

[Designation of Document] Specification

[Title of the Invention] ADDITIVE FOR FLUID CATALYTIC
CRACKING CATALYST

[Technical Field]

[0001]

The present invention relates to an ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST, which is to be added to a fluid catalytic cracking catalyst (FCC catalyst) and used in a fluid catalytic cracking unit (FCC unit) especially for cracking the heavy oil fraction (bottom product) of a feedstock to obtain a light fraction (in particular, gasoline).

[Background Art]

[0002]

Conventionally, a feedstock is cracked using a fluid catalytic cracking catalyst to produce light oil. However, with a rise in the price of crude oil, a heavier feedstock (heavy oil fraction) has also been treated. For the purpose of efficiently cracking such a heavy oil fraction (e.g., resid) with an FCC catalyst, the amount of active ingredient in the FCC catalyst, such as zeolite or alumina, is increased. However, an increase in the proportion of active ingredient in an FCC catalyst causes problems in that the strength of the catalyst decreases, for example, thereby degrading the physical properties.

Further, in the cracking of the heavy oil fraction of a feedstock in a fluid catalytic cracking unit to produce a light fraction, there are problems in that the amount of coke increases as the heavy oil fraction cracking proceeds, and further, the combustion of the produced coke is accompanied by a temperature rise and the generation of steam, degrading the quality of the FCC catalyst. In order to solve these problems, the following additives have been developed as auxiliary catalysts for FCC catalysts (FCC Additives).

[0003]

For example, Patent Document 1 discloses an ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST, which comprises a granular mixture of silica-alumina, clay, and silica. The silica-alumina has a silica content of 10 to 30 wt%, and the mixture has a silicon content of 10 to 60 wt% (calculated as SiO_2).

Patent Document 2 discloses an ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST, which comprises silica-alumina, clay, and silica. The additive includes particles having a total silicon content of 10 to 60 wt% (calculated as SiO_2), and has a specific surface area of 30 to 80 m^2/g and a total pore volume of 0.14 to 0.45 ml/g . Further, the volume of pores with a pore radius of 60 Å or less is 0.05 ml/g or less, and the total amount of

acid is within a range of 0.02 to 0.065 mmol/g.

Patent Document 3 discloses an ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST, which comprises a composite metal oxide, clay, and silica. The additive has a specific surface area of 30 to 80 m²/g and a total pore volume of 0.14 to 0.45 ml/g. Further, the volume of pores with a pore diameter of 60 to 200 Å is 45% or more based on the total pore volume.

Patent Document 4 discloses an additive catalyst for cracking heavy oil, which comprises a composite metal oxide, clay, and silica. The additive has a specific surface area of 30 to 80 m²/g and a total acid amount of 0.02 to 0.08 mmol/g. Further, the proportion of the amount of strong acid based on the total amount of acid is 10 to 50%.

In the additives disclosed in Patent Documents 1 to 4, the silica content of silica-alumina is 10 to 30 wt%, the silica content of the mixture is 10 to 60 wt%, the specific surface area is 30 to 80 m²/g, and the total amount of acid is 0.02 to 0.08 mmol/g.

[Related Art Documents]

[Patent Documents]

[0004]

[Patent Document 1] Japanese Patent No. 3,479,783;
specification

[Patent Document 2] Japanese Patent No. 3,467,608;
specification

[Patent Document 3] Japanese Patent No. 3,643,843;
specification

[Patent Document 4] Japanese Patent No. 3,920,966;
specification

[Summary of the Invention]

[Problems that the Invention is to Solve]

[0005]

Although the conventional additives are somewhat effective in cracking heavy oil fractions, there is a need to further increase the efficiency of heavy oil fraction cracking. When a heavy oil fraction is subjected to fluid catalytic cracking using such an additive, the yield of coke increases as the heavy oil fraction cracking proceeds. Such an increase in the yield of coke causes a rise in the temperature in a catalyst regenerator of an FCC unit, and, with the temperature rise or the steam generation during the combustion of coke, the quality of FCC catalysts is degraded.

