

DESCRIPTION

TESTING UNIT FOR FLUID CATALYTIC CRACKING CATALYST

Technical Field

5 [0001]

The present invention relates to a testing unit for a catalyst for fluid catalytic cracking of hydrocarbon oil. More particularly, the present invention relates to a testing unit for a fluid catalytic cracking catalyst, by which reaction results extremely similar to those obtained by a pilot unit for fluid catalytic cracking or a commercial fluid catalytic cracking unit (actual unit) are obtained and which is applicable to not only evaluation of a fluid catalytic cracking catalyst but also evaluation and research/development of a catalyst withdrawn from the commercial fluid catalytic cracking unit.

10

15

Background Art

[0002]

A fluid catalytic cracking process is a process for mainly producing gasoline from hydrocarbon oil.

20

[0003]

As a catalyst used for the fluid catalytic cracking process, for example, a catalyst containing zeolite, a binder and a filler such as kaolin or alumina and containing an additive if necessary

is known.

[0004]

For example, patent literature 1 describes a catalyst for catalytic cracking of hydrocarbon, in which (1) alumina particles
5 containing a metal component selected from one or more alkaline earth metals and rare earth metals and a phosphorus component and having particle diameters of 2 to 60 μm and (2) crystalline aluminosilicate zeolite have been homogeneously dispersed in (3) a porous inorganic oxide matrix. It describes that this catalyst has metal resistance,
10 high activity and selectivity and can inhibit production of hydrogen and coke.

[0005]

Patent literature 2 describes a catalyst composition for fluid catalytic cracking of hydrocarbon, which contains alumina,
15 crystalline aluminosilicate zeolite and a matrix of an inorganic oxide other than alumina, said each component containing a phosphorus atom. It describes that if this catalyst is used for catalytic cracking of heavy hydrocarbon oil, the catalyst exhibits excellent bottom (tower bottom oil) cracking ability, the amounts of hydrogen and coke produced
20 are small, and the amounts of gasoline and kerosene-gas oil fraction are increased.

[0006]

Patent literature 3 describes a porous molecular sieve catalyst of high hydrothermal stability obtained by the moisture evaporation

of a raw material mixture containing (1) a molecular sieve having a -Si-O-H-Al- framework, surface pores of said molecule sieve modified with a specific phosphate, (2) a water-insoluble metal salt and (3) a phosphoric acid compound. It describes that this catalyst has high hydrothermal stability and enhances gaseous olefin yield and selectivity.

[0007]

Patent literature 4 describes a production process for a catalytic cracking catalyst, comprising washing microspherical particles obtained by subjecting an aqueous slurry of a mixture composed of airflow-calcined alumina, clay containing silica and alumina as main components, a precursor of a silica-based inorganic oxide and crystalline aluminosilicate to spray drying in such a manner that the content of an alkali metal oxide becomes not more than 1.0% by mass in terms of an oxide and then introducing a rare earth. It describes that if this catalyst is used for catalytic cracking of a heavy hydrocarbon oil containing a metal in a large amount, the catalyst exhibits high cracking activity and high gasoline selectivity, the amounts of coke and gas produced are small, and the catalyst has high hydrothermal stability.

[0008]

Patent literature 5 describes a catalyst for fluid catalytic cracking of hydrocarbon oil, which is a mixture of two or more kinds of catalyst compositions each containing zeolite and an inorganic

oxide matrix composed of an active matrix component and an inactive matrix component and is characterized in that the catalyst compositions differ from each other in the content of zeolite (however, one of the catalyst compositions may be a composition having a zeolite content of 0). It describes that according to this catalyst, gasoline and middle distillate are obtained in high yields, the yield of coke is low, and further, the bottom cracking ability is high, that is, the yield of heavy distillate can be lowered.

[0009]

Patent literature 6 describes a catalyst for fluid catalytic cracking of hydrocarbon oil, which is characterized in that the catalyst is obtained by mixing a catalyst composition A containing zeolite and 10 to 30% by mass of a silica-based binder as a binder and a catalyst composition B containing zeolite and 10 to 30% by mass of an aluminum compound binder as a binder in an arbitrary mass ratio within the range of 10:90 to 90:10 ($W_A:W_B$) (W_A : mass of the catalyst composition A, W_B : mass of the catalyst composition B). It describes that according to this catalyst, gasoline and gas oil fraction are obtained in high yields, the yield of coke is low, and further, the bottom cracking ability is high, that is, production of heavy distillate can be inhibited.

[0010]

For testing such catalyst properties, a micro activity test (MAT) of ASTM-D3907 defined by American Society for Testing and

Materials (ASTM) is known, and this test is commonly used. A schematic diagram of the micro activity test is shown in Fig. 3. In Fig. 3, numeral (31) designates a fixed bed of catalyst, and a feedstock is injected into a reaction vessel through a feedstock injection nozzle (32) and a feedstock injection pump, together with a purge gas led out from a purge gas line (33). Numeral (35) designates a heating furnace, and numeral (36) designates a thermocouple. By adopting such a micro activity test, activity, selectivity, etc. of a catalyst withdrawn from a commercial catalytic cracking unit are evaluated and used as indications of operation.

[0011]

However, operating performance of the commercial catalytic cracking unit and test results in MAT do not always accord with each other in some cases with regard to activity level, yields of various products and selectivity though they roughly accord with each other with regard to a trend of activity level. The reason is thought to be that MAT uses a fixed bed reactor unit and this unit greatly differs in the contact time between feedstock hydrocarbon oil and a catalyst.

[0012]

For example, the contact time in the commercial catalytic cracking unit is approximately several seconds though it varies depending upon the type of feedstock hydrocarbon oil used, etc., but the contact time in MAT is approximately 50 to 120 seconds. Moreover, the amount of the catalyst used is as extremely small as several grams.

[0013]

On this account, a test of catalyst evaluation is sometimes carried out utilizing a fluidized bed pilot plant copied from a commercial catalytic cracking unit (actual unit). For example, Fig. 4 shows a schematic diagram of a pilot plant unit. In Fig. 4, numeral (41) designates a reaction tower bottom, numeral (42) designates a reaction tower top, numeral (43) designates a feedstock injection line, numeral (44) designates a separator, numeral (45) designates a stripper, numeral (46) designates a lift line, numeral (47) designates a regenerator, numeral (48) designates a catalyst transport line, numeral (49) designates a catalyst trap, numeral (50) designates a product oil receiver, numeral (51) designates a fractionator, and numeral (52) designates a product gas. The feedstock and the catalyst are injected into the bottom (41) through the line (43) and the line (48), respectively, then they are subjected to catalytic cracking reaction, and thereafter, the product is distilled out through (50) to (52).

