

DESULFURIZATION CATALYST FOR CATALYTIC CRACKED GASOLINE, METHOD OF PRODUCING THE SAME, AND METHOD FOR DESULFURIZING OF CATALYTIC CRACKED GASOLINE USING THE SAME

FIELD OF THE INVENTION

[0001]

The present invention relates to a desulfurization catalyst for catalytic cracked gasoline (abbreviated as a FCC gasoline hereinafter), a method of producing the same, and a method for desulfurization of FCC gasoline using the catalyst. The desulfurization catalyst for FCC gasoline is, as known, used for removing sulfur included in the produced FCC gasoline when heavy hydrocarbon oil and vacuum gas oil are catalytically cracked by a fluidized catalytic cracking unit (abbreviated as a FCC unit hereinafter).

BACKGROUND OF THE INVENTION

[0002]

The FCC gasoline obtained by means of the fluidized catalytic cracking of heavy hydrocarbon oil or vacuum gas oil contains sulfur compounds. Recently, in the view of environmental concerns such as prevention of air pollution, it is required that a sulfur content in FCC gasoline should be reduced because catalyst for removing NO_x contained in exhaust gas from vehicles rapidly decreases its activity due to the effect of by sulfur. An amount of sulfur contained in gasoline is regulated to be less than 50 ppm in Japan in 2005, and there have been proposed various methods for desulfurization of FCC gasoline in the FCC unit.

[0003]

For instance, Japanese Patent No.3545652 discloses a method for reducing sulfur content in catalytic cracked oil fractions. In this method, feed oil containing organic sulfur compounds is catalytically cracked by commercially available desulfurization catalyst at a high temperature in the FCC unit. This catalyst is a porous molecular sieve containing vanadium metal as cations in an oxidized state of more-than-zero inside small pore structure. With the features as described above, this catalyst is used for producing catalytic cracked products with reduced sulfur content.

However, this catalyst has a problem that, because this catalyst contains the vanadium metal in the oxidized state of more-than-zero in the small pore structure of the molecular sieve and the vanadium metal is ion-exchanged and present as cations in the small pores, the vanadium metal destroys crystal structure of the molecular sieve to lower an activity of the catalyst.

[0004]

Japanese Patent Laid-open Publication No. 2003-27065 discloses a method for desulfurization of FCC gasoline in a FCC unit or in a FCC unit especially for heavy oil (abbreviated as a RFCC unit hereinafter). This method uses a catalytic cracking catalyst for desulfurization containing at least one metal selected from a group consisting of vanadium, zinc, nickel, iron and cobalt, and in this catalyst the metal is homogeneously carried on an inorganic porous carrier. This document describes, moreover, that vanadium or zinc should preferably used for desulfurization of produced gasoline fractions.

However, when a catalyst homogeneously carrying vanadium on the inorganic porous carrier can not achieve desulfurization unless organic sulfur compound is diffused in the catalyst and contacts vanadium oxide contained therein, and therefore utilization efficiency of the carried vanadium oxide is low, and to overcome this defect, it

is necessary to use a large amount of vanadium carried on the catalyst. Moreover, when the inorganic porous carrier is a fluidized catalytic cracking catalyst including Y-type zeolite (abbreviated as a FCC catalyst hereinafter), although the catalyst is effective in removing sulfur components in the FCC gasoline fraction in the RFCC process, there is the problem that the Y-type zeolite is destroyed by vanadium with a cracking activity lowered and yield of hydrogen and coke generated in the cracking process disadvantageously increase.

SUMMARY OF THE INVENTION

[0005]

For solving the problems as described above, an object of the present invention is to provide desulfurization catalyst for FCC gasoline having high desulfurizing property for removing sulfur in gasoline fractions and also having high activity to control generation of hydrogen and coke in a FCC process.

Another object of the present invention is to provide a method of producing the desulfurization catalyst for FCC gasoline and a method for desulfurization of FCC gasoline using the same.

[0006]

The present inventors diligently made studies for achieving the objects as described above and found the fact that the desulfurization catalyst for FCC gasoline carrying vanadium oxide only on surfaces of porous inorganic oxide spherical particles has the high desulfurizing property in FCC process, and also that generation of hydrogen and coke is suppressed although the cracking activity is high. The inventors completed the present invention based on this newly found fact.