The invention was accomplished against the above background. An object of the invention is to provide an ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST, which is capable of increasing the efficiency of heavy oil fraction cracking and suppressing an increase in the yield of coke.

[Means for Solving the Problems]

[0006]

An ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to the invention for the object mentioned above is the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST, which is obtainable by spray-drying a mixed slurry including a binder and alumina-silica, characterized by having a specific surface area of 100 to 400 m²/g , and a total solid acid amount of 0.10 mmol/g or more and less than 0.50 mmol/g.

In the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to the invention, it is preferable that the proportion of the amount of strong acid based on the total solid acid amount is 20% or less.

In the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to the invention, it is preferable that the mixed slurry includes a porous silica or a zeolite.

In the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to the invention, it is preferable that the proportion of alumina-silica in the mixed slurry is 20 mass% or more and less than 80 mass%.

In the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to the invention, it is preferable that the alumina-silica has a silica content of more than 0 mass% and less than 10 mass%.

In the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to the invention, it is preferable that the binder is a silica compound or an aluminum compound.

[Advantage of the Invention]

[0007]

The additive of the invention has a specific surface area of 100 to 400 m²/g, and a total solid acid amount of 0.10 to 0.50 mmol/g. Therefore, as compared with conventional additives, the additive of the invention has an increased activity and provides a reduced yield of

(HCO:Heavy Cycle Oil), an increased yield of gasoline, and a comparative yield of coke. This can be attributed to the following reasons. Because the specific surface area and the total solid acid amount of the additive are higher than conventional, there is an increased contact area between a feedstock and the additive, as well as an increased number of active spots. As a result, the activity of the FCC catalyst increases, while the yield of HCO decreases. Further, because the proportion of strong acid based on the total solid acid is as small as 20% or less, an excessive cracking reaction is suppressed, whereby the yields of gasoline and FCC-cracked

(LCO:Light Cycle Oil) increase, and, further, an increase in the yield of coke is suppressed.

[Mode for Carrying Out the Invention]

[0008]

The following describes an ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to an embodiment of the invention.

The ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST of the invention (hereinafter sometimes referred to simply as "additive") is added to a fluid catalytic cracking catalyst made of an inorganic oxide porous body including a zeolite, and used in a fluid catalytic cracking unit (FCC unit) especially to crack the heavy oil fraction (bottom product) of a feedstock to obtain a light fraction.

The additive of the invention is obtained by spray-drying a mixed slurry including a binder and alumina-silica under known conditions. The additive has a specific surface area of 100 to 400 m²/g as measured by the BET method (JIS Z8830), preferably 150 to 380 m²/g, and more preferably 200 to 350 m²/g, and also has a total solid acid amount (the amount of ammonia adsorbed with a heat of adsorption of 70 kJ/mol or more) of 0.10 mmol/g or more and less than 0.50 mmol/g as measured by ammonia adsorption calorimetry (see Japanese Patent No. 3,784,852; the actual measurement was performed according to the method described in Example 1), preferably 0.20 to 0.45 mmol/g, and more preferably 0.25 to 0.40 mmol/g.

When the specific surface area of the additive is less than $100 \text{ m}^2/\text{g}$, this leads to a smaller number of reaction sites of the additive with a feedstock, reducing the efficiency of heavy oil fraction cracking, while when it is more than $400 \text{ m}^2/\text{g}$, the bulk density and strength of the additive are reduced. When the amount of solid acid in the additive is less than 0.10 mmol/g , the efficiency of heavy oil fraction cracking decreases, while when it is 0.50 mmol/g or more, the heavy oil fraction is excessively cracked, increasing the yield of coke.

The binder used may be a silica compound or an aluminum compound. As the silica compound, water glass, a silicic acid solution, or the like is usable, for example. As the aluminum compound, basic aluminum chloride, a boehmite alumina peptized sol, or the like is usable, for example.

As the alumina-silica, a product obtained by mixing a silica compound with a pseudo-boehmite gel or a boehmite gel, optionally followed by aging, is usable.

The alumina-silica preferably has a silica content of more than 0 mass% and less than 10 mass%, and preferably 1 to 9 mass%. When the silica content of the alumina-silica is 10 mass% or more, this leads to a decrease in specific surface area and the amount of acid.