[0014]

In the test in the pilot plant, the activity level, the yields and the qualities (octane value, etc.) of various products and the selectivity roughly accord with those of the commercial catalytic cracking unit (actual unit), but catalyst load is as large as several kg, and a long time is needed for the test including preparation, etc., so that this test has a disadvantage that the test efficiency

does not increase. Moreover, great expense is necessary for manufacture and maintenance of the pilot plant.

[0015]

Then, development of a novel testing unit adopting a fluidized
5 bed has been desired.

[0016]

Patent literature 7 discloses a small-sized testing unit adopting a fluidized bed, which is shown in Fig. 2. In Fig. 2, catalyst is loaded into a catalytic fluidized bed reactor (21), and feedstock,
10 etc. are injected through a feedstock and dispersing gas injection nozzle (22), while a fluidizing gas is fed through a catalyst-fluidizing gas feed nozzle (23) and a catalyst-fluidizing gas feed line (23'). Numeral (24) designates a discharge line for a product gas and a fluidizing gas. Catalytic cracking reaction is
15 carried out by a heating furnace (25) provided outside the reactor while detecting a temperature by a thermocouple (26).

[0017]

Then, the present applicant obtained a small-sized testing unit of the patent literature 7 and carried out various tests. In this
20 unit, the catalyst load is several grams, the contact time between the catalyst and the feedstock hydrocarbon oil is approximately 60 to 120 seconds, and the test efficiency is good, but the difference from the test results of the pilot plant is not always small, and therefore, it cannot be necessarily said that this unit is satisfactory

from the viewpoint of performance evaluation of a catalyst used for commercial unit.

Citation List

5 Patent Literature

[0018]

Patent literature 1: JP-B 1993-16908

Patent literature 2: JP-A 1996-173816

Patent literature 3: JP-A 2009-511245

10 Patent literature 4: JP-A 1985-193543

Patent literature 5: JP-A 2010-110698

Patent literature 6: WO 2009/145311

Patent literature 7: U.S. Patent No. 6,069,012

15 Summary

[0018a]

In one aspect of the present disclosure, there is provided a testing unit for a fluid catalytic cracking catalyst, comprising a reaction vessel in which a catalyst fluidization cell, a feedstock
20 injection nozzle and a catalyst-fluidizing gas feed nozzle are provided inside the vessel, said feedstock and said catalyst-fluidizing gas being fed from the upper part of vessel, and a product collection line is provided at the lower part of the vessel.

Technical Problem

[0019]

In order to solve such problems, the present inventors have earnestly studied, and as a result, they have found that test results
5 closely similar to the test results obtained by a pilot plant can be obtained by providing, in a small-sized testing unit, a completely isolated catalyst fluidization cell (1) inside a reaction vessel (6), loading a catalyst into the cell, supplying a catalyst-fluidizing gas from above to allow the catalyst to be in a fluidized state and

injecting a feedstock hydrocarbon oil to this fluidized catalyst region from above. Thus, the present inventors have accomplished the present invention.

5 Solution to Problem

[0020]

The testing unit for a fluid catalytic cracking catalyst according to the present invention is characterized by comprising a reaction vessel (6) in which a catalyst fluidization cell (1), a
10 feedstock injection nozzle (2) and a catalyst-fluidizing gas feed nozzle (3) are provided inside the vessel, said feedstock and said catalyst-fluidizing gas being fed from the upper part of the vessel, and a product collection line (5) is provided at the lower part of the vessel.

15 [0021]

It is preferable that the catalyst fluidization cell (1) is cylindrical, has an inner diameter (D_I) ranging from 1 to 4 cm, a height (T) ranging from 2 to 14 cm and a ratio of the height (T) to the inner diameter (D_I), $(T)/(D_I)$, ranging from 1.1 to 7.0, and has
20 a cell bottom having a downward concave conical structure.

[0022]

The catalyst fluidization cell (1) preferably has an internal volume in the range of 5 to 40 ml.

[0023]

The catalyst load in the catalyst fluidization cell (1) during testing is preferably in the range of 1 to 20 g.

[0024]

It is preferable that the catalyst has an average particle
5 diameter in the range of 40 to 100 μm , and a bulk specific gravity in the range of 0.5 to 1.1 /ml.

Advantageous Effects of Invention

[0025]

10 According to the present invention, there can be provided a testing unit for a catalyst for fluid catalytic cracking of a hydrocarbon oil, by which reaction results extremely similar to those obtained by a pilot unit for fluid catalytic cracking and further
by a commercial catalytic cracking unit are obtained even if the testing
15 unit is small-size and which can be preferably used for evaluation of a fluid catalytic cracking catalyst, and evaluation of a catalyst withdrawn from a commercial catalytic cracking unit.

Brief Description of Drawings

20 [0026]

[Fig. 1] Fig. 1 shows a schematic diagram of an embodiment of the testing unit for a fluid catalytic cracking catalyst according to the present invention.

[Fig. 2] Fig. 2 shows a schematic diagram of a small-sized

fluidized bed testing unit disclosed in the patent literature 7.

[Fig. 3] Fig. 3 shows a schematic diagram of a micro activity testing unit of ASTM-D3907 defined by American Society for Testing and Materials (ASTM).

5 [Fig. 4] Fig. 4 shows a schematic diagram of a fluidized bed pilot plant simulating a commercial catalytic cracking unit.

Description of Embodiments

[0027]

10 The testing unit for a fluid catalytic cracking catalyst according to the present invention will be described hereinafter.

Testing unit for fluid catalytic cracking catalyst

The testing unit for a fluid catalytic cracking catalyst according to the present invention is characterized by comprising
15 a reaction vessel (6) in which a catalyst fluidization cell (1), a feedstock injection nozzle (2) and a catalyst-fluidizing gas feed nozzle (3) are provided inside the vessel, said feedstock and said catalyst-fluidizing gas being fed from the upper part of the vessel, and a product collection line (5) is provided at the lower part of
20 the vessel.

