used as balance. Properties of Catalyst D are shown in Table 1.

[Example 3]

[0038]

Catalyst E is prepared using the same method as that employed in Example 1 except the point that a solution of aluminum dihydrogen phosphate $[\text{Al}(\text{H}_2\text{PO}_4)_3]$ so that the weight of total concentration of Al_2O_3 and P_2O_5 in the final catalytic composition is 20% by weight and kaolin is used as balance. Properties of Catalyst E are shown in Table 1.

[Comparative Example 4]

[0039]

Catalyst F is prepared using the same method as that employed in Example 1 except the point that a solution of aluminum dihydrogen phosphate $[\text{Al}(\text{H}_2\text{PO}_4)_3]$ to obtain 30 % by weight of total concentration of Al_2O_3 and P_2O_5 at a weight basis of the final catalytic composition, and using kaolin as balance. Properties of Catalyst F are shown in Table 1.

[Example 4]

[0040]

Catalyst G is prepared using the same method as that employed in Example 1 except the point that ZSM-5 zeolite is weighed so that the content in the final catalytic composition is 15% by weight and also a solution of aluminum dihydrogen phosphate $[\text{Al}(\text{H}_2\text{PO}_4)_3]$ is added so that the total concentration of Al_2O_3 and P_2O_5 in the final catalytic composition is 12% by weight with kaolin used as balance. Properties of Catalyst G are shown in Table 1.

[Example 5]

[0041]

Catalyst H is prepared using the same method as that employed in Example 1

except the point that ZSM-5 zeolite is weighed so that the content in the final catalytic composition is 40% by weight and a solution of aluminum dihydrogen phosphate [$\text{Al}(\text{H}_2\text{PO}_4)_3$] is added so that the total concentration of Al_2O_3 and P_2O_5 in the final catalytic composition is 16% by weight with kaolin used as balance. Properties of Catalyst H are shown in Table 1.

[Example 6]

[0042]

Catalyst I is prepared using the same method as that employed in Example 1 except the point that a solution of magnesium dihydrogen phosphate [$\text{Mg}(\text{H}_2\text{PO}_4)_2$] (Produced by Yoneyama Chemical Co., Ltd.) containing 8.0% by weight of MgO and 33.9% by weight of P_2O_5 is added in place of aluminum dihydrogen phosphate [$\text{Al}(\text{H}_2\text{PO}_4)_3$] so that the total concentration of MgO and P_2O_5 in the final catalytic composition is 15% by weight. Properties of Catalyst I are shown in Table 1.

[Comparative Example 5]

[0043]

100 kg of a diluted aqueous solution of sodium silicate having the SiO_2 concentration of 4.0% by weight is prepared by diluting sodium silicate having a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 3.20 and the SiO_2 concentration of 24% by weight. The solution is put in a 200-L tank having a steam jacket, 1000 grams of sodium sulfate is added by agitating the mixture at 600 rpm, and the mixture is heated up to 90 °C over 20 minutes. Then, silicate slurry with the pH of 7.0 is obtained by adding 8.07 kg of an aqueous solution of sulfuric acid with the concentration of 25% by weight over 50 minutes keeping the temperature at 90 °C.

[0044]

The silicate slurry is filtered and splashed and washed with 200 liters of warm water at the temperature of 60 °C to remove by-product Na_2SO_4 from the slurry. Pure

water is added to this washed cake to prepare slurry with the SiO₂ concentration of 8.0% by weight, and then the slurry is passed through a homogenizer to obtain a homogenized slurry. This homogenized slurry is spray-dried at the inlet temperature of 280 °C and the outlet temperature of 150 °C to obtain porous silica particles.

The porous silica particles are pulverized by a jet mill to prepare porous silica powder (X) having the average particle diameter of 8 µm. Properties of the porous silica powder (X) after calcinated at 600 °C for 2 hours are as follows, a surface area: 190 m²/g, a pore volume: 2.5 ml/g, and an average pore diameter: 53nm.

[0045]

Sulfuric acid with the concentration of 25% by weight is continuously added to water glass with the SiO₂ concentration of 17% by weight, and the mixture is processed at the temperature of 40 °C to prepare silica hydrosol with the pH of 1.6 and the SiO₂ concentration of 12.5%.