The mixed slurry may contain a clay mineral, a

porous silica, and a zeolite. Examples of clay minerals include kaolin, montmorillonite, dolomite, and calcite. Examples of porous silicas include wet silica and dry silica. Examples of zeolites include ultrastabilized Y-type zeolite (USY), H-Y, NH₄-Y, RE-Y, RE-USY, ZSM-5, and mordenite. By the addition of a porous silica or a zeolite, the specific surface area of the additive can be adjusted (increased), and it also contributes to the improvement of activity.

The proportion of alumina-silica in the mixed slurry is preferably 20 mass% or more and less than 80 mass%, and more preferably 40 to 70 mass%. Depending on the alumina-silica proportion, the specific surface area of the additive and the amount of solid acid therein can be controlled. When the proportion of alumina-silica in the mixed slurry is less than 20 mass%, the amount of active ingredient is insufficient to crack a heavy oil fraction, making it difficult to effectively crack the heavy oil fraction, while when it is 80 mass% or more, this leads to a decrease in the strength and bulk density of the additive, and when such an additive is used as an ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST, the fluidity decreases or dusting occurs, possibly making it difficult to operate the fluid catalytic cracking unit. The concentration of binder in the mixed slurry is about

10 to about 15 mass%, and the solid content of the mixed slurry is about 15 to about 30 mass%.

The proportion of the amount of strong acid (the amount of ammonia adsorbed with a heat of adsorption of 110 kJ/mol or more in ammonia adsorption calorimetry) based on the total amount of solid acid in the additive is 20% or less, preferably 10% or less, and more preferably 5% or less. When the amount of strong acid is more than 20%, this is likely to cause an excessive cracking reaction, increasing the yield of coke.

[Examples]

[0009]

Hereinafter, the invention will be described in further detail with reference to Examples and Comparative Examples. However, the invention is not limited thereto..

[0010]

<<Test Example 1: Effect of the Amount of Solid Acid>>

[Example 1: Additive 1]

To 7690 g of a boehmite slurry including 13.0 mass% alumina (Al_2O_3) (containing 1000 g of alumina) was added 300 g of silica sol a (including 10 mass% silica, i.e., containing 30 g of silica) prepared by adjusting water glass including 17.5 mass% silica (SiO_2) to pH 1.6 with a 25 mass% aqueous sulfuric acid solution. The resulting mixture was adjusted to pH 10.5 with a 48 mass% aqueous

sodium hydroxide solution, and further aged at 95°C for 1 hour to give alumina-silica slurry A including 3 mass% silica. The total concentration of alumina and silica in the alumina-silica slurry A was 14 mass%.

Further, a water glass including 17.5 mass% silica (SiO_2) (hereinafter, referred to as 17.5 mass% water glass) was adjusted to pH 1.6 with sulfuric acid to give silica sol b having a silica concentration of 12.5 mass% (an example of a binder made of a silica compound).

After 1430 g of the alumina-silica slurry A (containing 200 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, 1600 g of the silica sol b (containing 200 g of silica; the same applies hereinafter) was added thereto. Subsequently, 600 g of kaolin (dry mass; the same applies hereinafter) was added thereto and uniformly mixed. The resulting mixture was spray-dried under the following conditions: inlet temperature of 460°C, outlet temperature of 260°C, and residence time of 20 minutes (the same applies to the following examples), and then desalted by washing (ammonium sulfate in an amount of 20 mass% based on dry catalyst was added to remove alkali, and then sulfuric acid was removed by 15% aqueous ammonia; the same applies also to the following examples) to give additive 1 with an average particle diameter of 60 μm . Table 1 shows the composition of the

additive 1. Further, the specific surface area and bulk density of the additive 1 were measured by the BET method and the UOP method 254-65, respectively (the same applies to the following examples). Table 1 shows the properties of the additive 1.