[0028]

A schematic diagram of an embodiment of the testing unit for a fluid catalytic cracking catalyst according to the present invention is shown in Fig. 1.

[0029]

Fig. 1 includes a catalyst fluidization cell (1), a feedstock injection nozzle (2), a feedstock injection pump (2'), a catalyst-fluidizing gas feed nozzle (3), a catalyst-fluidizing gas feed source (3'), a nozzle support (4), a product collection line (5), a reaction vessel (6), a heating furnace (7) and a thermocouple (8).

[0030]

Catalyst fluidization cell (1)

10 Inside the catalyst fluidization cell (1), a given catalytic cracking catalyst is loaded, and the catalyst is fluidized to carry out catalytic cracking of hydrocarbon oil. The catalyst fluidization cell (1) is cylindrical and has a bottom at the lower part. The bottom preferably has a downward concave conical structure or semispherical structure. By virtue of such a structure, the catalyst during reaction comes to be in a homogeneously fluidized state as compared with the case where the catalyst fluidization cell is prismatic or the bottom of the cell is flat, and therefore, reproducibility of catalytic cracking test results of hydrocarbon oil is enhanced, and reaction results extremely similar to those obtained by a pilot unit are obtained.

[0031]

The catalyst fluidization cell (1) is arranged in such a manner that the interior of the reaction vessel and the interior of the cell

can be completely isolated from each other.

[0032]

By providing such a catalyst fluidization cell inside the reaction vessel, it becomes possible to obtain measurement results of the same level as that of the test results of a pilot plant with regard to gasoline yield, LPG yield, coke yield, etc. Although the reason for the above is not clear, the present inventors have thought that by using not a reaction vessel itself as patent literature 7 but a cell completely isolated from the reaction vessel, the product and the fluidized catalyst can be rapidly separated from each other, and secondary reaction (sometimes referred to as "side reaction") can be inhibited.

[0033]

A fixture, a stopper or the like to hold the catalyst fluidization cell may be provided on the outer surface of the cell, the bottom or the like, and by virtue of this, the catalyst fluidization cell (1) is arranged at a given position in the reaction vessel. The catalyst fluidization cell may be hung at the upper part from the later-described nozzles (2) and (3) or support (4).

20 [0034]

The inner diameter (D_1) of the cylindrical cell is preferably 1 to 4 cm, more preferably 1 to 3 cm.

[0035]

If the inner diameter (D_1) of the cylindrical cell is small,

the fluidized state of the catalyst is deteriorated, and measurement accuracy and reproducibility sometimes become insufficient. Also if the inner diameter (D_I) of the cylindrical cell is too large, diffusion of feedstock hydrocarbon oil in the lateral direction becomes
5 insufficient, and probably because the mixed condition between the catalyst and the hydrocarbon oil is deteriorated, the measurement accuracy tends to be lowered, and cracking tends to become insufficient.

[0036]

10 The height (T) of the cylindrical cell is preferably in the range of 2 to 14 cm, more preferably 3 to 12 cm.

[0037]

Here, the height (T) of the cylindrical cell refers to a distance between the lowermost part and the uppermost part of the cell.

15 [0038]

In the case of a cylindrical cell having a small height (T), a height needed to homogeneously fluidize the catalyst becomes insufficient, and probably because the mixed condition between the catalyst and the hydrocarbon oil is deteriorated, the measurement
20 accuracy tends to be lowered, and cracking tends to become insufficient.

[0039]

Also if the height (T) of the cylindrical cell is too large, the size of the testing unit is increased though there is no problem

in testing. In the micro activity test (MAT), therefore, the upper limit has only to be about the aforesaid value.

[0040]

The ratio of the height (T) to the inner diameter (D_I), $(T)/(D_I)$,
5 is preferably in the range of 1.1 to 7.0, more preferably 1.5 to 6.5.

[0041]

When the ratio $(T)/(D_I)$ is in the above range, a homogeneously fluidized state of the catalyst is obtained, and mixing of the feedstock hydrocarbon oil with the catalyst can be homogeneously carried out,
10 so that measurement accuracy can be increased.

[0042]

The internal volume of the catalyst fluidization cell (1) is preferably in the range of 5 to 40 ml, more preferably 6 to 30 ml.

[0043]

15 When the internal volume of the catalyst fluidization cell (1) is in the above range, a preferred fluidized state of the catalyst is obtained even if catalyst load is small, and therefore, reproducibility of catalytic cracking test results of a hydrocarbon oil is enhanced, and reaction results extremely similar to those
20 obtained by a pilot unit are obtained.

[0044]

The filling quantity of the catalyst in the catalyst fluidization cell (1) during testing is preferably in the range of 1 to 20 g, more preferably 2 to 15 g, though it varies depending upon the internal

volume of the catalyst fluidization cell (1), the particle diameter distribution of the catalyst, the bulk specific gravity of the catalyst, etc.

[0045]

5 If catalyst load is small, a homogeneously fluidized state is not obtained because of a small quantity of the catalyst, and contact of the catalyst with feedstock hydrocarbon oil become heterogeneous. Moreover, since the quantity of feedstock hydrocarbon oil used is decreased, the recovery rate of the product is lowered, and therefore,
10 the test accuracy tends to become insufficient. Also if catalyst load is too large, the quantity of feedstock hydrocarbon oil used is increased, and therefore, the quantity of gas product produced after the reaction increases and becomes excess based on the aforesaid internal volume of the catalyst fluidization cell (1). Consequently,
15 the internal pressure of the reaction vessel sometimes steeply increases, and troubles, such as heterogeneously fluidized state and back flow of the product gas into the catalyst-fluidizing gas feed nozzle (3), are liable to occur, so that the test accuracy sometimes becomes insufficient.

20 [0046]

When the test is intended to be carried out by increasing the loading quantity of the catalyst, the size of the catalyst fluidization cell (1) can be increased proportionally to the catalytic quantity. The testing unit of the present invention has been designed for purposes

of test and development of a catalyst used in a commercial catalytic cracking unit, and it is preferable to use a catalyst having an average particle diameter of 40 to 100 μm , preferably 50 to 80 μm .

[0047]

5 If the average particle diameter of the catalyst is not within the above range, a preferred fluidized state of the catalyst is not obtained, and therefore, the test accuracy sometimes becomes insufficient.

