DESCRIPTION

CATALYST FOR FLUID CATALYTIC CRACKING OF HYDROCARBON OIL AND METHOD FOR FLUID CATALYTIC CRACKING OF HYDROCARBON OIL WITH THE SAME

Technical Field

[0001]

The present invention relates to a catalyst for fluid catalytic cracking of hydrocarbon oil with which gasoline and a gas oil fraction can be obtained in high yields and a high degree of bottom cracking and a low coke yield are attained, and to a method for fluid catalytic cracking of hydrocarbon oil with it.

Background Art

[0002]

In fluid catalytic cracking of hydrocarbon oil, catalysts for fluid catalytic cracking containing a silica-based binder, such as silica sol, as a binding agent have been developed so far for the purpose of obtaining gasoline in a high yield and attaining a low coke yield (e.g., see PTL 1). However, catalysts for fluid catalytic cracking that contain a silica-based binder have been required to attain a higher degree of bottom cracking.

[0003]

And, in order to obtain gasoline and a kerosene/light oil fraction (a kerosene fraction and a light oil fraction, or light cycle oil; hereinafter, also referred to as "LCO") and to improve the degree of bottom cracking, in other words, to reduce the yield of a heavy fraction (heavy cycle oil; hereinafter, also referred to as "HCO"), catalysts for fluid catalytic cracking containing an aluminum-compound binder, such as basic aluminum chloride, as a binding agent are also under development (e.g., see PTL 2). However, catalysts for fluid catalytic cracking that contain an alumina-compound binder have been required to produce coke in a lower yield.

[0004]

Incidentally, fluid catalytic cracking apparatus (full-scale apparatus) is usually used with any catalyst for fluid catalytic cracking that may be changed to provide any intended formulation of resultant oil (e.g., "a high proportion of gasoline," "a high proportion of light cycle oil," and so forth). Also, different kinds of raw material oil provide different formulations of resultant oil, and thus the catalyst for fluid catalytic cracking is usually changed to provide any intended formulation of resultant oil. When the catalyst is changed, the following cases are possible: (1) A catalyst containing a silica-based binder is changed to

one that contains a different silica-based binder; (2) A catalyst containing an aluminum-compound binder is changed to one that contains a different aluminum-compound binder; (3) a catalyst containing a silica-based binder is changed to one that contains an aluminum-compound binder; and (4) a catalyst containing an aluminum-compound binder is changed to one that contains a silica-based binder. Here, when a catalyst is changed, some volume of a first catalyst is first taken out of the apparatus, and then the same volume of a second catalyst is put into the apparatus. In this case, the inside of the fluid catalytic cracking apparatus is subjected to a gradual change in the mixing proportion (mass proportion) of the first catalyst to the second catalyst, and finally the content inside the apparatus, the first catalyst, is replaced with the second catalyst. This has involved changes in catalytic activity, conversion rate, gasoline yield, and some other conditions; however, it has believed that these changes are attributable to a newly added catalyst or operating conditions of the apparatus.

[0005]

As for additive catalysts (added catalysts), which are added to a catalyst for fluid catalytic cracking, these are intended for supplementing the performance of the catalyst for fluid catalytic cracking (e.g., removal of NOx, removal

of SOx, resistance against metal, improvement of octane number, degree of bottom cracking, and so forth), not for obtaining gasoline and a gas oil fraction in high yields or attaining a high degree of bottom cracking and a low coke yield.

Citation List

Patent Literature

[0006]

PTL 1: Japanese Unexamined Patent Application Publication No. 2007-748

PTL 2: Japanese Unexamined Patent Application Publication No. 2006-142273

Summary

Technical Problem

[0007]

However, known catalysts for fluid catalytic cracking have had a problem that none of available ones satisfies all of a high gasoline yield, a high yield of a gas oil fraction, a low coke yield, and a high degree of bottom cracking.

[0008]

Made under these circumstances, the present disclosure aims to provide a catalyst for fluid catalytic cracking of hydrocarbon oil with which gasoline and a gas oil fraction can be obtained in high yields and a high degree of bottom

cracking and a low coke yield are attained, and a method for fluid catalytic cracking of hydrocarbon oil with it.

Solution to Problem

[0009]

More specifically, the gist of the present disclosure is as follows:

In a first aspect, there is provided a catalyst for fluid catalytic cracking of hydrocarbon oil, comprising a catalyst composition A that comprises FAU type (faujasite type) zeolite and 10 to 30 % by mass of a silica-based binder as a binding agent and a catalyst composition B that comprises FAU type (faujasite type) zeolite and 10 to 30 % by mass of an aluminum-compound binder as a binding agent, mixed therein in any mass proportion in the range of 10:90 to 90:10 (W_A:W_B), provided that W_A is the mass of the catalyst composition A and W_B is the mass of the catalyst composition B.

[1] There is provided a catalyst for fluid catalytic cracking of hydrocarbon oil, comprising Catalyst Composition A that comprises zeolite and 10 to 30 % by mass of a silica-based binder as a binding agent and Catalyst Composition B that comprises zeolite and 10 to 30 % by mass of an aluminum-compound binder as a binding agent, mixed therein in any mass proportion in the range of 10:90 to 90:10 (W_A:W_B), provided

that W_A is the mass of the catalyst composition A and W_B is the mass of the catalyst composition B.

[2] The catalyst for fluid catalytic cracking of hydrocarbon oil according to [1], wherein each of Catalyst Composition A and Catalyst Composition B has a K value as expressed by the following formula (1), which is equal to or higher than 1.

[0010]

K value = Conversion rate/(100-Conversion rate) (1)

where the conversion rate is expressed by the following formula (2);

[0011]

Conversion rate (% by mass) = (a-b)/a × 100 (2)

where the symbol "a" represents the mass of raw material oil, and "b" represents the total mass of light cycle oil and heavy cycle oil.

[3] The catalyst for fluid catalytic cracking of hydrocarbon oil according to [1] or [2], wherein, when the K values for Catalyst Composition A and for Catalyst Composition B are expressed as "K_A" and "K_B" respectively, the ratio of K_A:K_B is in the range as shown in the following formula (3);

[0012]

K_A:K_B=1:0.5 to 1:1.5 (3).

[4] The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of [1] to [3], wherein, when the K value for the above catalyst is expressed as "K_m", the K_m is greater than the K value for Catalyst Composition A (K_A) and the K value for Catalyst Composition B (K_B).

[5] The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of [1] to [4], wherein a gasoline yield by use of the above catalyst, when it is expressed as "G_m", is greater than a gasoline yield by use of Catalyst Composition A, when it is expressed as "G_A" and a gasoline yield by use of Catalyst Composition B, when it is

expressed as "G_B".

[6] The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of [1] to [5], wherein the above silica-based binder is one or more of the binding agent(s) selected from the group consisting of a silica sol, a water glass, and an acidic liquid of silicic acid.

[7] The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of [1] to [6], wherein the aluminum-compound binder is one or more of the binding agent(s) selected from the group consisting of the following compound (a) to (c);

(a) Basic aluminum chloride,

(b) Aluminum biphosphate,

(c) Alumina sol.