[0011]

(Method for Measuring the Amount of Solid Acid)

The amount of solid acid in the obtained additive 1 was measured as follows. First, 0.2 g of the additive 1 was fired at 500°C for 1 hour, and then heat-treated under a reduced pressure (1×10^{-4} torr) at 400°C for 4 hours. After that, ammonia gas was adsorbed thereon. The heat of adsorption thus generated was detected, and the total amount of solid acid was calculated. For the measurement, "Calorimeter" manufactured by TOKYO RIKOSHA was used. The amount of ammonia adsorbed with a heat of adsorption of 70 kJ/mol or more was taken as the total amount of solid acid, and the amount of ammonia adsorbed with a heat of adsorption of 110 kJ/mol or more was taken as the amount of strong acid (measurement was conducted in the same manner in the following examples). Table 1 shows results of the measurement of the amount of solid acid in the additive 1.

[0012]

[Example 2: Additive 2]

2860 g of the alumina-silica slurry A (containing 400 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was added thereto. Subsequently, 400 g of kaolin was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 2 with an average particle diameter of 60 μm . Table 1 shows the composition and properties of the additive 2.

[Example 3: Additive 3]

5000 g of the alumina-silica slurry A (containing 700 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was added thereto. Subsequently, 100 g of kaolin was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 3 with an average particle diameter of 60 μm . Table 1 shows the composition and properties of the additive 3.

[Comparative Example 1: Additive 4]

1070 g of the alumina-silica slurry A (containing 150 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was added thereto. Subsequently, 650 g of kaolin was added thereto and uniformly mixed. The

resulting mixture was spray-dried, and then desalted by washing to give additive 4 with an average particle diameter of 60 μm . Table 1 shows the composition and properties of the additive 4.

[Comparative Example 2: Additive 5]

5710 g of the alumina-silica slurry A (containing 800 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was thereto. After uniform mixing, the resulting mixture was spray-dried, and then desalted by washing to give additive 5 with an average particle diameter of 60 μm . Table 1 shows the composition and properties of the additive 5.

[0013]

[Activity Evaluation]

Using the additives 1 to 5, the effect of the amount of solid acid in an additive on its activity was evaluated.

The evaluation of the activity of an additive was performed using a pilot reaction apparatus manufactured by ARCO. This apparatus is a circulating fluidized bed, in which a catalyst alternately and repeatedly undergoes reaction and regeneration while circulating in the apparatus, and is modeled after an FCC unit for use on a commercial scale. The additives 1 to 5 were each mixed

with an FCC equilibrium catalyst in a mass ratio of 90:10 (1.8 Kg:0.2 Kg). Using a desulfurized atmospheric resid (DSAR) as a feedstock, the temperature of the reactor was set at 520°C and the temperature of the regenerator was set at 670°C, and an adjustment was made so that 5g or 7g of the catalyst would be present per 1 g of the feedstock in the apparatus. A catalytic cracking reaction was then carried out, and the reaction product and the residue (product liquor) were analyzed. Then, the gas produced in the reactor was analyzed by gas chromatography [Micro GC 3000A] manufactured by SHIMADZU, and the yields of hydrogen and C1 to C4 were measured. At the same time, CO and CO₂ produced in the regenerator were analyzed by an infrared absorption gas analyzer [CGT-7000] manufactured by SHIMADZU, and the yield of coke was calculated. Further, the product liquor was analyzed by distillation gas chromatography [GC System HP6890] manufactured by Hewlett Packard, and the amounts of the gasoline fraction, light cycle oil (LCO), and heavy cycle oil (HCO) produced were measured. Prior to the reaction, the additives 1 to 5 were each treated in 100% steam at 810°C for 12 hours. Table 1 shows evaluation results. Concerning the conversion, the measurement results from a sample containing no additive were used as the standard, and differences from the standard were expressed as the

evaluation results. Also, concerning measurement results of gasoline, LCO, HCO and coke, the amount containing no additive were used as the standard, the differences of the amount being calculated, on the assumption that the conversion is constant, from the standard were expressed as the evaluation results.

The evaluation was performed in the same manner in the following examples.