[0048]

10 The average particle diameter of the catalyst is determined by sieving the catalyst particles to classify them into samples of 20, 30, 45, 60, 75, 90, 105 and 150 μm by a dry micromesh sieve method, measuring wt% of the classified each sample, plotting the integrated wt%, and taking the value corresponding to 50 wt% as the average particle
15 diameter.

[0049]

 The bulk specific gravity of the catalyst is preferably in the range of 0.5 to 1.1 g/ml, more preferably 0.6 to 1.0 g/ml.

[0050]

20 Also if the bulk specific gravity of the catalyst is not within the above range, a preferred fluidized state of the catalyst is not obtained, and therefore, the test accuracy sometimes becomes insufficient.

[0051]

The bulk specific gravity of the catalyst is measured on the basis of UOP Method 254-65.

[0052]

Specifically, the measuring method comprises calcining the catalyst at 600°C for 2 hours, cooling the catalyst, then pouring the catalyst into a 25 ml cylinder up to overflowing, leveling off the catalyst overflowing from the top of the cylinder, measuring the weight of the catalyst and calculating the bulk specific gravity from the following formula.

10 [0053]

Bulk specific gravity (g/ml) = Weight of catalyst (g)/25 (ml)

At the top of the catalyst fluidization cell (1), a filter can be provided in order to prevent scattering of the catalyst, and the filter can be used in combination with glass wool or the like.

15 [0054]

A feedstock injection nozzle (2)

A feedstock injection nozzle (2) to inject the feedstock to the catalyst fluidization cell (1) is provided inside the cell. The feedstock injection nozzle (2) is arranged in such a manner that its tip is located in the catalyst fluidization cell (1) and can fluidize the catalyst. Particularly when the catalyst fluidization cell (1) has a conical structure or a semispherical structure at the lower part, the feedstock injection nozzle (2) is preferably provided in such a manner that the tip of the nozzle is located at the central

part of the structure.

[0055]

When the tip of the feedstock injection nozzle (2) is present at the central part of the conical structure or the semispherical structure, contact of the catalyst with the feedstock hydrocarbon oil is carried out more homogeneously, and the test accuracy is high.

[0056]

The sectional area of the tip of the feedstock injection nozzle (2) is preferably in the range of 0.1 to 4 mm², more preferably 0.2 to 2 mm².

[0057]

When the sectional area of the tip of the feedstock injection nozzle (2) is in the above range, the feedstock can be stably injected, and good test accuracy is obtained.

15 [0058]

The feedstock injection nozzle (2) lead the feedstock into the catalyst fluidization cell (1) from a feedstock source present outside, by means of a pump or the like.

[0059]

20 A catalyst-fluidizing gas feed nozzle (3) gas

Together with the feedstock injection nozzle (2), a catalyst-fluidizing gas feed nozzle (3), is provided at the catalyst fluidization cell (1) to supply the fluidization gas from the upper part of the reactor. In the fluidized catalytic reaction,

fluidization gas for the catalyst is usually supplied.

[0060]

In order to enhance contact efficiency between the catalyst and the feedstock, the catalyst-fluidizing gas feed nozzle (3) is preferably provided in such a manner that the tip of the nozzle is located at the central part of the conical region or the semispherical region present at the lower part.

[0061]

When the tip of the catalyst-fluidizing gas feed nozzle (3) is located at the central part of the conical region or the semispherical region, a preferred fluidized state of the catalyst is obtained, and therefore, good test accuracy is obtained.

[0062]

The feedstock injection nozzle (2) and the catalyst-fluidizing gas feed nozzle (3) are preferably provided closely to each other. When they are provided closely to each other, the catalyst in a preferred fluidized state made by a fluidizing gas comes into contact with the feedstock hydrocarbon oil homogeneously, and therefore, good test accuracy can be obtained.

20 [0063]

Particularly in the present invention, it is preferable to use a double tube in which an internal tube nozzle on the inner side is used as the feedstock injection nozzle (2), an external tube on the outer side is used as the catalyst-fluidizing gas feed nozzle (3),

and they are integrated with each other.

[0064]

In Fig. 1, an embodiment of the double tube is shown.

[0065]

5 When such a double tube is used for the feedstock injection
nozzle (2) and the catalyst-fluidizing gas feed nozzle (3), the
feedstock hydrocarbon oil can be injected to the catalyst that is
in a preferred fluidized state, and therefore, good test accuracy
can be obtained. Moreover, the fluidizing gas also serves to
10 disperse/diffuse the feedstock hydrocarbon oil homogeneously, and
good test accuracy can be obtained.

[0066]

 The external tube of the double tube can be used as the feedstock
injection nozzle (2) and the internal tube thereof can be used as
15 the catalyst-fluidizing gas feed nozzle (3), but in this case, the
mixed condition between the catalyst and the feedstock hydrocarbon
oil is lowered, and the test accuracy sometimes becomes insufficient.

[0067]

 The feedstock injection nozzle (2) and the catalyst-fluidizing
20 gas feed nozzle (3) can be used by appropriately designing them in
such a manner that a given amount of the feedstock can be injected
and the catalyst can be allowed to be in a homogeneously fluidized
state.

[0068]

The sectional area of the tip of the catalyst-fluidizing gas feed nozzle (3) is preferably in the range of 0.2 to 8 mm², more preferably 0.4 to 4 mm².

[0069]

5 When the sectional area of the tip of the catalyst-fluidizing gas feed nozzle (3) is in the above range, the catalyst can be allowed to be in a homogeneously fluidized state, and good test accuracy is obtained.

[0070]

10 As the catalyst-fluidizing gas, an inert gas is used, and in the unit of the present invention, nitrogen gas is recommended from the viewpoint of economy.

[0071]

Support (4)

15 In order that the feedstock injection nozzle (2) and the catalyst-fluidizing gas feed nozzle (3) can be fixed at given positions, a support (4) is provided.

[0072]

20 By providing the support (4), the fluidized state of the catalyst can be kept constant, and besides, the position to feed the raw material hydrocarbon oil can be kept constant, so that excellent test accuracy is obtained.

[0073]

A support for the catalyst fluidization cell (1) can be

appropriately provided though such a support is not shown in the figure. For example, a support of such a shape as to hang the catalyst fluidization cell (1) at the nozzles (2) and (3) can be provided.