[0007]

Namely, the present invention relates to the desulfurization catalyst for FCC gasoline carrying vanadium oxide only on surfaces of porous inorganic oxide spherical particles and the vanadium oxide is carried at least on a portion of the surface of each particle.

It is preferable that said vanadium oxide forms a vanadium oxide thin layer at least on a portion of the surface of each porous inorganic oxide spherical particle.

[0008]

A quantity of carried vanadium oxide is preferably in a range from 0.3 to 3 wt% when calculated as V_2O_5 .

More preferably, antimony is also carried on the porous inorganic oxide spherical particles.

Preferably, the porous inorganic oxide spherical particle includes crystalline aluminosilicate zeolite and a porous inorganic oxide matrix. Further, the porous inorganic oxide matrix includes heat-resistant metal oxide functioning as a binder, clay mineral, porous silica xerogel, alumina powder and a metal-trap agent.

[0009]

In a method of manufacturing desulfurization catalyst for FCC gasoline according to the present invention, porous inorganic oxide spherical particles are dried and sintered after impregnated using vanadium oxide sol. Preferably, vanadium oxide particles in the vanadium oxide sol have an average diameter ranging from 1 to 1,000 nanometers.

[0010]

In a method of desulfurizing a FCC gasoline according to the present invention, heavy hydrocarbon gas and/or vacuum gas oil is contacted to a mixture of the desulfurization catalyst for FCC gasoline and FCC catalyst mixed at a rate in a range

from 5/95 to 50/50 by weight for the purpose to catalytically crack and desulfurize the heavy hydrocarbon oil and/or vacuum gas oil.

[0011]

When the desulfurization catalyst for FCC gasoline according to the present invention is mixed with the FCC catalyst in an FCC unit, the organic sulfur compounds efficiently contact the vanadium oxide carried only on a portion of surface of the desulfurization catalyst for FCC gasoline. Because of this feature, only a small amount of vanadium oxide (carried only on a portion of the surface of the catalyst) is needed to obtain the desired desulfurization activity.

Furthermore, when the FCC catalyst including crystalline aluminosilicate zeolite is used as porous inorganic spherical particles, the vanadium oxide does not damage the zeolite crystal, so that the catalytic cracking activity is high, and the generation of hydrogen and coke is suppressed.

[0012]

When antimony is carried, in addition to vanadium oxide, on the desulfurization catalyst according to the present invention, antimony provides excellent hydrogenation activity and also provides an effect to suppress generation of hydrogen.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1 is a photo showing a surface of the catalyst α in Example 1 observed and photographed with a scanning electron microscope (SEM); and

FIG. 2 provides an image of the catalyst α obtained with an electron probe microanalyzer (WDS), and an element distribution chart illustrating a result of the line analysis of the catalyst α on a white line in the image.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0014]

DESULFURIZATION CATALYST FOR FCC GASOLINE

The porous inorganic oxide spherical particles according to the present invention have substantially same size as that of the typical FCC catalyst. Specifically exemplified are spherical fine particles having an average particle diameter in a range from 40 to 90 micrometers.

In this invention described therein, the term "a surface portion of the porous inorganic oxide spherical particle" refers to an inner portion ranging from an outer surface of the spherical particle down to $1/2$ of the radius of the particle. The desulfurization catalyst for FCC gasoline according to the present invention carries vanadium oxide at least on a portion of the surface thereof.

[0015]

In the conventional desulfurization catalyst for FCC gasoline in which vanadium is carried uniformly thereon, or in the catalyst in which vanadium oxide is carried in the portion including the inner portion below the surface and ranging down to a depth over a half of the radius of the particle and sometimes even down to the center, organic sulfur compound needs to be penetrated into the inner portion of the catalyst and contact the vanadium oxide carried therein for desulfurization. Because of this feature, the vanadium therein is not used efficiently, and it is necessary to increase the quantity of vanadium carried therein for obtaining the desired desulfurization activity.