[8] The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of [1] to [7], wherein the zeolite has a crystal structure selected from the group consisting of FAU type (faujasite type), MFI type, CHA type, and MOR type, or a mixture thereof and is contained in Catalyst Composition A and Catalyst Composition B in the range of 15 to 60 % by mass respectively on a catalyst basis.

[9] The catalyst for fluid catalytic cracking of hydrocarbon oil according to [8], wherein the zeolite, when it has a crystal structure of the FAU type, is any one of

hydrogen Y-type zeolite (HY), ultrastable Y-type zeolite (USY), rare-earth exchanged Y-type zeolite (REY), and rare-earth exchanged ultrastable Y-type zeolite (REUSY).

[10] The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of [1] to [9], wherein Catalyst Composition A and Catalyst Composition B further comprise, besides the zeolite and the binding agent, a clay mineral.

In a second aspect, there is provided a method for fluid catalytic cracking of hydrocarbon oil, with use of the above catalyst as defined above.

[11] There is provided a method for fluid catalytic cracking of hydrocarbon oil, with use of the above catalyst according to any of [1] to [10].

[12] The method for fluid catalytic cracking of hydrocarbon oil according to [11], wherein the hydrocarbon oil comprises a residual oil.

[13] The method for fluid catalytic cracking of hydrocarbon oil according to [12], wherein the hydrocarbon oil comprises vanadium and nickel being equal to or more than 0.5 ppm by mass for each.

[14] The method for fluid catalytic cracking of hydrocarbon oil according to any of [11] to [13], wherein the above catalyst comprises vanadium and nickel being equal to or more than 300 ppm by mass for each.

Advantageous Effects

[0013]

A catalyst for fluid catalytic cracking of hydrocarbon oil according to the present disclosure comprises two catalyst compositions for cracking of different kinds of oil, more specifically, Catalyst Composition A comprising a silica-based binder and Catalyst Composition B comprising an aluminum-compound binder, mixed therein. This means that in fluid catalytic cracking of hydrocarbon oil, oil cracked by one of the catalyst compositions can be further cracked by the other catalyst composition, and thus oil left after cracking is lighter than ever; as a result, gasoline and a gas oil fraction can be obtained in high yields, coke is produced in a low yield, and the degree of bottom cracking can be high enough to prevent the formation of heavy cycle oil.

[0014]

In particular, when the raw material oil is heavy oil, which contains large amounts of vanadium, nickel, and other metals poisonous to catalysts, alumina contained in Catalyst Composition B, which comprises an alumina-compound binder, binds to these poisonous metals to detoxify them, and thus Catalyst Composition A, which comprises a silica-based binder, becomes unlikely to be poisoned by the poisoning metals; as a result, a high gasoline yield and a high yield of a gas oil fraction as well as a high degree of bottom cracking are

achieved while the high gasoline yield and a low coke yield are maintained.

Brief Description of Drawings

[0015]

[Fig. 1] Fig. 1 is a plot of K values obtained for an example of the present invention.

[Fig. 2] Fig. 2 is a plot of gasoline yields obtained for an example of the present invention.

Description of Embodiments

[0016]

A catalyst for fluid catalytic cracking of hydrocarbon oil according to an embodiment of the present invention comprises Catalyst Composition A that comprises zeolite and 10 to 30 % by mass of a silica-based binder as a binding agent and Catalyst Composition B that comprises zeolite and 10 to 30 % by mass of an aluminum-compound binder as a binding agent, mixed therein in any mass proportion in the range of 10:90 to 90:10 (W_A:W_B), provided that W_A is the mass of Catalyst Composition A and W_B is the mass of Catalyst Composition B. The following details the individual catalyst compositions.

[0017]

Incidentally, fluid catalytic cracking apparatus (full-scale apparatus) sometimes reaches the above-mentioned mass

proportion during the change from a catalyst comprising a silica-based binder to one that comprises an aluminum-compound binder and vise versa because of gradual addition of the replacing catalyst. However, this is not the case in the present invention because a catalyst mixture having a fixed mass proportion is continuously added and thus the mass proportion of catalyst compounds in the apparatus is kept constant.

[0018]

Also, the catalyst used in the present invention is a mixture of catalyst compositions each comprising a different binder. These catalyst compositions are intended for initiating fluid catalytic cracking and thus are different from additive catalysts (added catalysts), which are added to a catalyst for fluid catalytic cracking to supplement the catalyst's performance.

[Catalyst Composition A]

Catalyst Composition A comprises, for example, 15 to 60 % by mass, preferably 20 to 50 % by mass of zeolite, 10 to 30 % by mass, preferably, 15 to 25 % by mass of a silica-based binder as a binding agent, and inorganic oxides other than zeolite as the balance.

<<Silica-based Binder>>

The silica-based binder can be any one of or two or more

of silica sol, water glass (sodium silicate), and silicic acid liquid. And, silica sol can be produced from water glass. For example, silica sol comprising SiO_2 at a concentration in the range of 10 to 15 % by mass can be prepared by adding water glass comprising SiO_2 at a concentration in the range of 12 to 23 % by mass and sulfuric acid having a concentration in the range of 20 to 30 % by mass simultaneously and continuously.

<<Zeolite>>

The zeolite used here can be any kind of zeolite commonly used in a catalyst for catalytic cracking of hydrocarbon oil, for example, any one of or two or more of FAU type (faujasite type; e.g., Y-type zeolite, X-type zeolite, and so forth), MFI type (e.g., ZSM-5, TS-1, and so forth), CHA type (Examples are chabasite, SAPO-34, and so forth), and MOR type (e.g., mordenite, Ca-Q, and so forth). The FAU type is particularly preferable. Faujasite-type zeolite includes hydrogen Y-type zeolite (HY), ultrastable Y-type zeolite (USY), rare-earth exchanged Y-type zeolite (REY), and rare-earth exchanged ultrastable Y-type zeolite (REUSY). The latter two types of zeolite can be obtained by making HY and USY carry rare-earth metals by ion exchange or some other means.

[0019]

When the content ratio of zeolite to Catalyst Composition A is lower than 15 % by mass, the cracking activity is often low. When it exceeds 60 % by mass, the bulk density is often high, leading to a decreased strength.

<<Inorganic Oxides>>

The inorganic oxides can be, besides kaolin and other clay minerals, activated alumina, porous silica, rare-earth metal compounds, and metal capture agents (metal-trapping agents).

[0020]

Any rare-earth metal oxide may be contained in Catalyst Composition A, in the form of RE_2O_3, at a content ratio in the range of 0.5 to 2.0 % by mass. Rare-earth metals used here include cerium (Ce), lanthanum (La), praseodium (Pr), and neodymium (Nd), and Catalyst Composition A may carry any one of or two or more of these as metal oxides.

[0021]

The following describes an example of the manufacturing method of Catalyst Composition A. First, kaolin, porous silica powder, and activated alumina are added to silica sol mentioned above (an example of the silica-based binder), and then slurry of ultrastable Y-type zeolite (USY) prepared with 20 to 30 % by mass sulfuric acid to have pH in the range of 3 to 5; in this way, a slurry mixture is prepared. This slurry

mixture is spray-dried to form spherical particles. The obtained spherical particles are washed, brought into contact with an aqueous solution of a rare earth metal (RE) chloride for ion exchange for the content ratio of RE_2O_3 to be in the range of 0.5 to 2.0 % by mass, and then dried; in this way, Catalyst Composition A is obtained. The average particle diameter of Catalyst Composition A obtained is not particularly limited as long as the composition can be mixed with Catalyst Composition B described later; however, it is on the order of 60 to 70 μm.