[0074]

5 Product collection line (5)

At the lower part of the reaction vessel (6), a product collection line (5) is provided. Products (gas product, liquid product) distilled out along with the initiation of the reaction in the catalyst fluidization cell, and the catalyst-fluidizing gas are collected

10 through the product collection line (5), and they are subjected to composition analysis, etc.

[0075]

Reaction vessel (6)

The reaction vessel (6) mainly includes therein the catalyst

15 fluidization cell (1), the feedstock injection nozzle (2), the catalyst-fluidizing gas feed nozzle (3) and the support (4) described above, and has the product collection line (5) at the lower part. The structure of the reaction vessel (6), involving size, shape, etc., is preferably one capable of not only including the aforesaid catalyst

20 fluidization cell (1) but also being uniformly heated by a heating furnace (7) that is provided outside the reaction vessel.

[0076]

Heating furnace (7), temperature detector (8)

In order that the reaction vessel (6) may be inserted inside,

an annular heating furnace (7) is provided. The heating furnace (7) is properly controlled so that a given reaction temperature may be maintained. The heating method is not specifically restricted, and a well-known one is adoptable, and as the temperature detector, a well-known one such as a thermocouple is usually used.

[0077]

Next, a test method using the testing unit for a fluid catalytic cracking catalyst according to the present invention will be described.

[0078]

10 Catalyst

As the catalyst, any of catalysts for fluid catalytic cracking of hydrocarbon oils can be tested without specific restriction. In this test, the average particle diameter and the bulk specific gravity of the catalyst are preferably in the aforesaid ranges.

15 [0079]

As the catalyst, a catalyst (also referred to as a "fresh catalyst") obtained by spray drying a mixed slurry of crystalline aluminosilicate zeolite disclosed in the patent literatures 5 and 6, an inorganic oxide matrix component, a binder, clay mineral, etc. can be used, but a catalyst (also referred to as an "equilibrium catalyst") withdrawn from a commercial catalytic cracking unit, or the like can be also used.

[0080]

In the case of the fresh catalyst, it is preferable to carry

out measurement after the catalyst is previously subjected to hydrothermal treatment at approx. 650 to 850°C and thereby pseudo-equilibrated. Further, the measurement can be also carried out after the fresh catalyst is allowed to support a metal component
5 contained in an equilibrium catalyst, such as Ni, V or Fe, and then subjected to pseudo-equilibration. In the case of the equilibrium catalyst, test is usually carried out after the catalyst is calcined by heating to remove a carbon deposit, though it depends upon the purpose of the test.

10 [0081]

Hydrocarbon oil (feedstock)

Examples of the feedstock employable include vacuum distillation gas oil, atmospheric distillation residual oil, vacuum distillation residual oil, deasphalted oil, light cycle oil (LCO),
15 heavy cycle oil (HCO) and mixed oils of these oils.

[0082]

Test method

First, a given amount of the catalyst is loaded into the catalyst fluidization cell (1) in the reaction vessel (6), then the reaction
20 vessel (6) is arranged in the heating furnace (7), subsequently a fluidizing gas is fed at a given rate to fluidize the catalyst in the catalyst fluidization cell (1), and the temperature is raised in such a manner that the temperature of the catalyst bed becomes a given reaction temperature.

[0083]

After the temperature is raised, a feedstock is injected through the feedstock injection nozzle (2) at a given rate for a given period of time to allow the feedstock to undergo reaction.

5 [0084]

While carrying out the reaction, the product is collected through the product collection line (5) provided at the lower part of the reaction vessel (6), then the product gas and the product oil are subjected to separation by a condenser having been cooled to -10°C ,
10 and thereafter, components contained in the product gas and the product oil are subjected to separation and quantitative determination.

[0085]

In the case of separation and quantitative determination of the gas components, hydrogen and hydrocarbon of 1 to 6 carbon atoms
15 are separated and quantitatively determined by, for example, gas chromatography (GC-20B-3S, manufactured by Shimadzu Corporation).

[0086]

In the case of separation and quantitative determination of the product oils, gasoline, LCO and HCO are separated and
20 quantitatively determined by gas chromatography (GC-2014, manufactured by Shimadzu Corporation).

Examples

[0087]

The present invention is more specifically described with reference to the following examples and comparative examples, but it should be construed that the present invention is in no way limited to those examples.

5 [0088]

[Example 1]

Testing unit for fluid catalytic cracking catalyst

The testing unit for a fluid catalytic cracking catalyst had a structure shown in Fig. 1. The reaction vessel 6 had a height of
10 26 cm and an inner diameter of 2.2 cm. The cell (1) had a height of 7.7 cm and an inner diameter of 1.6 cm. The bottom of the cell had a conical shape, and the cone angle against a perpendicular line was 45°. The nozzle had a double tube structure, the sectional area of a tip of feedstock injection nozzle (2) was 1.1 mm², and the sectional
15 area of a tip of the catalyst-fluidizing gas feed nozzle (3) was 2.4 mm². The nozzle tip was located at the central position of the conical bottom of the cell (1).

[0089]

The shape of the catalyst fluidization cell is cylindrical,
20 and the cell has an inner diameter (D₁) of 1.6 cm, a height (T) of 7.7 cm and an internal volume of 14.4 ml.

[0090]

Fluid catalytic cracking catalyst

As the catalyst, CVZ manufactured by JGC CATALYSTS AND CHEMICALS

LTD. and having an average particle diameter of 65 μm , a bulk specific gravity of 0.77 g/ml and a zeolite content of 25% by weight was used.

[0091]

Pseudo-equilibration

5 The fluid catalytic cracking catalyst (CVZ manufactured by JGC CATALYSTS AND CHEMICALS LTD., average particle diameter: 65 μm , bulk specific gravity: 0.77 g/ml, zeolite content: 25% by weight) was calcined at 600°C for 1 hour. Thereafter, the catalyst was allowed to absorb a toluene solution of nickel naphthenate and vanadium
10 naphthenate in such a manner that the contents of nickel and vanadium became 3000 ppm and 500 ppm, respectively. Subsequently, the catalyst was dried at 110°C, thereafter calcined at 600°C for 1.5 hours, then subjected to steam treatment at 810°C for 12 hours and calcined again at 600°C for 1 hour to pseudo-equilibrate the catalyst.