As shown by Table 1, when the amount of solid acid was 0.1 to 0.4 mmol/g, with an increase in the amount of solid acid, the efficiency of heavy oil fraction cracking increased, and the amount of HCO fraction decreased, producing excellent results. However, when the amount of solid acid was 0.08 mmol/g, the efficiency of heavy oil fraction cracking was low, resulting in an increased amount of HCO fraction, while when the amount of solid acid was 0.5 mmol/g, although the efficiency of heavy oil fraction cracking increased, and the amount of HCO fraction decreased, the amount of coke produced increased.

[0014]

[Table 1]

		Example 1		Example 2		Example 3		Comparative Example 1		Comparative Example 2	
		Additive 1		Additive 2		Additive 3		Additive 4		Additive 5	
Composition											
Binder (Silica)	mass%	20		20		20		20		20	
Kaolin	mass%	60		40		10		65		-	
Alumina-Silica	mass%	20		40		70		15		80	
Properties											
Bulk Density	ml/g	0.85		0.84		0.80		0.90		0.76	
Specific Surface Area	m ² /g	100		200		300		85		330	
Total Amount of Solid Acid	mmol/g	0.10		0.20		0.40		0.08		0.50	
Amount of Strong Acid/ Total Amount of Solid Acid	%	0		0		0		0		0	
Activity Evaluation											
Conversion	Δmass%	+0.1		+0.4		+0.7		+0.1		+0.8	
Gasoline	Δmass%	+0.1		+0.3		+0.4		±0		+0.4	
LCO	Δmass%	+0.2		+0.4		+0.7		+0.1		+0.8	
HCO	Δmass%	-0.3		-0.4		-0.7		-0.1		-0.8	
Coke	Δmass%	-0.1		-0.2		±0		±0		+0.3	

[0015]

<<Test Example 2: Effect of Specific Surface Area>>

[Example 4: Additive 6]

2860 g of the alumina-silica slurry A (containing 400 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was added thereto. Subsequently, 100 g of kaolin and 300 g of ultrastabilized Y-type zeolite (dry weight; the same applies hereinafter) were added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 6 with an average particle diameter of 60 μm . Table 2 shows the composition and properties of the additive 6.

[Comparative Example 3: Additive 7]

1430 g of the alumina-silica slurry A (containing 200 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was added thereto. Subsequently, 100 g of kaolin and 500 g of ultrastabilized Y-type zeolite were added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 7 with an average particle diameter of 60 μm . Table 2 shows the composition and properties of the additive 7.

[Activity Evaluation]

Using the additive 1, the additive 3, the additive 4, the additive 6, and the additive 7, the effect of specific surface area on activity was evaluated. Table 2 shows evaluation results. The additive 7 has a low bulk density and is difficult to use in the actual unit, so the activity thereof was not evaluated.

As shown by Table 2, when the specific surface area was 100 to 350 m²/g, the number of reaction sites with the heavy oil fraction increased, whereby the yield of HCO decreased, producing excellent results. However, when the specific surface area was 85 m²/g, there were a small number of reaction sites, so the HCO yield increased, while when it was 410 m²/g, although there are expected to be a large number of reaction sites, whereby the heavy oil fraction can be cracked efficiently, such an additive had a low bulk density and thus was not practical.

[0016]

[Table 2]

	Example 1	Example 3	Example 4	Comparative	Comparative
	Additive 1	Additive 3	Additive 6	Example 1	Example 3
Composition					
Binder (Silica)	20	20	20	20	20
Kaolin	60	10	10	65	10
Alumina-Silica	20	70	40	15	20
Zeolite	-	-	30	-	50
Properties					
Bulk Density	0.85	0.80	0.70	0.90	0.58
Specific Surface Area	100	300	350	85	410
Total Amount of Solid Acid	0.10	0.40	0.25	0.08	0.20
Amount of Strong Acid/ Total Amount of Solid Acid	0	0	5	0	10
Activity Evaluation					
Conversion	+0.1	+0.7	+0.7	+0.1	-
Gasoline	+0.1	+0.4	+0.5	±0	-
ICO	+0.2	+0.7	+0.4	+0.1	-
HCO	-0.3	-0.7	-0.4	-0.1	-
Coke	-0.1	±0	+0.1	±0	-

[0017]

<<Test Example 3: Effect of Silica Content of Alumina-Silica>>

[Example 5: Additive 8]

To 7690 g of a boehmite slurry including 13.0 mass% alumina was added 500 g of the silica sol a (i.e., containing 50 g of silica). The resulting mixture was adjusted to pH 10.5 with a 48 mass% aqueous sodium hydroxide solution, and further aged at 95°C for 1 hour to give alumina-silica slurry B including 5 mass% silica. The total concentration of alumina and silica in the alumina-silica slurry B was 15 mass%.