On the other hand, when the desulfurization catalyst for FCC gasoline according to the present invention is used, vanadium oxide can be used efficiently because organic sulfur compounds efficiently contacts the vanadium oxide carried only in the surface portion of the porous inorganic oxide spherical particle. Therefore, only a small amount

of vanadium is needed to obtain the desired desulfurization activity. Furthermore, when the FCC catalyst including crystalline aluminosilicate zeolite described later is used as the porous inorganic spherical particles, high cracking activity is obtained and generation of hydrogen and coke is suppressed, because crystal of the crystalline aluminosilicate zeolite is not damaged by vanadium oxide carried thereon.

[0016]

In the desulfurization catalyst for FCC gasoline according to the present invention, it is preferable that at least 90 wt% of vanadium oxide carried thereon is preferably in a portion ranging from the outer surface down to 30% of the radius of the particle, and more preferably in a portion ranging from the outer surface down to 20% of the radius of the particle. How the vanadium oxide is carried on a portion of the surface of porous inorganic oxide spherical particle can be observed with a scanning electron microscope (SEM) and an electron probe microanalyzer (WDS).

Furthermore, in the desulfurization catalyst for FCC gasoline according to the present invention, it is preferable that vanadium carried in the surface portion of the porous inorganic particles ranging from the outer surface down to a half of the radius of the particle forms a vanadium oxide thin layer at least on a portion of the surface of the porous inorganic oxide spherical particle. The vanadium oxide thin layer can be observed by photographing the surface of the porous inorganic oxide spherical particle with an SEM.

[0017]

In the desulfurization catalyst for FCC gasoline according to the present invention, when vanadium oxide is carried at least on the surface portion of porous inorganic oxide spherical particle, especially when a vanadium oxide thin layer is formed thereon, the desulfurization efficiency is high because the desulfurizing reaction

proceeds only when the surface of the porous inorganic particles contact organic sulfur compounds, so that the catalyst can be used for removing sulfur compounds not only in the gasoline fractions but also in other high molecular weight oil fractions having higher boiling points.

[0018]

In the desulfurization catalyst for FCC gasoline according to the present invention, it is preferable that a quantity of carried vanadium oxide is in a range from 0.3 to 3 wt% when calculated as V_2O_5 . When the quantity is less than 0.3 wt%, the desulfurizing performance for removing sulfur compounds in the gasoline fraction may become low in the FCC process. When the quantity is more than 3 wt%, the desulfurizing performance for removing sulfur compounds in the gasoline fraction becomes higher, the generation of hydrogen and coke in the reaction increase, and the yield of gasoline fraction will generally become lower. More preferably, the quantity of carried vanadium oxide is in the range from 0.5 to 2 wt% when calculated as V_2O_5 .

[0019]

In the desulfurization catalyst for FCC gasoline according to the present invention, it is preferable that antimony is carried, in addition to vanadium oxide, on the porous inorganic oxide spherical particles. When also antimony is carried thereon in addition to vanadium oxide, the effect for suppressing the generation of hydrogen and coke is enhanced with the yield of the gasoline fraction improved. It is guessed that, in the FCC process, the generation of hydrogen in this reaction decreases because compounds, such as $SbVO_4$, Sb_2VO_5 , and $Sb_{0.9}V_{0.1}O_4$, synthesized from antimony and vanadium suppress dehydrogenation reaction by vanadium.

[0020]

Preferably, a quantity of carried antimony is in the range from 0.3 to 5 wt%, and

more preferably in the range from 0.5 to 4 wt% based on catalyst when calculated as Sb_2O_3 . Furthermore, in the desulfurization catalyst for FCC gasoline according to the present invention, in addition to vanadium oxide described above, a metal, such as zinc, nickel, iron, and cobalt, that is typically used as a desulfurization catalyst for FCC gasoline can also be carried thereon.

There is no specific requirement where antimony and the other metal such as zinc should be carried. It is, however, preferable that the antimony or the other metal is carried near vanadium oxide carried thereon.

[0021]

As the porous inorganic oxide spherical particles, it is possible to use spherical particles made of an organic oxide typically used in a FCC catalyst.

The porous inorganic oxide spherical particles include crystalline aluminosilicate zeolite such as Y-zeolite, ultra stable Y-zeolite (USY), X-zeolite, mordenite, beta-zeolite and ZSM zeolite; heat-resistant metal oxides such as silica, alumina, silica-alumina, silica-magnesia, alumina-boria, titania, zirconia, silica-zirconia, calcium silicate, calcium aluminate; and clay minerals such as kaolin, bentonite, and halloysite.