15 [0092]

Reaction test

4.8 g of the pseudo-equilibrated catalyst was loaded into the catalyst fluidization cell (1) of the testing unit for a fluid catalytic cracking catalyst, and while feeding N_2 gas as a fluidizing gas under
20 the conditions of 30 ml (STP)/min to fluidize the catalyst, the temperature was raised to 550°C. Subsequently, reaction (No. 1) was carried out under the following conditions.

[0093]

Reaction (No. 1)

As feedstock hydrocarbon oil, the mixture of desulfurized atmospheric residual oil (DSAR) and desulfurized vacuum distillation gas oil (DSVGO) in a ratio of 1:1 was fed at an oil injection rate of 0.096 g/sec for 10 seconds. At this time, the catalyst/feedstock
5 hydrocarbon oil ratio (C/O) was 5, the space velocity (WHSV) was 72 hr^{-1} , and the reaction time was 10 seconds.

[0094]

Along with the initiation of the reaction, the product was collected through the product collection line (5), and after completion
10 of feedstock injection, the product remaining on the catalyst was collected while feeding N_2 gas to the feedstock injection nozzle (2) under the conditions of 30 ml/min and feeding N_2 gas to the catalyst-fluidizing gas feed nozzle (3) under the conditions of 30 ml/min. Thereafter, the product gas and the product oil were separated
15 by a condenser having been cooled to -10°C , and then the components contained in the product gas and the product oil were separated and quantitatively determined.

[0095]

After completion of the reaction, the catalyst was taken out
20 of the catalyst fluidization cell (1), and coke remaining on the catalyst was quantitatively determined by a carbon analyzer (EMIA-321V manufactured by HORIBA, Ltd.). Based on the results of the separation and the quantitative determination, a conversion and a yield of each component were determined in accordance with the following definition.

[0096]

Range of boiling point of gasoline: 36 to 204°C, range of boiling point of light cycle oil (LCO): 204 to 343°C, range of boiling point of heavy cycle oil (HCO): not lower than 343°C

5 Conversion (wt%) = 100 - (LCO wt% + HCO wt%) (wt%)

Reaction (No. 2)

Reaction (No. 2) was carried out in the same manner as in Reaction (No. 1), except that 5.76 g of the catalyst was loaded into the cell, the feedstock hydrocarbon oil was injected at an oil injection rate
10 of 0.096 g/sec for 10 seconds, the catalyst/feedstock hydrocarbon oil ratio (C/O) was changed to 6, the space velocity (WHSV) was changed to 57 hr⁻¹, and the reaction time was 10 seconds. Then, a conversion and a yield of each component were determined.

[0097]

15 Reaction (No. 3)

Reaction (No. 3) was carried out in the same manner as in Reaction (No. 1), except that 6.72 g of the catalyst was loaded into the cell, the feedstock hydrocarbon oil was injected at an oil injection rate of 0.096 g/sec for 10 seconds, the catalyst/feedstock hydrocarbon
20 oil ratio (C/O) was changed to 7, the space velocity (WHSV) was changed to 49 hr⁻¹, and the reaction time was 10 seconds. Then, a conversion and a yield of each component were determined.

[0098]

The results of the reactions No.1 to No. 3 were graphically

plotted as a relation between the conversion ratio and the yield of each component, and from the graph, a yield of each component corresponding to a conversion of 68% by weight was determined. The results are shown in the table. Further, differences from yields of the components in the results of the following Reference Example 1 are shown in the table.

[Reference Example 1]

Testing unit for fluid catalytic cracking catalyst

Performance evaluation test was carried out using a hitherto known pilot plant of catalyst circulation regeneration type (Midget-2 manufactured by JGC CATALYSTS AND CHEMICALS LTD.) shown in Fig. 4. The diameter of the reaction tower bottom (41) was 1.28 cm, the diameter of the reaction tower top (42) was 0.94 cm as the lower part smallest diameter and was 2.14 cm as the upper part largest diameter, and the total height of the reaction tower was 81.7 cm.

[0099]

Fluid catalytic cracking catalyst

A catalyst having been pseudo-equilibrated in the same manner as in Example 1 was used.

20 [0100]

Reaction test

In the catalyst circulation type testing unit for a fluid catalytic cracking catalyst (Midget-2 manufactured by JGC CATALYSTS AND CHEMICALS LTD.), 2 kg of the pseudo-equilibrated catalyst was

loaded, and while circulating the catalyst, the mixture of desulfurized atmospheric residual oil (DSAR) and desulfurized vacuum distillation gas oil (DSVGO) in a ratio of 1:1 was injected as a feedstock hydrocarbon oil at a rate of 10 g/min. At this time, temperature control was

5 carried out by an electric heater in such a manner that the temperature of the reaction tower top became 520°C and the temperature of the reaction tower bottom became 550°C.

[0101]

After the reaction, the catalyst was transferred to a

10 regeneration tower (47) through a stripper (45) and a lift line (46), and while supplying air at a temperature of 680°C, the catalyst was regenerated in such a manner that the amount of coke on the regenerated catalyst became not more than 0.05% by mass. The regenerated catalyst was circulated to the reaction tower.

15 [0102]

Reaction (No. 1)

In the above test, reaction was carried out under the conditions of a catalyst circulation quantity of 50 g/min and a catalyst/feedstock hydrocarbon oil ratio (C/O) of 5.

20 [0103]

The resulting product was separated into a product oil and a product gas by a fractionator having been cooled to -20°C, and they were collected. Thereafter, each component was separated and quantitatively determined.

[0104]

A conversion and a yield of each component were determined in accordance with the same definition as in Example 1.

[0105]

5 Reaction (No. 2)

In the above test, reaction (No.2) was carried out under the conditions of a catalyst circulation quantity of 70 g/min and a catalyst/feedstock hydrocarbon oil ratio (C/O) of 7.

[0106]

10 The resulting product was separated and quantitatively determined in the same manner as in the reaction (No. 1).

[0107]

Reaction (No. 3)

15 In the above test, reaction (No.3) was carried out under the conditions of a catalyst circulation quantity of 80 g/min and a catalyst/feedstock hydrocarbon oil ratio (C/O) of 8.

[0108]

The resulting product was separated and quantitatively determined in the same manner as in the reaction (No. 1).