[Catalyst Compound B]

Catalyst Composition B comprises, for example, 15 to 60 % by mass, preferably 20 to 50 % by mass of zeolite, 10 to 30 % by mass, preferably 15 to 25 % by mass of an aluminum-compound binder as a binding agent, and inorganic oxides other than zeolite as the balance.

<<Aluminum-compound Binder>>

The aluminum-compound binder can be (a) basic aluminum chloride, (b) aluminum biphosphate, or (c) alumina sol. A solution obtained by dissolving any kind of or two or more kinds of crystalline alumina, such as gibbsite, bayerrite, and boehmite, in an acid solution may be used as the aluminum-compound binder instead.

[0022]

Here, basic aluminum chloride is expressed by Formula 4.

[0023]

$$[Al_2(OH)_nCl_{6-n}]_m \quad (4)$$

(where, $0<n<6$ and $1\leq m\leq 10$, preferably, $4.8\leq n\leq 5.3$ and $3\leq m\leq 7$, and the symbol m represents a natural number.)

Aluminum biphosphate, also referred to as aluminum dihydrogen phosphate or primary aluminum phosphate, is expressed by $Al(H_2PO_4)_3$. Alumina sol can be produced by, for example, pH adjustment of pseudoboehmite-type alumina with an acid.

<<Zeolite and Inorganic Oxides>>

Zeolite and inorganic oxides that can be used for Catalyst Composition B are the same as those for Catalyst Composition A described above and can be prepared in the same content ratios as those for Catalyst Composition A.

[0024]

The following describes an example of the manufacturing method of Catalyst Composition B. First, kaolin, activated alumina, and USY slurry are added to, for example, a solution of basic aluminum chloride with an Al_2O_3 concentration in the range of 20 to 25 % by mass; in this way, a slurry mixture is prepared with a slurry concentration in the range of 35 to 45%. This slurry mixture is spray-dried to form spherical particles. These spherical particles are washed, brought

into contact with a solution of a rare earth metal chloride for ion exchange for the content ratio of RE_2O_3 to be in the range of 0.5 to 2.0 % by mass, and then dried; in this way, Catalyst Composition B is obtained. The average particle diameter of Catalyst Composition B obtained is not particularly limited; however, it is on the order of 60 to 70 μm.

[Catalyst for Fluid Catalytic Cracking]

A catalyst for fluid catalytic cracking according to the present invention is a mixture obtained by mixing Catalyst Composition A and Catalyst Composition B in any mass proportion in the range of 10:90 to 90:10 (W_A:W_B), provided that W_A is the mass of Catalyst Composition A and W_B is the mass of Catalyst Composition B. When the mass proportion of the catalyst compositions deviates from the specified range, the difference from the case where the catalyst compositions are individually used for fluid catalytic cracking is small, and thus an explicit advantage is unlikely to be obtained. Note that the mixing proportion (mass proportion) of Catalyst Composition A and Catalyst Composition B is preferably determined in such a manner that the cracking products obtained by cracking of hydrocarbon oil using this catalyst for fluid catalytic cracking (in particular, gasoline and LCO) can have intended formulations (yields).

[Method for Fluid Catalytic Cracking]

Fluid catalytic cracking based on a catalyst for fluid catalytic cracking according to the present invention can be performed under ordinary conditions for fluid catalytic cracking of hydrocarbon oil. For example, the conditions described below can be suitably used.

[0025]

The raw material oil for catalytic cracking can be ordinary raw material hydrocarbon oil, for example, hydro desulfurized vacuum gas oil (DSVGO) or vacuum gas oil (VGO), or residual oil such as residual oil of atmospheric distillation (AR), residual oil of vacuum distillation (VR), desulfurized residual oil of atmospheric distillation (DSAR), desulfurized residual oil of vacuum distillation (DSVR), and deasphaltened oil (DAO). These kinds of oil can be used alone or in combination thereof. A catalyst for fluid catalytic cracking according to the present invention can process any residual oil that contains nickel and vanadium at a content ratio equal to or higher than 0.5 ppm by mass each, and can be used with apparatus for fluid catalytic cracking of residual oil (Resid FCC, or RFCC), which involves the use of residual oil alone. Note here that when a known catalyst for fluid catalytic cracking is used with RFCC, nickel and vanadium contained in residual oil adhere to the catalyst and

reduce the activity of it; however, with a catalyst for fluid catalytic cracking according to the present invention, even processing of any residual oil that contains vanadium and nickel at a content ratio equal to or higher than 0.5 ppm by mass each would not affect the excellent catalytic performance of the catalyst. Furthermore, a catalyst for fluid catalytic cracking according to the present invention keeps its catalytic performance even when it contains vanadium and nickel at a content ratio equal to or higher than 300 ppm by mass each. The maximum acceptable limit of vanadium and nickel contained in a catalyst for fluid catalytic cracking according to the present invention is about 10000 ppm by mass each.

[0026]

As for reaction temperature for catalytic cracking of the above-mentioned raw material hydrocarbon oil, a temperature in the range of 470 to 550°C is suitably used. As for reaction pressure, a pressure on the order of 1 to 3 kg/cm^2 is usually preferable. The mass proportion of catalyst/oil (catalyst/oil ratio) is preferably in the range of 2.5 to 7.0, and the contact time is preferably in the range of 10 to 60 hr^{-1}.

<<K value>>

The K value can be determined in the following way: Raw

material oil is catalytically cracked by the method described above, the fractions having a boiling point higher than that of gasoline (on the order of 30 to 220°C), or light cycle oil (LCO) and heavy cycle oil (HCO), are weighed, the conversion rate is determined from the mass of the raw material oil and the total mass of LCO and HCO by Formula (2), and then the K value is determined from the conversion rate by Formula (1).

[0027]

K value = Conversion rate/(100-Conversion rate) (1)

Conversion rate (% by mass) = (a-b)/a × 100 (2)

where the symbol "a" represents the mass of raw material oil, and "b" represents the total mass of light cycle oil and heavy cycle oil.

[0028]

Here, the K values for Catalyst Composition A and Catalyst Composition B (K_A and K_B, respectively) are at least 1 (conversion rate: ≥50%), preferably equal to or higher than 1.5 (conversion rate: ≥60%), and more preferably equal to or higher than 2.3 (conversion rate: ≥70%). Any K value for Catalyst Composition A or Catalyst Composition B being less than 1 (conversion rate: <50%) results in low yields of gasoline and LCO and thus is impractical.

[0029]

Also, the K values for Catalyst Composition A and

Catalyst Composition B follow a relationship of K_A:K_B in the range of 1:0.5 to 1:1.5, preferably 1:0.8 to 1:1.2, and more preferably 1:0.9 to 1:1.1. In the case where K_A:K_B is 1:<0.5(lower than 0.5) or K_A:K_B is 1:>1.5(higher than 1.5), the difference in K value between the two catalyst compositions is too great, and thus it is difficult to exceed K_A and K_B.