[0022]

Preferably the porous inorganic oxide spherical particles according to the present invention are made of crystalline aluminosilicate zeolite such as Y-zeolite, ultra stable Y-zeolite and ZSM-5, and an inorganic oxide matrix. Preferably the inorganic oxide matrix includes heat-resistant metal oxide functioning as a binder for silica, alumina, and silica-alumina, and clay mineral such as kaolin, and further includes, if necessary, an appropriate amount of porous silica xerogel and either alumina powder or a metal-trap agent.

Preferably a quantity of the crystalline aluminosilicate zeolite is in the range

from 5 to 50 weight percent based on catalyst. As is often the case with a catalytic cracking catalyst, the crystalline aluminosilicate zeolite is ion-exchanged with at least one kind of cation selected from the group consisting of hydrogen, ammonium, and polyvalent metals.

[0023]

It is especially preferable to use, as the porous inorganic oxide spherical particles, a FCC catalyst including typical crystalline aluminosilicate zeolite used in an apparatus FCC unit.

The porous inorganic oxide spherical particles described above are manufactured in the same manner as that employed when a typical FCC catalyst is manufactured. For instance, the spherical particles are manufactured by spray-drying a mixture of the ultra stable Y- zeolite and a precursor of the inorganic oxide matrix including silica sol, kaolin, porous silica xerogel and alumina hydrate, and the obtained spherical particles are then washed, dried and, if necessary, sintered. Preferably, the spherical particles have an average particle diameter in the range from 40 to 90 micrometers.

[0024]

METHOD OF PRODUCING THE DESULFURIZATION CATALYST

The desulfurization catalyst for FCC gasoline according to the present invention is produced by impregnating the porous inorganic oxide spherical particles described above with vanadium oxide sol, further by drying and sintering the same.

The vanadium oxide sol may be prepared, for instance, by the method described in Japanese Patent Laid-open Publication No. HEI 7-507532, or the commercial vanadium oxide sol may be used.

[0025]

Any impregnating method may be employed for impregnating the porous inorganic oxide spherical particles into the vanadium oxide sol. For instance, the spraying method, the pore-filling method, the incipient wetness method, or the evaporation to dryness method may be employed. In the producing method according to the present invention, the porous inorganic oxide spherical particles are impregnated in the vanadium oxide sol by the well-known method, and dried until water content is less than 20 wt%, more preferably in a range from 5 to 15 wt%, and then sintered at a temperature of approximately 500 to 600 degrees Celsius. The sintering of catalyst may be executed under the condition of catalyst regeneration in regenerator of FCC unit.

[0026]

An average particle diameter of vanadium oxide spherical particles included in the vanadium oxide sol is preferably in a range from 1 to 1,000 nanometers. When the average particle diameter is less than 1 nanometer, vanadium oxides supported on the surface of the porous inorganic oxide spherical particles described above decrease in quantity, and may also be carried on the interior of the spherical particles so that sometimes the desired effect described above is not achieved. When the average particle diameter is more than 1,000 nanometers, the binding power between the vanadium oxides carried on the surface of the porous inorganic oxide spherical particles described above and the porous inorganic oxide spherical particles may be weakened so that the obtained desulfurization catalyst is possibly unable to achieve the desired sulfur retention due to decrease of the supporting vanadium oxides during use.

[0027]

According to the present invention, the average particle diameter of vanadium oxide spherical particles is calculated by measuring the major axis of each of one hundred vanadium oxide spherical particle images taken by a transmission electron

microscope (TEM) with a micrometer caliper.

Said average particle diameter of vanadium oxide spherical particle is more preferably in the range from 20 to 500 nanometers.

[0028]

When the desulfurization catalyst for FCC gasoline supports antimony in addition to the vanadium oxides, for instance, the porous inorganic oxide spherical particles described above are mixed into a hydrochloric solution with antimony chloride being dissolved therein; neutralized with sodium hydroxide; dehydrated; dried; and sintered, and after that, according to the method described above, the porous inorganic oxide spherical particles are impregnated with the vanadium oxide sol; dried; and sintered if needed, so that the desulfurization catalyst for FCC gasoline is produced. Alternatively, as described in the examples described later, antimony oxide sol may be used.