4670 g of the alumina-silica slurry B (containing 700 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was added thereto. Subsequently, 100 g of kaolin was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 8 with an average particle diameter of 60 μm . Table 3 shows the composition and properties of the additive 8.

[Comparative Example 4: Additive 9]

5385 g of a boehmite slurry including 13.0 mass% alumina (containing 700 g of alumina) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b

(containing 200 g of silica) was added thereto. Subsequently, 100 g of kaolin was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 9 with an average particle diameter of 60 μm . Table 3 shows the composition and properties of the additive 9.

[Comparative Example 5: Additive 10]

To 7690 g of a boehmite slurry including 13.0 mass% alumina, 17.5% water glass was adjusted to pH 1.6 with sulfuric acid, and 1200 g of the silica sol a (i.e., containing 120 g of silica) was added. The resulting mixture was adjusted to pH 10.5 with a 48 mass% aqueous sodium hydroxide solution, and further aged at 95°C for 1 hour to give alumina-silica slurry C including 11 mass% silica. The total concentration of alumina and silica in the alumina-silica slurry C was 15 mass%.

4670 g of the alumina-silica slurry C (containing 700 g of alumina-silica) was adjusted to pH 4.0 with sulfuric acid, and 1600 g of the silica sol b (containing 200 g of silica) was added thereto. Subsequently, 100 g of kaolin was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 10 with an average particle diameter of 60 μm . Table 3 shows the composition and properties of the additive 10.

[Activity Evaluation]

Using the additive 3, the additive 8, the additive 9, and the additive 10, the effect of the silica content of alumina-silica on the activity was evaluated. Table 3 shows evaluation results.

As shown by Table 3, the yield of HCO decreased with an increase in the silica content of alumina-silica, producing excellent results. However, when the silica content was 0 mass%, the amount of solid acid was small, and there thus was a small decrease in the yield of HCO, while when the silica content is 11 mass%, the yield of coke increased.

[0018]

[Table 3]

	Example 3		Example 5		Comparative Example 4		Comparative Example 5	
	Additive 3		Additive 8		Additive 9		Additive 10	
Composition								
Binder (Silica)	mass%	20		20		20		20
Kaolin	mass%	10		10		10		10
Alumina-Silica	mass%	70		70		-		70
Alumina	mass%	-		-		70		-
Silica Content of Alumina-Silica	mass%	3		5		0		11
Properties								
Bulk Density	ml/g	0.80		0.80		0.78		0.81
Specific Surface Area	m ² /g	300		310		210		350
Total Amount of Solid Acid	mmol/g	0.40		0.40		0.20		0.50
Amount of Strong Acid/Total Amount of Solid Acid	%	0		1		0		4
Activity Evaluation								
Conversion	Δmass%	+0.7		+0.7		+0.2		+0.8
Gasoline	Δmass%	+0.4		+0.5		±0		+0.3
LCO	Δmass%	+0.7		+0.4		+0.1		+0.7
HCO	Δmass%	-0.7		-0.4		-0.1		-0.8
Coke	Δmass%	±0		+0.1		±0		+0.3

[0019]

<<Test Example 4: Effect of the Amount of Solid Acid>>

[Example 6: Additive 11]

To 858 g of basic aluminum chloride solution b having an Al_2O_3 concentration of 22.3 mass% (an example of a binder made of an alumina compound; containing 200 g of alumina) was added 500 g of kaolin. Subsequently, 2140 g of the alumina-silica slurry A (containing 300 g of alumina-silica) adjusted to pH 5.0 with sulfuric acid was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 11 with an average particle diameter of 60 μm . Table 4 shows the composition and properties of the additive 11.