[0030]

Additionally, the K value for the catalyst for fluid catalytic cracking (K_m) is preferably greater than the K value for Catalyst Composition A (K_A) and the K value for Catalyst Composition B (K_B).

<<Gasoline Yield G>>

The gasoline yield for the catalyst for fluid catalytic cracking, G_m, is preferably greater than the gasoline yield for Catalyst Composition A, G_A, and the gasoline yield for Catalyst Composition B, G_B. The gasoline yield mentioned here is calculated from the mass of gasoline obtained by catalytic cracking of raw material performed by the method described above and the mass of the raw material oil.

[0031]

In addition, a catalyst for fluid catalytic cracking according to the present invention often provides LCO in a higher yield, and hydrogen, C1+C2, LPG, HCO, and coke in

lower yields than Catalyst Composition A or Catalyst Composition B used alone does. In other words, the use of a catalyst for fluid catalytic cracking according to the present invention, when compared with the use of Catalyst Composition A or Catalyst Composition B alone, often increases the yields of liquid fuels, such as gasoline and LCO, but decreases the yields of gas, heavy oil, coke, and so forth.

EXAMPLES

[0032]

[Production of Silica-based Binders]

<<Catalyst Composition A_1>>

Silica sol comprising SiO_2 at a concentration of 12.5 % by mass (an example of the silica-based binder) was prepared with a weight of 4000 g by adding 2941 g of water glass comprising SiO_2 at a concentration of 17 % by mass and 1059 g of sulfuric acid having a concentration of 25 % by mass simultaneously and continuously. To this silica sol, 800 g of kaolin, 175 g of porous silica powder, and 250 g of activated alumina, the weights on a dry weight basis, were added, and then 800 g of slurry of ultrastable Y-type zeolite (USY) prepared with 25 % by mass sulfuric acid to have pH of 3.9 was added; in this way, a slurry mixture was prepared. This slurry mixture was spray-dried to form spherical

particles having an average particle diameter of 60 μm.

[0033]

The obtained spherical particles were washed, brought into contact with an aqueous solution of a rare earth metal (RE) chloride (this solution contained chlorides of cerium and lanthanum; the same applies hereinafter) for ion exchange for the content ratio of RE_2O_3 to be 1.0 % by mass, and then dried in an oven at 135°C. In this way, Catalyst Composition A_1 was prepared.

[0034]

The formulation of Catalyst Composition A_1 was as follows: SiO_2 of silica sol origin: 20 % by mass; kaolin: 32 % by mass; SiO_2 of porous silica powder origin: 7 % by mass; activated alumina: 10 % by mass; USY: 30 % by mass. The properties of Catalyst Composition A_1 are shown in Table 1.

<<Catalyst Composition A_2>>

Silica sol comprising SiO_2 at a concentration of 12.5 % by mass (an example of the silica-based binder) was prepared with a weight of 4000 g by adding 2941 g of water glass comprising SiO_2 at a concentration of 17 % by mass and 1059 g of sulfuric acid having a concentration of 25 % by mass simultaneously and continuously. To this silica sol, 800 g of kaolin, 175 g of porous silica powder, and 250 g of

activated alumina, the weights on a dry weight basis, were added, and then 800 g of slurry of RE ultrastable Y-type zeolite (REUSY) prepared with 25 % by mass sulfuric acid to have pH of 3.9 was added as Y-type zeolite; in this way, a slurry mixture was prepared. This slurry mixture was spray-dried to form spherical particles having an average particle diameter of 60 μm.

[0035]

The obtained spherical particles were washed and then dried in an oven at 135°C. In this way, Catalyst Composition A_2 was prepared. The properties of Catalyst Composition A_2 are shown in Table 1.

<<Catalyst Composition A_3>>

To 2941 g of water glass comprising SiO_2 at a concentration of 17 % by mass (an example of the silica-based binder), 800 g of kaolin, 175 g of porous silica powder, and 250 g of activated alumina, the weights on a dry weight basis, were added, and then 800 g of slurry of RE ultrastable Y-type zeolite (REUSY) prepared with 25 % by mass sulfuric acid to have pH of 3.9 as Y-type zeolite was added; in this way, a slurry mixture was prepared. This slurry mixture was spray-dried to form spherical particles having an average particle diameter of 60 μm.

[0036]

The obtained spherical particles were washed and then dried in an oven at 135°C. In this way, Catalyst Composition A_3 was prepared. The properties of Catalyst Composition A_3 are shown in Table 1.

[0037]

[Table 1]

Table 1

		Composition A_1	Composition A_2	Composition A_3
Zeolite		USY	REUSY	REUSY
Binder		Silica sol	Silica sol	Water glass
Chemical properties				
Loss on carcination	% by mass	13.6	12.6	14.6
Al_2O_3	% by mass	30.4	28.8	28.0
RE_2O_3	% by mass	0.99	3.70	3.78
Na_2O	% by mass	0.13	0.15	0.23
SO_4	% by mass	0.23	0.32	0.36
Physical properties				
Specific surface area	m^2/g	259	263	238
Bulk specific gravity	g/m	0.73	0.65	0.67

[0038]

Note that the specific surface area and the bulk specific gravity were measured by the BET method and UOP Method 254-65, respectively. And, the loss on carcination represents a decrease in mass observed after carcination at 1000°C for one hour. (The same applies hereinafter.)

[Production of Aluminum-compound Binders]

<<Catalyst Composition B_1>>

To 1201 g of a basic aluminum chloride solution comprising Al_2O_3 at a concentration of 23.3 % by mass (an example of the aluminum-compound binder), 840 g of kaolin, 260 g of activated alumina, and 640 g of USY slurry were added; in this way, a slurry mixture was prepared with a slurry concentration of 41%. This slurry mixture was spray-dried to form spherical particles having an average particle diameter of 60 μm. These spherical particles were washed, brought into contact with an aqueous solution of a rare earth metal chloride for ion exchange for the content ratio of RE_2O_3 to be 1.0 % by mass, and then dried in an oven at 135°C. In this way, Catalyst Composition B1 was prepared. The formulation of Catalyst Composition B_1 obtained was as follows: Al_2O_3 of basic aluminum chloride solution origin: 14 % by mass; kaolin: 41 % by mass; activated alumina: 13 % by mass; USY: 32 % by mass. The properties of Catalyst Composition B_1 are shown in Table 2.

<<Catalyst Composition B_2>>

To 1201 g of a basic aluminum chloride solution comprising Al_2O_3 at a concentration of 23.3 % by mass (an example of the aluminum-compound binder), 840 g of kaolin, 260 g of activated alumina, and 640 g of REUSY slurry as Y-type zeolite were added; in this way, a slurry mixture was

prepared with a slurry concentration of 43%. This slurry mixture was spray-dried to form spherical particles having an average particle diameter of 60 μm. These spherical particles were washed and then dried in an oven at 135°C. In this way, Catalyst Composition B_2 was prepared. The properties of Catalyst Composition B_2 are shown in Table 2.