The silica hydrosol is weighed so that a content of SiO₂ in the catalytic composition is 18.7% by weight, and then kaolin, alumina (CATAPAL-A: Produced by Sasol Chemical Industries Ltd.) and the porous silica powder (X) are added to the silica hydrosol so that the contents in the catalytic composition are 36% by weight, 4.7% by weight and 5.6% by weight respectively in the catalytic composition, to prepare a matrix precursor slurry.

Further, a slurry with the content of ZSM-5 zeolite (830NHA: Produced by Tosoh Corporation) of about 30% by weight is added to the matrix precursor slurry so that a content of the zeolite in the final composition is 28% by weight, to prepare a mixed slurry with the pH of 2.6 and the temperature of 35 °C.

[0046]

This mixed slurry is spray-dried to prepare spherical fine particles, which are washed with an aqueous solution of ammonium sulfate with the concentration of 5% by

weight until a content of Na_2O is dropped to 0.1% by weight or below and then dried at 135 °C in a drying machine. Then, the dried catalyst particles are impregnated with an aqueous solution of H_3PO_4 so that a content of P_2O_5 in the dried catalyst particle is 7.0% by weight and is dried overnight at 135 °C. The dried particles are calcinated for 2 hours at 600 °C to prepare Catalyst J. Properties of Catalyst J are shown in Table 1.

[Example 7]

[0047]

An evaluation test is performed for each of Catalysts A to J produced in the examples and the comparative examples respectively with the ACE-MAT (Advanced Cracking Evaluation – Micro Activity Test) system by using the same feedstock oil and applying the reaction conditions. Before the evaluation tests, each catalyst is pretreated for 13 hours under the temperature of 750 °C and in 100 % steam atmosphere.

Each pretreated catalyst is blended with an FCC equilibrium catalyst so that a content of ZSM-5 is stabilized at 0.6% by weight in the mixed catalyst, and evaluated by the ACE-MAT system. The specific content value of 0.6% by weight as used herein means 4.0 % by weight for a catalyst having the ZSM-5 content of 15% by weight, 2.4% by weight for a catalyst with the ZSM-5 content of 25% by weight, and 1.5% by weight for a catalyst with the ZSM-5 content of 40% by weight.

[0048]

The reaction conditions are as follows.

Reaction temperature: 510 °C

Feed oil: Blended oil of 50 wt % of desulfurized reduced crude (DSAR) and 50 wt % of desulfurized vacuum gas oil (DSVGO)

WHSV: 8 hr^{-1}

Ratio of Catalyst/Oil: 5 wt % / wt %

[0049]

A result of the evaluation test is shown in Table 2.

From the result shown in Table 2, it is understood that an octane number of gasoline is higher and a content of light olefins fractions such as propylene and butylenes is larger for the catalysts according to the present invention as compared to the catalysts prepared in the comparative examples.

Also, it is understood that each of the catalysts prepared in the examples has a small value of average attrition rate (wt %/hr) resulting in a superior attrition resistance. The spherical fine particles are flowed in a catalytic tube constituting the attrition testing machine and the attrition rate is measured for a period 12 hours to 20 hours after the beginning of the testing, and the average attrition rate is described as attrition rate per hour.

Table 1

		E.1	CE.1	CE.2	E.2	E.3	CE.4	E.4	E.5	E.6	CE.5
Catalyst Sign		A	B	C	D	E	F	G	H	I	J
Catalyst Composition											
Aluminum dihydrogen phosphate	wt%	15	-	5	10	20	30	12	16	-	-
Magnesium dihydrogen phosphate	wt%	-	-	-	-	-	-	-	-	15	-
Phosphoric acid	wt%	-	15	-	-	-	-	-	-	-	7
Silica binder	wt%	-	-	-	-	-	-	-	-	-	18.7
ZSM-5	wt%	25	25	25	25	25	25	15	40	25	28
Active alumina	wt%	-	-	-	-	-	-	-	-	-	4.7
Porous Aluminum silicate	wt%	-	-	-	-	-	-	-	-	-	5.6
Kaolin	wt%	60	60	70	65	55	45	73	44	60	36
Properties											
P ₂ O ₅	wt%	11.9	15.0	4.0	7.9	15.8	23.7	9.5	12.6	12.2	7.0
P ₂ O ₅ (Surface)	wt%	11.4	14.9	2.9	7.7	15.6	23.4	9.3	12.5	12.1	7.0
P ₂ O ₅ (Center)	wt%	10.3	14.8	2.7	7.1	13.6	20.0	8.2	11.8	10.7	7.1
Surface P / Center P	%	1.11	1.01	1.07	1.08	1.15	1.17	1.13	1.06	1.13	0.99
*1	μ m	70	73	70	71	73	69	71	72	71	72
*2	μ m	67	66	64	63	70	68	67	66	67	69