[0029]

METHOD OF DESULFURIZING FCC GASOLINE

In the method of desulfurization for FCC gasoline according to the present invention, the desulfurization is performed together with a catalytic cracking by contacting heavy hydrocarbon oil and/or vacuum gas oil with the mixed catalyst of the desulfurization catalyst for FCC gasoline described above and the FCC catalyst under the catalytic cracking condition.

[0030]

As the FCC catalyst, the commercial FCC catalyst may be used, and especially the FCC catalyst containing faujasite zeolite is preferably used because of the high degradation activity. The FCC catalyst containing faujasite zeolite is, for instance, a catalyst containing faujasite zeolite (USY) with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5 to 6, in the range from 10 to 50 wt%; silica as a binder in the range from 15 to 20 wt%; porous

silica xerogel in the range from 0 to 15 wt%; active alumina in the range from 0 to 20 wt%; metal trap agent in the range from 0 to 10 wt%; and kaolin in the range from 25 to 65 wt%.

As the FCC catalyst as described above, ACZ, DCT, STW, BLC, HMR, and the like (which are trademarks or registered trademarks of FCC catalysts produced by Catalysts & Chemicals Industries Co., Ltd.) are exemplified. As the FCC catalyst according to the present invention, an equilibrium catalyst of the FCC catalyst used for the catalyzed degradation of hydrocarbon oil in the FCC unit may be employed.

[0031]

In the mixed catalyst described above, the mixing ratio of the desulfurization catalyst for FCC gasoline and the FCC catalyst is in the range from 5/95 to 50/50 by weight. When the mixing ratio of the desulfurization catalyst for FCC gasoline is less than 5/95 by weight, sulfur compounds in the gasoline fraction may not be removed sufficiently because the desulfurization catalyst is not enough. When the mixing ratio of the desulfurization catalyst for FCC gasoline is more than 50/50 by weight, the catalytic cracking activity and the yield of gasoline become lower.

The mixing ratio of the desulfurization catalyst for FCC gasoline and the FCC catalyst is preferably in the range from 10/90 to 30/70 by weight.

[0032]

In the method of desulfurization for FCC gasoline according to the present invention, desulfurization is performed together with catalytic cracking by contacting heavy hydrocarbon oil and/or vacuum gas oil to the mixed catalyst described above under the catalytic cracking condition. As the catalytic cracking condition, the catalytic cracking condition commonly used in this field conventionally may be employed, and, for instance, the catalytic cracking temperature is approximately in the range from

400 to 600 degrees Celsius, and the regeneration temperature is approximately in the range from 500 to 800 degrees Celsius.

EXAMPLES

Examples are shown below to describe the present invention further specifically, however, the present invention is not limited to the examples in any way.

[0033]

Example of Production 1

4,000 grams of silica hydrosol with the SiO_2 concentration of 12.5 wt% is prepared by continuously adding 1,059 grams of sulfuric acid solution with the sulfuric acid concentration of 25 wt% into 2,941 grams of water glass with the SiO_2 concentration of 17 wt% so that the SiO_2 concentration of the final catalyst composition is 20 wt% on the dry base. Kaolin, porous silica xerogel, active alumina, a metal trap agent, and ultra stable Y-zeolite slurry adjusted at pH 3.0 with 25 wt% sulfuric acid are added respectively by 975 grams, 125 grams, 125 grams, 25 grams, and 750 grams respectively into the silica hydrosol so that weight percents of the components in the final catalyst composition are 39%, 5%, 5%, 1%, and 30% respectively. After spherical particles are prepared by spray-drying the mixed slurry, the spherical particles are cleaned until the Na_2O content is less than 0.5 wt%, and then dried at a temperature of 135 degrees Celsius to obtain a catalyst A.