<<Catalyst Composition B_3>>

Alumina sol (an example of the aluminum-compound binder) was prepared by adding 63% nitric acid to 2400 g of an aqueous solution of pseudoboehmite-type alumina (Catapal-A, a product from Sasol) comprising Al_2O_3 at a concentration of 12.5 % by mass until pH was 3.0. To this alumina sol, 840 g of kaolin, 260 g of activated alumina, and 640 g of REUSY slurry as Y-type zeolite were added; in this way, a slurry mixture was prepared with a slurry concentration of 43%. This slurry mixture was spray-dried to form spherical particles having an average particle diameter of 60 μm. These spherical particles were carcinated in an electric furnace at 600°C. In this way, Catalyst Composition B_3 was prepared. The properties of Catalyst Composition B_3 are shown in Table 2.

<<Catalyst Composition B_4>>

To 1723 g of a 17.4 % by mass aluminum biphosphate solution (an example of the aluminum-compound binder), 840 g

of kaolin, 260 g of activated alumina, and 640 g of REUSY slurry as Y-type zeolite were added; in this way, a slurry mixture was prepared with a slurry concentration of 43%. This slurry mixture was spray-dried to form spherical particles having an average particle diameter of 60 μm. These spherical particles were carcinated in an electric furnace at 600°C. In this way, Catalyst Composition B_4 was prepared. The properties of Catalyst Composition B_4 are shown in Table 2.

[0039]

[Table 2]

Table 2

	Composition B_1	Composition B_2	Composition B_3	Composition B_4
Zeolite	USY	REUSY	REUSY	REUSY
Binder	ACH	ACH	Alumina sol	Aluminum biphosphate
Chemical properties				
Loss on carcination mass%	17.3	14.3	3.7	4.4
Al_2O_3 mass%	49.7	40.2	40.4	39.8
RE_2O_3 mass%	0.97	3.79	3.81	3.17
Na_2O mass%	0.26	0.15	0.18	0.17
SO_4 mass%	2.64	2.33	0.03	0.08
Physical properties				
Specific surface area m^2/g	261	274	283	156
Bulk specific gravity g/m	0.73	0.78	0.67	0.56

[0040]

<<Experiment 1: A_1-B_1>>

(Example 1: Catalyst 1)

Catalyst Composition A_1 and Catalyst Composition B_1 were mixed in a mass proportion of 70:30 on a dry weight basis to

form Catalyst for Fluid Catalytic Cracking 1.

(Example 2: Catalyst 2)

Catalyst Composition A_1 and Catalyst Composition B_1 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 2.

(Example 3: Catalyst 3)

Catalyst Composition A_1 and Catalyst Composition B_1 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 3.

(Comparative Example 1: Catalyst 4)

Catalyst Composition A_1 was used as Catalyst for Fluid Catalytic Cracking 4.

(Comparative Example 2: Catalyst 5)

Catalyst Composition B_1 was used as Catalyst for Fluid Catalytic Cracking 5.

(Test 1)

With Catalysts for Fluid Catalytic Cracking 1 to 5, catalytic cracking reaction test was performed using a pilot reaction test unit (a product from ARCO) with the same raw material oil and under the same reaction conditions. The pilot reaction test unit, which had a circulation moving bed for the circulation of a catalyst inside and alternately repeated reaction and catalyst regeneration, was a simulator of apparatus for fluid catalytic cracking in commercial use.

(The same also applies to the examples described below.)

First, prior to the reaction test, Catalysts for Fluid Catalytic Cracking 1 to 5 were pretreated by the cyclic metal deposition (CMD) method in such a manner that they should each contain vanadium octylate and nickel octylate at, on a mass basis, 4000 ppm by mass in terms of vanadium and 2000 ppm by mass in terms of nickel, respectively. Here, the CMD method is a method in which impregnation of a catalyst for fluid catalytic cracking with small amounts of vanadium and nickel and subsequent regeneration of the catalyst for fluid catalytic cracking at a high temperature are repeated until vanadium and nickel depositions reach a target concentration in the catalyst for fluid catalytic cracking, and then oxidation and reduction are repeated at a high temperature in the range of 400 to 800°C; this method is a simulator of apparatus for fluid catalytic cracking in commercial use. (The same also applies to the examples described below.)

The fluid catalytic cracking mentioned here was performed under the reaction conditions shown in Table 3. Table 4 and Figs. 1 and 2 show the results of reaction. In Table 4, the calculations for Catalysts 1 to 3 were derived (by the weighed average method) from the result of reaction test for Catalyst 4 (i.e., Catalyst Composition A_1 only), that for Catalyst 5 (i.e., Catalyst Composition B_1 only), and

the mixing proportion of catalysts. (The same also applies to the examples described below.) Note that the K values were calculated from the conversion rates.

[0041]

The K values and gasoline yields shown in Table 4 are plotted in Figs. 1 and 2, respectively. Note that in Figs. 1 and 2, the symbol "■" represents measurements, and ● represents "calculations." As shown in Table 4, with Catalysts 1 to 3, "Gasoline" and "LCO" were obtained in high yields, and "HCO" and "Coke" were in low yields, compared with the calculations. In Fig. 1, examples with a mass proportion of Catalyst Composition A_1 in the range of 10 to 40 % by mass (in other words, the ratio W_A:W_B in the range of 10:90 to 40:60) provided a K value for Catalyst 1 (K_m) higher than those for Catalyst Composition A_1 (K_A) and Catalyst Composition B_1 (K_B). In Fig. 2, examples with a mass proportion of Catalyst Composition A1 in the range of 10 to 90 % by mass (in other words, the ratio W_A:W_B in the range of 10:90 to 90:10) provided a gasoline yield for Catalyst 1 higher than each of those for Catalyst Composition A_1 and Catalyst Composition B_1.

[0042]

[Table 3]

Table 3

Reaction temperature	520°C
Regeneration temperature	670°C
Raw material oil	Desulfurized Atmosphere residual oil(DSAR) Nickel content 2 ppm by mass Vanadium content 2 ppm by mass
Catalyst/Oil ratio	7 % by mass/% by mass

[0043]

[Table 4]

Table 4

	Catalyst 1		Catalyst 2		Catalyst 3		Catalyst 4	Catalyst 5
Catalyst Composition A_1	70		50		30		100	0
Catalyst Composition B_1	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	72.9	72.6	73.2	72.8	73.5	73.0	72.2	73.4
K value	2.69	2.64	2.73	2.68	2.77	2.71	2.60	2.76
Hydrogen %	0.51	0.54	0.51	0.55	0.52	0.55	0.53	0.56
C1+C2 %	2.3	2.4	2.3	2.4	2.3	2.4	2.3	2.5
LPG %	13.3	13.6	13.2	13.6	13.2	13.5	13.7	13.4
Gasoline %	52.9	50.8	52.3	51.0	52.5	51.2	50.6	51.4
LCO %	18.6	18.5	18.7	18.6	18.8	18.7	18.3	18.8
HCO %	8.5	9.0	8.1	8.7	7.7	8.3	9.5	7.8
Coke %	4.8	5.2	4.8	5.3	4.9	5.4	5.0	5.5

[0044]

Note the following:

- Conversion rate (% by mass)=(a-b)/a × 100

a: Mass of raw material oil

b: Total mass of light cycle oil (LCO) and heavy cycle oil (HCO)

- K value=Conversion rate/(100-Conversion rate)

- Hydrogen (% by mass)=c/a × 100

c: Mass of hydrogen in the gas produced

- C1+C2 (% by mass)=d/a × 100

d: Mass of C1 (methane) and C2 (ethane and ethylene) in the gas produced

- LPG (liquefied petroleum gas; % by mass)=e/a × 100

e: Mass of propane, propylene, butane, and butylene in the gas produced

- Gasoline (% by mass)=f/a × 100

f: Mass of gasoline (boiling point range: the boiling point of C5 (butane) (20°C) to 204°C) in the oil produced

- LCO (% by mass)=g/a × 100

g: Mass of light cycle oil (boiling point range: 204 to 343°C) in the oil produced

- HCO (% by mass)=h/a × 100

h: Mass of heavy cycle oil (boiling point range: ≥343°C) in the oil produced

- Coke (% by mass)=i/a × 100

i: Mass of coke precipitated on the catalyst mixture

The same also applies to the examples described below.