*1: Average particle diameter of catalyst before measurement of attrition

*2: Average particle diameter of catalyst after measurement of attrition

Table 2

Catalyst Sign		E.1	CE.1	CE.2	E.2	E.3	CE.4	E.4	E.5	E.6	CE.5
Assessment of activity		A	B	C	D	E	F	G	H	I	J
Mix Ratio in Eq. Catalyst	wt%	0	2.4	2.4	2.4	2.4	2.4	4.0	1.5	2.4	2.4
ZSM in total catalyst	wt%	0	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.7
Conversion ratio	wt%	72.1	72.0	71.9	72.0	72.0	72.0	71.9	71.9	71.9	72.0
Dry gas	wt%	2.3	2.1	2.2	2.2	2.2	2.0	2.2	2.2	2.2	2.2
Propane (C3)	wt%	1.3	1.3	2.2	1.7	1.6	1.2	1.6	1.6	1.6	1.4
Propylene (C3 ⁼)	wt%	4.2	4.8	6.4	6.6	6.1	4.3	6.8	6.3	6.5	5.5
n-Butane (n-C4)	wt%	1.5	1.6	1.9	2	1.9	1.5	1.9	1.9	2	1.7
i-butane (i-C4)	wt%	3.6	3.4	3.7	3.7	3.7	3.3	3.5	3.6	3.7	3.4
Butylenes (C4 ⁼)	wt%	4.9	5.4	6.4	6.6	6.2	5.2	6.7	6.4	6.7	5.8
Gasoline	wt%	48.0	47.2	42.8	43.0	44.0	48.1	42.8	43.7	43.1	45.8
Light cycle oil (LCO)	wt%	16.5	16.5	16.5	16.6	16.5	16.4	16.5	16.5	16.6	16.4
Bottom (HCO+CLO)	wt%	11.4	11.5	11.6	11.4	11.5	11.6	11.6	11.6	11.5	11.6
Coke	wt%	6.4	6.4	6.3	6.3	6.4	6.2	6.3	6.3	6.2	6.2
Octane number (RON)	-	91.7	93.3	92.2	93.1	93.0	91.8	93.3	93.1	93.2	92.5
Properties											
Average attrition rate	wt%/hr		0.23	0.60	1.10	0.13	0.10	0.27	0.43	0.30	0.13
Bulk density	g/ml		0.67	0.68	0.64	0.65	0.76	0.73	0.65	0.66	0.69

CLAIMS

1. A catalytic composition for fluidized catalytic cracking of hydrocarbons, the composition having a form of spherical fine particles and comprising phosphorus pentoxide (P_2O_5) by 5 to 20% by weight, pentacyl-type zeolite by 10 to 50% by weight, and a porous inorganic oxide by 30 to 85% by weight, wherein a content of P_2O_5 in a surface portion of the fine particle is 1.05 times or more higher than that in the central portion.
2. A method of producing the catalytic composition for fluidized catalytic cracking of hydrocarbons according to claim 1, wherein the spherical fine particle is prepared by spray-drying a slurry obtained by mixing an aqueous solution of primary phosphate as P_2O_5 by 5 to 20% by weight, pentacyl-type zeolite by 10 to 50% by weight, and a precursor for porous inorganic oxides including those other than P_2O_5 in the composition primary phosphate by 30 to 85% by weight.
3. A method of producing the catalytic composition for fluidized catalytic cracking of hydrocarbons according to claim 2, wherein the primary phosphate is at least one selected from the group consisting of aluminum primary phosphate, magnesium primary phosphate, calcium primary phosphate, zinc primary phosphate, and manganese primary phosphate.