The compositions and characteristics of the catalyst A are described as follows;

[0034]

(1) Compositions

Silica:	20 wt%
Kaolin:	39 wt%
Zeolite:	30 wt%
Porous silica xerogel:	5 wt%
Active alumina:	5 wt%
Metal trap agent:	1 wt%

(2) Characteristics

Loss of ignition (1000°C – 1 hour):	11.3 wt%
Remaining Na ₂ O:	0.1 wt%
Remaining SO ₄ :	0.2 wt%
Al ₂ O ₃ :	25.2 wt%
Average particle diameter:	72 micrometers
Apparent bulk specific gravity:	0.76 gram per milliliter
Specific surface area:	211 square meter per gram
Attrition resistance:	0.1 wt% per hour

[0035]

Example 1

A solution prepared by mixing 125.0 grams of vanadium pentoxide sol with the vanadium pentoxide concentration of 2 wt% into 58.8 grams of water was impregnated in 497.5 grams of the catalyst A as the dry base so that the vanadium pentoxide concentration in the catalyst was 0.5 wt%, and the catalyst was dried at a temperature of 135 degrees Celsius for 12 hours, and then sintered at a temperature of 600 degrees Celsius for two hours to prepare a desulfurization catalyst for FCC gasoline carrying

vanadium pentoxide thereon (hereinafter referred to as "a catalyst α "). The used vanadium pentoxide sol was the one (the average major axis: 250 nanometers, the average minor axis: 1 nanometer) produced by Shinko Chemical Industry K.K.

[0036]

Fig. 1 is an image showing a surface condition of the catalyst α observed with a scanning electron microscope (SEM), and it is recognized that a thin layer is formed on a surface of the catalyst α .

From an image photographed with an electron probe microanalyzer (WDS) shown in Fig. 2 and the result of line analysis, a diameter of the catalyst particles and a portion where the vanadium pentoxide is carried are measured. From a result of measurement of 20 catalyst particles, it is recognized that the vanadium pentoxide is carried on in a portion ranging from the outer surface of the catalyst down to the depth of less than 14% of a radius of the catalyst α .

The properties of the catalyst α are shown in Table 1.

[0037]

Example 2

Like in the case of the catalyst α in Example 1, the solution prepared by mixing 125.0 grams of vanadium pentoxide sol into 57 grams of water was impregnated in 495.0 grams of the catalyst A as the dry base so that the concentration of vanadium pentoxide in the catalyst was 1.0 wt%, and the process described above one was repeated once more for impregnating an appropriate volume of the sol suited to the water absorption rate of the catalyst A, and then the catalyst is sintered at a temperature of 600 degrees Celsius for two hours to prepare the desulfurization catalyst for FCC gasoline supporting vanadium pentoxide (hereinafter referred to as "a catalyst β ").

Examination with the SEM like in Examination 1 shows that a thin layer is formed on the surface of the catalyst β .

From the result of line analysis with the WDS, it is recognized that the vanadium pentoxide is carried on in a portion of the catalyst ranging from the outer surface down to the depth of approximately less than 15% of a radius of the catalyst β . The properties of the catalyst β are shown in Table 1.

[0038]

Example 3

Like in the case of the catalyst α in Example 1, the solution prepared by mixing 165.0 grams of vanadium pentoxide sol into 16.6 grams of water was impregnated in 490.0 grams of the catalyst A as the dry base so that the concentration of vanadium pentoxide in the catalyst was 2.0 wt%, and the process described above one was repeated twice more for impregnating an appropriate volume of the sol suited to the water absorption rate of the catalyst A, and then the catalyst was sintered at a temperature of 600 degrees Celsius for two hours to prepare the desulfurization catalyst for FCC gasoline supporting vanadium pentoxide (hereinafter referred to as "a catalyst γ ").

Examination with the SEM like in Examination 1 shows that a thin layer is formed on the surface of the catalyst γ .

From the result of line analysis with the WDS, it is recognized that the vanadium pentoxide is carried on in a portion of the catalyst ranging from the outer surface down to the depth of approximately less than 17% of a radius of the catalyst γ . The properties of the catalyst γ are shown in Table 1.