<<Experiment 2: A_2-B_2>>

(Example 4: Catalyst 6)

Catalyst Composition A_2 and Catalyst Composition B_2 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 6.

(Example 5: Catalyst 7)

Catalyst Composition A_2 and Catalyst Composition B_2 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 7.

(Example 6: Catalyst 8)

Catalyst Composition A_2 and Catalyst Composition B_2 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 8.

(Comparative Example 3: Catalyst 9)

Catalyst Composition A_2 was used as Catalyst for Fluid Catalytic Cracking 9.

(Comparative Example 4: Catalyst 10)

Catalyst Composition B_2 was used as Catalyst for Fluid Catalytic Cracking 10.

(Test 2)

With Catalysts for Fluid Catalytic Cracking 6 to 10,

fluid catalytic cracking was performed as in Test 1. Table 5 shows the results of reaction. As shown in Table 5, with Catalysts 6 to 8, "Gasoline" and "LPG" were obtained in high yields, and "HCO" and "Coke" were in low yields, compared with the calculations.

[0045]

[Table 5]

Table 5

	Catalyst 6		Catalyst 7		Catalyst 8		Catalyst 9	Catalyst 10
Catalyst Composition A_2	70		50		30		100	0
Catalyst Composition B_2	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	77.7	77.5	78.6	78.2	79.2	78.9	76.4	79.9
K value	3.48	3.43	3.67	3.58	3.81	3.73	3.24	3.98
Hydrogen %	0.35	0.36	0.35	0.37	0.36	0.37	0.35	0.38
C1+C2 %	2.3	2.3	2.4	2.4	2.4	2.4	2.3	2.4
LPG %	18.8	18.7	19.0	18.8	19.0	18.9	18.5	19.1
Gasoline %	47.8	47.5	48.2	47.8	48.5	48.1	47.0	48.5
LCO %	13.4	13.3	13.4	13.4	13.4	13.4	13.3	13.4
HCO %	8.9	9.2	8.0	8.5	7.4	7.8	10.3	6.7
Coke %	8.4	8.6	8.6	8.9	8.9	9.1	8.2	9.5

[0046]

<<Experiment 3: A_2-B_3>>

(Example 7: Catalyst 11)

Catalyst Composition A_2 and Catalyst Composition B_3 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 11.

(Example 8: Catalyst 12)

Catalyst Composition A_2 and Catalyst Composition B_3 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 12.

(Example 9: Catalyst 13)

Catalyst Composition A_2 and Catalyst Composition B_3 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 13.

(Comparative Example 5: Catalyst 14)

Catalyst Composition B_3 was used as Catalyst for Fluid Catalytic Cracking 14.

(Test 3)

With Catalysts for Fluid Catalytic Cracking 9 and 11 to 14, fluid catalytic cracking was performed as in Test 1. Table 6 shows the results of reaction. As shown in Table 6, with Catalysts 11 to 13, "Conversion rate," "Gasoline," and "LPG" were obtained in high yields, and "HCO" and "Coke" were in low yields, compared with the calculations.

{0047}

[Table 6]

Table 6

	Catalyst 11		Catalyst 12		Catalyst 13		Catalyst 9	Catalyst 14
Catalyst Composition A_2	70		50		30		100	0
Catalyst Composition B_3	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	77.6	77.2	78.0	77.7	78.5	78.2	76.4	78.9
K value	3.46	3.38	3.55	3.47	3.65	3.58	3.24	3.74
Hydrogen %	0.35	0.36	0.35	0.36	0.36	0.36	0.35	0.37
C1+C2 %	2.3	2.3	2.4	2.4	2.4	2.4	2.3	2.4
LPG %	18.9	18.9	19.0	18.9	19.0	18.9	18.8	19.0
Gasoline %	47.8	47.3	48.0	47.6	48.1	47.8	47.0	48.1
LCO %	13.4	13.3	13.4	13.4	13.4	13.4	13.3	13.4
HCO %	9.0	9.5	8.6	9.0	8.1	8.5	10.3	7.7
Coke %	8.2	8.4	8.3	8.6	8.6	8.8	8.2	9.0

[0048]

<<Experiment 4: A_2-B_4>>

(Example 10: Catalyst 15)

Catalyst Composition A_2 and Catalyst Composition B_4 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 15.

(Example 11: Catalyst 16)

Catalyst Composition A_2 and Catalyst Composition B_4 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 16.

(Example 12: Catalyst 17)

Catalyst Composition A_2 and Catalyst Composition B_4 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 17.

(Comparative Example 6: Catalyst 18)

Catalyst Composition B_4 was used as Catalyst for Fluid Catalytic Cracking 18.

(Test 4)

With Catalysts for Fluid Catalytic Cracking 9 and 15 to 18, fluid catalytic cracking was performed as in Test 1. Table 7 shows the results of reaction. As shown in Table 7, with Catalysts 15 to 17, "Additive rate," "Gasoline," and "LPG" were obtained in high yields, and "Hydrogen," "C1+C2," "LCO," "HCO," and "Coke" were in low yields, compared with

the calculations.

[0049]

[Table 7]

Table 7

	Catalyst 15		Catalyst 16		Catalyst 17		Catalyst 9	Catalyst 18
Catalyst Composition A_2	70		50		30		100	0
Catalyst Composition B_4	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	73.7	62.5	72.0	53.3	50.6	44.0	76.4	30.1
K value	2.80	1.67	2.57	1.14	1.02	0.79	3.24	0.43
Hydrogen %	0.34	0.36	0.33	0.36	0.35	0.36	0.35	0.37
C1+C2 %	2.0	2.1	1.8	2.0	1.7	1.8	2.3	1.6
LPG %	16.9	13.9	15.7	10.8	9.3	7.7	18.5	3.0
Gasoline %	46.9	37.9	47.2	31.8	31.4	25.7	47.0	16.6
LCO %	14.3	15.1	14.8	16.3	17.1	17.4	13.3	19.2
HCO %	12.0	22.4	13.2	30.5	32.3	38.6	10.3	50.7
Coke %	7.5	8.3	6.9	8.4	7.8	8.4	8.2	8.5

[0050]

<<Experiment 5: A_3-B_2>>

(Example 13: Catalyst 19)

Catalyst Composition A_3 and Catalyst Composition B_2 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 19.

(Example 14: Catalyst 20)

Catalyst Composition A_3 and Catalyst Composition B_2 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 20.

(Example 15: Catalyst 21)

Catalyst Composition A_3 and Catalyst Composition B_2 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 21.