[Example 7: Additive 12]

To 858 g of the basic aluminum chloride solution b (containing 200 g of alumina) was added 300 g of kaolin. Subsequently, 3570 g of the alumina-silica slurry A (containing 500 g of alumina-silica) adjusted to pH 4.5 with sulfuric acid was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 12 with an average particle diameter of 60 μm . Table 4 shows the composition and properties of the additive 12.

[Example 8: Additive 13]

To 858 g of the basic aluminum chloride solution b (containing 200 g of alumina) was added 100 g of kaolin. Subsequently, 5000 g of the alumina-silica slurry A (containing 700 g of alumina-silica) adjusted to pH 4.0 with sulfuric acid was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 13 with an average particle diameter of 60 μm . Table 4 shows the composition and properties of the additive 13.

[Comparative Example 6: Additive 14]

To 858 g of the basic aluminum chloride solution b (containing 200 g of alumina) was added 600 g of kaolin. Subsequently, 1430 g of the alumina-silica slurry A (containing 200 g of alumina-silica) adjusted to pH 4.0 with sulfuric acid was added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 14 with an average particle diameter of 60 μm . Table 4 shows the composition and properties of the additive 14.

[Comparative Example 7: Additive 15]

To 858 g of the basic aluminum chloride solution b (containing 200 g of alumina) was added 5710 g of the alumina-silica slurry A (containing 800 g of alumina-silica) adjusted to pH 4.0 with sulfuric acid. After uniform mixing, the resulting mixture was spray-dried, and

then desalted by washing to give additive 15 with an average particle diameter of 60 μm . Table 4 shows the composition and properties of the additive 15.

[Activity Evaluation]

Using the additives 11 to 15, the effect of the amount of solid acid in an additive on its activity was evaluated. Table 4 shows evaluation results.

As shown by Table 4, also in the case of an alumina sol binder, as in the case of a silica sol binder, when the amount of solid acid was 0.1 to 0.4 mmol/g, with an increase in the amount of solid acid, the efficiency of heavy oil fraction cracking increased, and the amount of HCO fraction decreased, producing excellent results. However, when the amount of solid acid was 0.07 mmol/g, the efficiency of heavy oil fraction cracking increased, and the amount of HCO fraction increased, while when the amount of solid acid was 0.5 mmol/g, the amount of coke produced increased.

[0020]

[Table 4]

		Example 6		Example 7		Example 8		Comparative Example 6		Comparative Example 7	
		Additive 11		Additive 12		Additive 13		Additive 14		Additive 15	
Composition											
Binder (Alumina)	mass%	20		20		20		20		20	
Kaolin	mass%	50		30		10		60		-	
Alumina-Silica	mass%	30		50		70		20		80	
Properties											
Bulk Density	ml/g	0.80		0.75		0.70		0.82		0.65	
Specific Surface Area	m ² /g	100		210		280		90		310	
Total Amount of Solid Acid	mmol/g	0.10		0.30		0.40		0.07		0.50	
Amount of Strong Acid/ Total Amount of Solid Acid	%	0		0		0		0		0	
Activity Evaluation											
Conversion											
Gasoline	Δmass%	+0.1		+0.3		+0.5		+0.1		+0.8	
LCO	Δmass%	+0.1		+0.3		+0.4		±0		+0.4	
HCO	Δmass%	+0.2		+0.4		+0.7		+0.1		+0.8	
	Δmass%	-0.3		-0.4		-0.7		-0.1		-0.8	
Coke	Δmass%	±0		+0.1		+0.1		±0		+0.3	

[0021]

<<Test Example 5: Effect of Specific Surface Area>>

[Example 9: Additive 16]

To 858 g of the basic aluminum chloride solution b (containing 200 g of alumina) was added 100 g of kaolin. Subsequently, 2860 g of the alumina-silica slurry A (containing 400 g of alumina-silica) adjusted to pH 4.0 with sulfuric acid and 300 g of ultrastabilized Y-type zeolite were added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 16 with an average particle diameter of 60 μm . Table 5 shows the composition and properties of the additive 16.