20 [0109]

The results of the reactions No.1 to No. 3 were graphically plotted as a relation between the conversion and the yield of each component, and from the graph, a yield of each component corresponding to a conversion ratio of 68% by weight was determined. The results

are shown in the table.

[Comparative Example 1]

Testing unit for fixed bed catalytic cracking catalyst

A testing unit for a fixed bed catalytic cracking catalyst
 5 (ASTM-MAT manufactured by JGC CATALYSTS AND CHEMICALS LTD.) shown
 in Fig. 3 was used. In the ASTM-MAT, the inner diameter of the reactor
 (34) was 1.56 cm, the height thereof was 25.7 cm, and the sectional
 area of the stock oil feed nozzle (32) was 0.6 mm².

[0110]

10 Fluid catalytic cracking catalyst

A catalyst having been pseudo-equilibrated in the same manner
 as in Example 1 was used.

[0111]

Reaction test

15 The lower part of the reactor of the testing unit for a fixed
 bed catalytic cracking catalyst (ASTM-MAT manufactured by JGC
 CATALYSTS AND CHEMICALS LTD.) was filled with glass wool, then on
 the glass wool, 4 g of a catalyst having been pseudo-equilibrated
 in the same manner as in Example 1 was loaded, and on the catalyst,
 20 glass wool was placed to set the reactor.

[0112]

Reaction (No. 1)

The internal temperature of the reactor was set at 550°C, and
 as a feedstock hydrocarbon oil, the mixture of desulfurized atmospheric

residual oil (DSAR) and desulfurized vacuum distillation gas oil (DSVGO) in a ratio of 1:1 was injected at an oil injection rate of 0.0177 g/sec for 75 seconds. At this time, the catalyst/feedstock hydrocarbon oil ratio (C/O) was 3, the space velocity (WHSV) was 16
5 hr^{-1} , and the reaction time was 75 seconds.

[0113]

Along with the initiation of the reaction, the product was collected through the product collection line, and after completion of feedstock injection, the product remaining on the catalyst was
10 collected while supplying N_2 gas to the feedstock injection nozzle (32) under the conditions of 30 ml/min. Thereafter, the product gas and the product oil were separated by a condenser having been cooled to -10°C , , and then the components contained in the product gas and the product oil were separated and quantitatively determined.

15 [0114]

After completion of the reaction, the catalyst was taken out of the catalyst fluidization cell (1), and coke remaining on the catalyst was quantitatively determined by a carbon analyzer (EMIA-321V manufactured by HORIBA, Ltd.).

20 [0115]

A conversion and a yield of each component were determined in accordance with the same definition as in Example 1.

[0116]

Reaction (No. 2)

Reaction (No. 2) was carried out in the same manner as in the reaction (No. 1), except that the feed time was changed to 64.4 seconds, the catalyst/feedstock hydrocarbon oil ratio (C/O) was changed to 3.5, and the reaction time was changed to 64.4 seconds, though the oil injection rate of the feedstock hydrocarbon oil remained at 0.0177 g/sec. Then, a conversion and a yield of each component were determined.

[0117]

Reaction (No. 3)

Reaction (No. 3) was carried out in the same manner as in the reaction (No. 1), except that the feed time was changed to 56.4 seconds, the catalyst/feedstock hydrocarbon oil ratio (C/O) was changed to 4, and the reaction time was changed to 56.4 seconds, though the oil injection rate of the feedstock hydrocarbon oil remained at 0.0177 g/sec. Then, a conversion and a yield of each component were determined.

[0118]

The results of the reactions No.1 to No. 3 were graphically plotted as a relation between the conversion and the yield of each component, and from the graph, a yield of each component corresponding to a conversion of 68% by weight was determined. The results are shown in the table. Further, differences from yields of the components in the results of the aforesaid Reference Example 1 are shown in the table.

[0119]

[Comparative Example 2]

Testing unit for fluid catalytic cracking catalyst

A testing unit for a fluid catalytic cracking catalyst (ACE-MAT,
5 model R+, manufactured by Kayser) shown in Fig. 2 was used.

[0120]

The inner diameter of the lower part of the reactor (21) was
1.58 cm, the inner diameter of the upper part thereof was 2.29 cm,
the total height thereof was 38.4 cm, the sectional area of the feedstock
10 and dispersing gas injection nozzle (22) was 0.2 mm^2 , and the sectional
area of the dispersing gas feed part thereof was 1.8 mm^2 .

[0121]

Fluid catalytic cracking catalyst

A catalyst having been pseudo-equilibrated in the same manner
15 as in Example 1 was used.

[0122]

Reaction test

The reactor of the testing unit for a fluid catalytic cracking
catalyst (ACE-MAT, model R+, manufactured by Kayser) was filled with
20 9 g of a catalyst having been pseudo-equilibrated in the same manner
as in Example 1, and reaction was carried out under the following
conditions.

[0123]

Reaction (No. 1)

The internal temperature of the reactor was set at 550°C, and as a feedstock hydrocarbon oil, the mixture of desulfurized atmospheric residual oil (DSAR) and desulfurized vacuum distillation gas oil (DSVGO) in a ratio of 1:1 was injected at an oil injection rate of 5 0.02 g/sec for 120 seconds. At this time, the catalyst/raw material hydrocarbon oil ratio (C/O) was 3.75, the space velocity (WHSV) was 8 hr⁻¹, and the reaction time was 120 seconds.

[0124]

Along with the initiation of the reaction, the product was 10 collected through the product collection line (24), and after completion of injecting of the feedstock hydrocarbon oil, N₂ gas was fed, and the product on the catalyst was collected. The product collected was separated into a product gas and a product oil by a condenser having been cooled to -15°C, and they were quantitatively 15 determined. Then, the components contained in the product gas and the product oil were separated and quantitatively determined. Thereafter, the temperature of the reactor was raised to 700°C in air flow, and while subjecting coke remaining on the catalyst to combustion, the coke was quantitatively determined by a carbon analyzer 20 (1440D manufactured by Servomex).

[0125]

A conversion and a yield of each component were determined in accordance with the same definition as in Example 1.

[0126]

Reaction (No. 2)

Reaction (No. 2) was carried out in the same manner as in the reaction (No. 1), except that the feed time was changed to 90 seconds, the catalyst/feedstock hydrocarbon oil ratio (C/O) was changed to 5, and the reaction time was changed to 90 seconds, though the oil injection rate of the feedstock hydrocarbon oil was remained at 0.02 g/sec. Then, a conversion and a yield of each component were determined.