[0039]

Example 4

A solution prepared by mixing 20.5 grams of antimony pentoxide sol into 166.0 grams of water was impregnated in 485.0 grams of the catalyst A as the dry base so that the concentration of antimony trioxide (Sb_2O_3) in the catalyst was 2.0 wt%, and the catalyst was dried at a temperature of 135 degrees Celsius for 12 hours. Furthermore, the operations of impregnating a solution by mixing 125.0 grams of vanadium pentoxide sol into 57.9 grams of water in the catalyst above so that the concentration of vanadium pentoxide is 1.0 wt% and then drying the catalyst were repeated twice for impregnating an appropriate volume of the sol suited to the water absorption rate of the catalyst A, and the catalyst was sintered for two hours at a temperature of 600 degrees Celsius to prepare the desulfurization catalyst for FCC gasoline carrying antimony pentoxide and vanadium pentoxide (hereinafter referred to as "a catalyst δ ").

Examination with the SEM shows that, like Example 1, a thin layer is formed on the surface of the catalyst δ .

From the result of line analysis of the WDS, it is recognized that the vanadium pentoxide is carried in a portion of the catalyst δ ranging from the outer surface thereof down to the depth of approximately less than 14% of radius of the catalyst δ . The properties of the catalyst δ are shown in Table 1.

[0040]

Comparative Example 1

6.4 grams of ammonium metavanadate was dissolved in 165.0 grams of an aqueous solution of amine so that the concentration of the ammonium metavanadate when calculated as vanadium pentoxide in the catalyst was 1.0 wt%. The obtained solution was impregnated into 495.0 grams of Catalyst A as the dry base, and the catalyst A was dried at 135 degrees Celsius for 12 hours and then sintered at 600 degrees Celsius for two hours to prepare the desulfurization catalyst for FCC gasoline

(Catalyst a) carrying vanadium pentoxide thereon.

From the result of the WDS line analysis similar to that in Example 1, it is confirmed that vanadium pentoxide is homogeneously carried on the Catalyst a even at the core thereof. Properties of the Catalyst a are shown in Table 1.

[0041]

Comparative Example 2

12.9 grams of ammonium metavanadate was dissolved in 165.0 grams of an aqueous solution of amine so that the concentration of the ammonium metavanadate when calculated as vanadium pentoxide in the catalyst was 2.0 wt%. The obtained solution was impregnated into 490.0 grams of catalyst A as the dry base, and the catalyst A was dried at 135 degrees Celsius for 12 hours and then sintered at 600 degrees Celsius for two hours to prepare the desulfurization catalyst for FCC gasoline (Catalyst b) carrying vanadium pentoxide thereon.

From the result of the WDS line analysis similar to that in Example 1, it is confirmed that vanadium pentoxide is homogeneously carried on Catalyst b even at the core thereof. Properties of the Catalyst b are shown in Table 1.

[Table 1] Properties of Catalyst α to δ , a, and b

	E x a m p l e s				Comparative Examples	
	1	2	3	4	1	2
Desulfurization catalyst	α	β	γ	δ	a	b
Loss of ignition [1000°C-1h] (wt%)	4.3	5.1	4.6	4.1	3.4	5.8
Remaining Na ₂ O (wt%)	0.1	0.1	0.1	0.1	0.1	0.1
Remaining SO ₄ (wt%)	0.2	0.2	0.2	0.2	0.2	0.2
V ₂ O ₅ (wt%)	0.48	1.00	1.98	1.00	1.03	1.98
Sb ₂ O ₅ (wt%)	0.00	0.00	0.00	2.26	0.00	0.00

[0042]

Example 5

Activities of the catalysts above mentioned were accessed with a pilot equipment. The pilot equipment is a circulating fluidized bed in which catalyst circulates inside the equipment while repeating the processes of reaction and regeneration alternately. The equipment imitates the FCC unit.

Each of the desulfurization catalysts α to δ , a, and b was processed, before reaction, at a temperature of 750 degrees Celsius for 13 hours with 100 percents steam, and was mixed with 2 kilograms of FCC equilibrium catalyst at 10 wt% of the catalyst. Then the catalyst was put in the equipment to perform the reaction.

[0043]

The reaction conditions are as described bellow.

Feed oil:	Desulfurized vacuum gas oil
Reaction temperature:	500 degrees Celsius
Catalyst to oil ratio:	5 g/g or 7 g/g
Feed oil supplying speed:	10 g/min
CRC (carbon concentration on regenerated catalyst): 0.05 wt%.	