(Comparative Example 7: Catalyst 22)

Catalyst Composition A_3 was used as Catalyst for Fluid Catalytic Cracking 22.

(Test 5)

With Catalysts for Fluid Catalytic Cracking 10 and 19 to 22, fluid catalytic cracking was performed as in Test 1. As shown in Table 8, with Catalysts 19 to 21, "Gasoline" and "LCO" were obtained in high yields, and "HCO" and "Coke" were in low yields, compared with the calculations.

[0051]

[Table 8]

Table 8

	Catalyst 19		Catalyst 20		Catalyst 21		Catalyst 22	Catalyst 10
Catalyst Composition A_3	70		50		30		100	0
Catalyst Composition B_2	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	73.9	73.0	78.3	75.0	79.0	77.0	70.1	79.9
K value	2.83	2.71	3.61	3.00	3.76	3.34	2.34	3.98
Hydrogen %	0.33	0.34	0.34	0.35	0.36	0.36	0.32	0.38
C1+C2 %	2.3	2.3	2.3	2.3	2.3	2.3	2.2	2.4
LPG %	17.8	17.4	19.2	17.9	19.0	18.4	16.6	19.1
Gasoline %	44.7	44.0	47.4	45.3	47.8	46.6	42.1	48.5
LCO %	13.2	13.1	13.2	13.2	13.2	13.3	12.9	13.4
HCO %	12.9	13.9	8.5	11.9	7.8	9.8	17.0	6.7
Coke %	8.8	9.0	9.0	9.2	9.2	9.3	8.8	9.5

[0052]

<<Experiment 6: A_3-B_3>>

(Comparative Example 16: Catalyst 23)

Catalyst Composition A_3 and Catalyst Composition B_3 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 23.

(Example 17: Catalyst 24)

Catalyst Composition A_3 and Catalyst Composition B_3 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 24.

(Example 18: Catalyst 25)

Catalyst Composition A_3 and Catalyst Composition B_3 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 25.

(Test 6)

With Catalysts for Fluid Catalytic Cracking 14, 22, and 23 to 25, fluid catalytic cracking was performed as in Test 1. Table 9 shows the results of reaction. As shown in Table 9, with Catalysts 23 to 25, "Gasoline" and "LCO" were obtained in high yields, and "HCO" and "Coke" were in low yields, compared with the calculations.

[0053]

[Table 9]

Table 9

	Catalyst 23		Catalyst 24		Catalyst 25		Catalyst 22	Catalyst 14
Catalyst Composition A_3	70		50		30		100	0
Catalyst Composition B_3	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	73.2	72.7	75.4	74.5	76.8	76.3	70.1	78.9
K value	2.73	2.67	3.07	2.92	3.31	3.21	2.34	3.74
Hydrogen %	0.33	0.34	0.34	0.35	0.35	0.36	0.32	0.37
C1+C2 %	2.3	2.3	2.3	2.3	2.3	2.3	2.2	2.4
LPG %	17.3	17.3	18.1	17.8	18.5	18.3	16.6	19.0
Gasoline %	44.4	43.9	45.8	45.1	46.8	46.3	42.1	48.1
LCO %	13.0	13.1	13.2	13.2	13.3	13.3	12.9	13.4
HCO %	13.8	14.2	11.4	12.4	9.9	10.5	17.0	7.7
Coke %	8.8	8.9	8.8	8.9	8.8	8.9	8.8	9.0

[0054]

<<Experiment 7: A_3-B_4>>

(Example 19: Catalyst 26)

Catalyst Composition A_3 and Catalyst Composition B_4 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 26.

(Example 20: Catalyst 27)

Catalyst Composition A_3 and Catalyst Composition B_4 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 27.

(Example 21: Catalyst 28)

Catalyst Composition A_3 and Catalyst Composition B_4 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 28.

(Test 7)

With Catalysts for Fluid Catalytic Cracking 18, 22, and 26 to 28, fluid catalytic cracking was performed as in Test 1. Table 10 shows the results of reaction. As shown in Table 10, with Catalysts 26 to 28, "Gasoline" and "LCO" were obtained in high yields, and "HCO" and "Coke" were in low yields, compared with the calculations.

[0055]

[Table 10]

Table 10

	Catalyst 26		Catalyst 27		Catalyst 28		Catalyst 22	Catalyst 18
Catalyst Composition A_3	70		50		30		100	0
Catalyst Composition B_4	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	67.2	58.1	65.0	50.1	47.5	42.1	70.1	30.1
K value	2.05	1.39	1.86	1.00	0.90	0.73	2.34	0.43
Hydrogen %	0.31	0.34	0.31	0.35	0.33	0.36	0.32	0.37
C1+C2 %	2.0	2.0	1.9	1.9	1.7	1.8	2.2	1.6
LPG %	15.1	12.5	13.8	9.8	8.4	7.1	16.6	3.0
Gasoline %	41.5	34.5	41.3	29.4	29.0	24.3	42.1	16.6
LCO %	14.0	14.8	14.8	16.1	17.0	17.3	12.9	19.2
HCO %	18.8	27.1	20.2	33.9	35.5	40.6	17.0	50.7
Coke %	8.2	8.7	7.6	8.7	8.0	8.6	8.8	8.5

[0056]

<<Experiment 8: A_2-A_3>>

(Comparative Example 8: Catalyst 29)

Catalyst Composition A_2 and Catalyst Composition A_3 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 29.

(Comparative Example 9: Catalyst 30)

Catalyst Composition A_2 and Catalyst Composition A_3 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 30.

(Comparative Example 10: Catalyst 31)

Catalyst Composition A_2 and Catalyst Composition A_3 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 31.

(Test 8)

With Catalysts for Fluid Catalytic Cracking 9, 22, and 29 to 31, fluid catalytic cracking was performed as in Test 1. Table 11 shows the results of reaction. As shown in Table 11, Catalysts 29 to 31 resulted in measurements similar to the calculations for the yields of "Gasoline," "LCO," "HCO," and "Coke."

[0057]

[Table 11]

Table 11

	Catalyst 29		Catalyst 30		Catalyst 31		Catalyst 9	Catalyst 22
Catalyst Composition A_2	70		50		30		100	0
Catalyst Composition A_3	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	74.7	74.5	73.4	73.3	72.1	72.0	76.4	70.1
K value	2.95	2.92	2.76	2.74	2.58	2.57	3.24	2.34
Hydrogen %	0.34	0.34	0.33	0.34	0.33	0.33	0.35	0.32
C1+C2 %	2.3	2.3	2.3	2.3	2.2	2.2	2.3	2.2
LPG %	17.9	17.9	17.5	17.6	17.4	17.2	18.5	16.6
Gasoline %	45.6	45.5	44.8	44.6	43.5	43.6	47.0	42.1
LCO %	13.2	13.2	13.0	13.1	13.0	13.0	13.3	12.9
HCO %	12.1	12.3	13.6	13.7	14.9	15.0	10.3	17.0
Coke %	8.5	8.4	8.4	8.5	8.6	8.6	8.2	8.8

[0058]

<<Experiment 9: B_2-B_3>>

(Comparative Example 11: Catalyst 32)

Catalyst Composition B_2 and Catalyst Composition B_3 were mixed in a mass proportion of 70:30 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 32.