[0127]

10 Reaction (No. 3)

Reaction (No. 3) was carried out in the same manner as in the reaction (No. 1), except that the feed time was changed to 75 seconds, the catalyst/feedstock hydrocarbon oil ratio (C/O) was changed to 6, and the reaction time was changed to 75 seconds, though the oil passing rate of the feedstock hydrocarbon oil remained at 0.02 g/sec. Then, a conversion and a yield of each component were determined.

[0128]

The results of the reactions No.1 to No. 3 were graphically plotted as a relation between the conversion and the yield of each component, and from the graph, a yield of each component corresponding to a conversion of 68% by weight was determined. The results are shown in the table. Further, differences from yields of the components in the results of the aforesaid Reference Example 1 are shown in the table.

[0129]

[Table 1]

		Ex. 1	Ref. Ex. 1	Comp. Ex. 1	Comp. Ex. 2
Reaction temperature		550°C	520°C	550°C	550°C
H ₂	%	0.33 (-0.24)	0.57	0.75 (+0.18)	0.49 (-0.08)
C ₁	%	0.6 (-0.1)	0.7	1.2 (+0.5)	1.0 (+0.3)
C ₂ +C ₂ =	%	1.2 (+0.1)	1.1	1.8 (+0.7)	1.3 (+0.2)
LPG	%	13.2 (+1.2)	12	16.8 (+4.8)	16.7 (+4.7)
C ₃	%	0.5 (-0.1)	0.6	1.1 (+0.5)	1.0 (+0.4)
C ₃ =	%	4.3 (+0.1)	4.2	5.6 (+1.4)	5.2 (+1.0)
n-C ₄	%	0.4 (±0)	0.4	0.7 (+0.3)	0.7 (+0.3)
i-C ₄	%	1.9 (+0.3)	1.6	2.3 (+0.7)	2.6 (+1.0)
C ₄ =	%	6.1 (+0.9)	5.2	7.1 (+1.9)	7.2 (+2.0)
Gasoline	%	46.7 (-1.0)	47.7	40.5 (-7.2)	42.0 (-5.7)
LCO	%	18.3 (-1.9)	20.2	17.5 (-2.7)	17.7 (-2.5)
HCO	%	13.7 (+1.9)	11.8	14.5 (+2.7)	14.3 (+2.5)
Coke	%	6.0 (+0.1)	5.9	6.9 (+1.0)	6.5 (+0.6)
LPG olefinicity	-	0.79 (+0.01)	0.78	0.76 (-0.02)	0.74 (-0.05)
Olefins in Gasoline	%	36.4 (+1.7)	34.7	-	-

Numerical values in parentheses indicate differences from Reference Example 1.

5 [0130]

From the results of the above examples, it can be seen that the testing unit of Example 1 produced test results having small differences from the test results of Reference Example using the pilot testing unit, and showed results almost similar to the results obtained by the pilot testing unit. On the other hand, in Comparative Example 2 using the testing unit of the patent literature 7, test results of LPG and gasoline production ratios had large differences from those of Reference Example 1.

15 Industrial Applicability

[0131]

By adopting the testing unit of the present invention, evaluation of a fluid catalytic cracking catalyst in a commercial catalytic cracking unit and evaluation of a catalyst withdrawn from a commercial catalytic cracking unit can be carried out by a small-scale testing unit. On this account, this testing unit is a testing unit capable of greatly contribute to research and development of catalytic cracking catalysts.

10 Reference Signs List

[0132]

- 1: catalyst fluidization cell
- 2: feedstock injection nozzle
- 2': feedstock injection pump
- 15 3: catalyst-fluidizing gas feed nozzle
- 3': catalyst-fluidizing gas feed source
- 4: support
- 5: product collection line
- 6: reaction vessel
- 20 7: heating furnace
- 8: thermocouple (temperature detector)
- 21: reactor (catalyst fluidized bed)
- 22: feedstock and dispersing gas injection nozzle 23:
- catalyst-fluidizing gas feed nozzle

- 23': catalyst-fluidizing gas feed line
- 24: product collection line
- 25: heating furnace
- 26: thermocouple (temperature detector)
- 5 31: catalyst bed (fixed bed)
- 32: feedstock injection nozzle
- 32': feedstock injection pump
- 33: purge gas line
- 34: reactor
- 10 35: heating furnace
- 36: thermocouple (temperature detector)
- 41: reaction tower bottom
- 42: reaction tower top
- 43: feedstock injection line
- 15 44: separator
- 45: stripper
- 46: lift line
- 47: regenerator
- 48: catalyst transport line
- 20 49: catalyst trap
- 50: product oil receiver
- 51: fractionator
- 52: product gas

CLAIMS

[Claim 1]

A testing unit for a fluid catalytic cracking catalyst, comprising a reaction vessel in which a catalyst fluidization cell, a feedstock injection nozzle and a catalyst-fluidizing gas feed nozzle are provided inside the vessel, said feedstock and said catalyst-fluidizing gas being fed from the upper part of vessel, and a product collection line is provided at the lower part of the vessel.

[Claim 2]

The testing unit for a fluid catalytic cracking catalyst as claimed in claim 1, wherein the catalyst fluidization cell is cylindrical, has an inner diameter (D_I) ranging from 1 to 4 cm, a height (T) ranging from 2 to 14 cm and a ratio of the height (T) to the inner diameter (D_I), $(T)/(D_I)$, ranging from 1.1 to 7.0, and has a cell bottom having a downward concave conical structure or semispherical structure.

[Claim 3]

The testing unit for a fluid catalytic cracking catalyst as claimed in claim 1 or 2, wherein the catalyst fluidization cell has an internal volume in the range of 5 to 40 ml.

[Claim 4]

The testing unit for a fluid catalytic cracking catalyst as claimed in any one of claims 1 to 3, wherein catalyst load in the catalyst fluidization cell during testing is in the range of 1 to
5 20 g.

[Claim 5]

The testing unit for a fluid catalytic cracking catalyst as claimed in any one of claims 1 to 4, wherein the catalyst has an average
10 particle diameter in the range of 40 to 100 μm , and a bulk specific gravity in the range of 0.5 to 1.1 g/ml.