[Comparative Example 8: Additive 17]

To 858 g of the basic aluminum chloride solution b (containing 200 g of alumina) was added 100 g of kaolin. Subsequently, 1430 g of the alumina-silica slurry A (containing 200 g of alumina-silica) adjusted to pH 4.0 with sulfuric acid and 500 g of ultrastabilized Y-type zeolite were added thereto and uniformly mixed. The resulting mixture was spray-dried, and then desalted by washing to give additive 17 with an average particle diameter of 60 μm . Table 5 shows the composition and properties of the additive 17.

[Activity Evaluation]

Using the additive 11, the additive 13, the additive 14, the additive 16, and the additive 17, the effect of specific surface area on activity was evaluated. Table 5 shows evaluation results. The additive 17 has a low bulk density and is difficult to use in the actual unit, so the activity thereof was not evaluated.

As shown by Table 5, when the specific surface area was 100 to 350 m²/g, the number of reaction sites with the heavy oil fraction increased, whereby the yield of HCO decreased, producing excellent results. However, when the specific surface area was 90 m²/g, there were a small number of reaction sites, so the HCO yield increased, while when it was 410 m²/g, although there are expected to be a large number of reaction sites, whereby the heavy oil fraction can be cracked efficiently, such an additive had a low bulk density and thus was not practical.

[0022]

[Table 5]

		Example 6	Example 8	Example 9	Comparative Example 6	Comparative Example 8
		Additive 11	Additive 13	Additive 16	Additive 14	Additive 17
Composition						
Binder (Alumina)	mass%	20	20	20	20	20
Kaolin	mass%	50	10	10	60	10
Alumina-Silica	mass%	30	70	40	20	20
zeolite	mass%	-	-	30	-	50
Properties						
Bulk Density	ml/g	0.80	0.70	0.70	0.82	0.56
Specific Surface Area	m ² /g	100	280	350	90	410
Total Amount of Solid Acid	mmol/g	0.10	0.40	0.30	0.07	0.20
Amount of Strong Acid/ Total Amount of Solid Acid	%	0	0	5	0	10
Activity Evaluation						
Conversion	Δmass%	+0.1	+0.5	+0.3	+0.1	-
Gasoline	Δmass%	+0.1	+0.4	+0.5	±0	-
LCO	Δmass%	+0.2	+0.7	+0.2	+0.1	-
HCO	Δmass%	-0.3	-0.7	-0.5	-0.1	-
Coke	Δmass%	±0	+0.1	+0.1	±0	-

[0023]

As described above, the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST of the invention allowed the heavy oil fraction in a feedstock to be effectively cracked, and also suppressed the yield of coke, making it possible to obtain high yields of gasoline and LCO. This can be attributed to the following reasons. The additive is characterized by its high specific surface area, and also in that the proportion of strong acid based on the total solid acid is low. Generally, when the proportion of strong acid is high, the reaction activity is high; however, there is a problem in that the cracking reaction proceeds excessively, resulting in a high yield of coke. Therefore, when the proportion of strong acid based on the total solid acid in the additive is suppressed, and further the specific surface area is increased to reduce the amount of solid acid per unit surface area, an increase in the yield of coke due to the excessive cracking of the feedstock can be suppressed.

[Designation of Document] Claims

[Claim 1]

An ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST obtainable by spray-drying a mixed slurry including a binder and alumina-silica, wherein

the ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST being characterized by having a specific surface area of 100 to 400 m²/g and a total solid acid amount of 0.10 mmol/g or more and less than 0.50 mmol/g.

[Claim 2]

The ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to claim 1, characterized in that the proportion of strong acid based on the total solid acid amount is 20% or less.

[Claim 3]

The ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to claim 1, characterized in that the mixed slurry includes a porous silica or a zeolite.

[Claim 4]

The ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to claim 1, characterized in that the proportion of alumina-silica in the mixed slurry is 20 mass% or more and less than 80 mass%.

[Claim 5]

The ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST

according to claim 1, characterized in that the alumina-silica has a silica content of more than 0 mass% and less than 10 mass%.

[Claim 6]

The ADDITIVE FOR FLUID CATALYTIC CRACKING CATALYST according to claim 1, characterized in that the binder is a silica compound or an aluminum compound.