[0044]

It is to be noted that analysis of product gas and product oil was made using gas chromatography, and the product oil obtained in a range from C₅ to the boiling point of 204°C was taken as the gasoline fraction. The product oil was fractionated to gasoline and cycle oil with the rotary band (theoretical plate number: 45 plates, manufactured by TOUKA SEIKI K.K.) method, and was analyzed for a sulfur concentration in the gasoline fraction with the coulometric titration method (ASTM D-3120).

Table 2 shows a yield of each product and sulfur concentration in gasoline for each catalyst when the catalyst to oil ratio is 7g/g.

[Table 2] Activity assessment of catalysts α to δ , a, and b

	Equilibrium Catalyst	E x a m p l e s				Comparative Examples	
		1	2	3	4	1	2
		α	β	γ	δ	a	b
Hydrogen (wt%)	0.15	0.16	0.19	0.21	0.12	0.21	0.25
C1+C2+C2 ⁼ *5) (wt%)	1.7	1.7	1.7	1.6	1.6	1.6	1.6
LPG *1) (wt%)	17.9	17.4	16.6	16.1	16.8	15.7	15.0
Gasoline *2) (wt%)	51.0	50.8	50.6	50.5	52.5	50.3	50.1
LCO *3) (wt%)	17.5	17.7	18.0	18.1	17.5	18.3	18.4
HCO *4) (wt%)	6.6	7.1	7.7	8.1	7.0	8.5	9.1
Coke (wt%)	6.1	5.1	5.2	5.3	4.4	5.3	5.5
Research octane number of gasoline	93.0	92.8	92.5	92.2	92.8	92.3	92.0
Sulfur conc. in gasoline (wt-ppm)	23	15	12	10	5	17	16

[0045]

Notes in Table 2

*1) LPG (liquefied petroleum gas) includes propane, propylene, n-butane, i-butane, and butylenes.

*2) Gasoline is a product fractionated in a range from C₅ to the boiling point of 204°C.

*3) LCO (light cycle oil) is a product fractionated in a range from the boiling point of 204°C to 343°C.

*4) HCO (heavy cycle oil) is a product fractionated in a range over the boiling point of 343°C.

*5) C1: methane, C2: ethane, C2⁼: ethylene

WHAT IS CLAIMED IS:

1. Desulfurization catalyst for FCC gasoline with porous inorganic oxide spherical particles, said catalyst carrying vanadium oxide on a surface thereof only, wherein the vanadium oxide is carried at least on a portion of the surface.

2. The desulfurization catalyst for FCC gasoline as claimed in Claim 1, wherein said vanadium oxide forms a vanadium oxide thin layer at least on a portion of the surface of porous inorganic oxide spherical particle.

3. The desulfurization catalyst for FCC gasoline as claimed in any of Claims 1 or 2, wherein a quantity of carried vanadium oxide is in a range from 0.3 to 3 wt% when calculated as V_2O_5 .

4. The desulfurization catalyst for FCC gasoline as claimed in any of Claims 1 to 3, wherein said porous inorganic oxide spherical particle carries antimony thereon.

5. The desulfurization catalyst for FCC gasoline as claimed in any of Claims 1 to 4, wherein said porous inorganic oxide spherical particle comprises crystalline aluminosilicate zeolite and porous inorganic oxide matrix.

6. The desulfurization catalyst for FCC gasoline as claimed in Claim 5, wherein said porous inorganic oxide matrix comprises heat-resistant metal oxide functioning as a binder, clay mineral, porous silica xerogel, alumina powder, and a metal-trap agent.

7. A method of manufacturing desulfurization catalyst for FCC gasoline as claimed in any of Claims 1 to 6, wherein said porous inorganic oxide spherical particle is dried and sintered after impregnation of vanadium oxide sol.

8. The method of manufacturing desulfurization catalyst for FCC gasoline as claimed in Claim 7, wherein vanadium oxide particles in the vanadium oxide sol have an average diameter ranging from 1 to 1000 nanometers.

9. A method of desulfurizing a FCC gasoline, wherein heavy hydrocarbon oil and/or vacuum gas oil is contacted to catalyst composed of desulfurization catalyst and FCC catalyst mixed at a rate in a range from 5/95 to 50/50 by weight under the catalytic cracking conditions to catalytically crack and desulfurize the heavy hydrocarbon oil and/or vacuum gas oil.