(Comparative Example 12: Catalyst 33)

Catalyst Composition B_2 and Catalyst Composition B_3 were mixed in a mass proportion of 50:50 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 33.

(Comparative Example 13: Catalyst 34)

Catalyst Composition B_2 and Catalyst Composition B_3 were mixed in a mass proportion of 30:70 on a dry weight basis to form Catalyst for Fluid Catalytic Cracking 34.

(Test 9)

With Catalysts for Fluid Catalytic Cracking 10, 14, and 32 to 34, fluid catalytic cracking was performed as in Test 1. Table 12 shows the results of reaction. As shown in Table 12, Catalysts 32 to 34 resulted in measurements similar to the calculations for the yields of "Gasoline," "LCO," "HCO," and "Coke."

[0059]

[Table 12]

Table 12

	Catalyst 32		Catalyst 33		Catalyst 34		Catalyst 10	Catalyst 14
Catalyst Composition B_2	70		50		30		100	0
Catalyst Composition B_3	30		50		70		0	100
	Measurement	Calculation	Measurement	Calculation	Measurement	Calculation	Measurement	Measurement
Conversion rate %	79.7	79.6	79.4	79.4	79.3	79.2	79.9	78.9
K value	3.93	3.90	3.85	3.85	3.83	3.81	3.98	3.74
Hydrogen %	0.38	0.38	0.37	0.38	0.37	0.37	0.38	0.37
C1+C2 %	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
LPG %	19.1	19.1	19.1	19.1	19.0	19.0	19.1	19.0
Gasoline %	48.4	48.4	48.2	48.3	48.3	48.2	48.5	48.1
LCO %	13.4	13.4	13.4	13.4	13.4	13.4	13.4	13.4
HCO %	6.9	7.0	7.2	7.2	7.3	7.4	6.7	7.7
Coke %	9.4	9.4	9.3	9.3	9.2	9.2	9.5	9.0

[0060]

Therefore, the present invention, namely, a catalyst for fluid catalytic cracking comprising Catalyst Composition A that comprises a silica-based binder and Catalyst Composition B that comprises an aluminum-compound binder mixed therein in any mass proportion in the range of 10:90 to 90:10, provides "Gasoline" and "LPG" in higher yields and "HCO" and "Coke" in lower yields than the calculations to a greater extent than any catalyst based only on Catalyst Composition A, any catalyst based only on Catalyst Composition B, any catalyst as a mixture of two catalyst compositions comprising a silica-based binder, and any catalyst as a mixture of two catalyst compositions comprising an aluminum-compound binder. This can be understood as follows: alumina contained in Catalyst Composition B, which comprises an alumina-compound binder, binds to metals poisonous to catalysts, such as vanadium and nickel, to detoxify them, and thus Catalyst Composition A, which comprises a silica-based binder, becomes unlikely to be poisoned by these poisonous metals; as a result, a high gasoline yield and a high yield of a gas oil fraction as well as a high degree of bottom cracking are achieved while the high gasoline yield and a low coke yield are maintained.

[0061]

The present invention is not limited to the embodiment described above and can be modified within the gist of the present invention. For example, any catalyst for fluid catalytic cracking according to the present invention constituted as a combination of some or all of the embodiments described above or modifications is also included in what is claimed by the present invention.

[0062]

In the examples above, a kind of Catalyst Composition A, which comprises a silica-based binder, and a kind of Catalyst Composition B, which comprises an aluminum-compound binder are combined to produce a catalyst for fluid catalytic cracking; however, for example, two or more kinds of Catalyst Composition A and/or Catalyst Composition B may be combined to constitute a catalyst for fluid catalytic cracking, respectively.

CLAIMS

[Claim 1]

A catalyst for fluid catalytic cracking of hydrocarbon oil, comprising a catalyst composition A that comprises FAU type (faujasite type) zeolite and 10 to 30 % by mass of a silica-based binder as a binding agent and a catalyst composition B that comprises FAU type (faujasite type) zeolite and 10 to 30 % by mass of an aluminum-compound binder as a binding agent, mixed therein in any mass proportion in the range of 10:90 to 90:10 (W_A:W_B), provided that W_A is the mass of the catalyst composition A and W_B is the mass of the catalyst composition B.

[Claim 2]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to Claim 1, wherein each of the catalyst composition A and the catalyst composition B has a K value as expressed by the following formula (1), which is equal to or higher than 1.

K value = Conversion rate/(100-Conversion rate) (1)

where the conversion rate is expressed by the following formula (2);

Conversion rate (% by mass) = (a-b)/a × 100 (2)

where the symbol "a" represents the mass of raw material oil, and "b" represents the total mass of light cycle oil and heavy cycle oil.

[Claim 3]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to Claim 2, wherein, when the K values for the catalyst composition A and for the catalyst composition B are expressed as "K_A" and "K_B" respectively, the ratio of K_A:K_B is in the range as shown in the following formula (3);

K_A:K_B = 1:0.5 to 1:1.5 (3)

[Claim 4]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of Claims 1 to 3, wherein, when the K value for the above catalyst is expressed as "K_m", the K_m is greater than the K value for the catalyst composition A (K_A) and the K value for the catalyst composition B (K_B).

[Claim 5]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of Claims 1 to 4, wherein a gasoline yield by use of the above catalyst, when it is expressed as "G_m", is greater than a gasoline yield by use of the catalyst composition A, when it is expressed as "G_A" and a gasoline yield by use of the catalyst composition B, when it is expressed as "G_B".

[Claim 6]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of Claims 1 to 5, wherein the above

silica-based binder is one or more of the binding agent(s) selected from the group consisting of a silica sol, a water glass, and an acidic liquid of silicic acid.

[Claim 7]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of Claims 1 to 6, wherein the aluminum-compound binder is one or more of the binding agent(s) selected from the group consisting of the following compound (a) to (c);

(a) Basic aluminum chloride,

(b) Aluminum biphosphate,

(c) Alumina sol.

[Claim 8]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to Claim 1, wherein the FAU type (faujasite type) zeolite is any one of hydrogen Y-

type zeolite (HY), ultrastable Y-type zeolite (USY), rare-earth exchanged Y-type zeolite (REY), and rare-earth exchanged ultrastable Y-type zeolite (REUSY).

[Claim 9]

The catalyst for fluid catalytic cracking of hydrocarbon oil according to any of Claims 1 to 8, wherein the catalyst composition A and the catalyst composition B further comprise, besides the zeolite and the binding agent, a clay mineral.

[Claim 10]

A method for fluid catalytic cracking of hydrocarbon oil, with use of the above catalyst according to any of Claims 1 to 9.

[Claim 11]

The method for fluid catalytic cracking of hydrocarbon oil according to Claim 10, wherein the hydrocarbon oil comprises a residual oil.

[Claim 12]

The method for fluid catalytic cracking of hydrocarbon oil according to Claim 11, wherein the hydrocarbon oil comprises vanadium and nickel being equal to or more than 0.5 ppm by mass for each.

[Claim 13]

The method for fluid catalytic cracking of hydrocarbon oil according to any of Claims 10 to 12, wherein the above

catalyst comprises vanadium and nickel being equal to or more than 300 ppm by mass for each.