

Catalyst for Catalytic Cracking Fluidized-bed

Technical Field

The present invention relates to a catalyst for catalytic cracking
5 fluidized-bed, especially a catalyst for fluidized-bed to produce
ethylene-propylene by catalytically cracking naphtha.

Background Art

Currently, the primary process for producing
10 ethylene-propylene is the steam pyrolysis, and the commonly
used materials are naphtha. However, there are several
shortcomings for steam pyrolysis of naphtha, *e.g.* high reaction
temperature, rigorous technological conditions, high
requirements on the devices, particularly on the furnace tube
15 materials, and high-loss. Various meaningful studies thus are
carried out. Catalytic cracking is the most attracting and
promising one, and the object thereof is to find a suitable
cracking catalyst to increase the selectivity of
ethylene-propylene, decrease the reaction temperature and
20 have some certain flexibility of the ethylene-propylene yield.

From the current documents, most catalytic cracking
researchers generally use the molecular sieves having a high
silica alumina ratio as the catalytic materials and use high
valent metallic ions for exchanging and impregnating. However,
25 the molecular sieves have a worse hydrothermal stability and
are difficult to regenerate.

USP6211104 and CN1504540A disclosed a catalyst
comprising 10~70 wt % of clay, 5~85 wt % of inorganic oxides
and 1-50 wt % of molecular sieves. Various materials for the
30 conventional steam pyrolysis therein exhibited excellent
activity stability and high yields of light olefin, especially

ethylene, wherein said molecular sieves were produced by impregnating 0~25 wt % of Y type zeolite having a high silica alumina ratio or ZSM molecular sieves having MFI structure with phosphorus/alumina, magnesium or calcium, and were
5 substantially the pure molecular sift catalysts.

In addition, oxides are also used as catalysts.

US4620051 and US4705769 of PHILLIPS PETROLEUM CO (US) disclosed using the oxide catalyst having manganese oxide and iron oxide as active ingredients and added with rare
10 earth element La and alkaline earth metal Mg to crack C₃ and C₄ materials. Under the circumstance that Mn,Mg/Al₂O₃ catalyst was placed in the fixed-bed reactor in the laboratory, water and butane are in a molar ratio of 1:1 at a temperature of 700°C; the butane conversion rate may achieve 80%; and ethylene and
15 propylene had the selectivity of 34% and 20% respectively. Said patents also alleged that naphtha and fluidized-bed reactors could be used therein.

CN1317546A of ENICHEM SPA (IT) disclosed a steam cracking catalyst having the chemical formula of 12CaO·7Al₂O₃.
20 Naphtha may be used as the raw materials. The reaction was carried out at a temperature of 720-800°C and under 1.1-1.8 atmospheric pressure, and the contact time was 0.07-0.2 s. The yield of ethylene and propylene may achieve 43%.

USSR Pat1298240.1987 disclosed feeding Zr₂O₃ and
25 potassium vanadate loaded on pumice or ceramic into a medium-size apparatus having a temperature of 660-780°C and a space velocity of 2-5 hour⁻¹, wherein the weight ratio of water/straight-run gasoline may be 1:1. The normal alkane C₇₋₁₇, cyclohexane and straight-run gasoline were used as the raw
30 materials, wherein the ethylene yield could achieve 46%, and propylene 8.8%.

CN1480255A introduced an oxide catalyst for producing ethylene-propylene by catalytically cracking naphtha as the raw materials at a temperature of 780 °C , wherein the ethylene-propylene yield may achieve 47%.

5 In conclusion, molecular sieves as the primary cracking catalysts are attached great importance. However, the examples regarding mixing with oxides are rarely reported.

Contents of the Invention

10 The technical problems to be solved by the present invention are high reaction temperature, low cryogenic activity of catalysts and worse selectivity during the preparation of ethylene-propylene by catalytic cracking in the prior art, and to provide a novel catalyst for catalytic cracking fluidized-bed.
15 Said catalyst is used to produce ethylene-propylene by catalytically cracking naphtha, which not only decreases the catalytic cracking temperature, but also enhances the selectivity of the catalyst.

In order to solve the problems above, the present invention
20 carries out the technical solution of a catalyst for catalytic cracking fluidized-bed, comprising at least one support selected from the group consisting of SiO₂, Al₂O₃, molecular sieves and composite molecular sieves, and a composition having the chemical formula (on the basis of atom ratio):

25 $A_aB_bP_cO_x$,

wherein A therein is at least one selected from the group consisting of rare earth elements; B is at least one element selected from the group consisting of VIII, IB, IIB, VIIB, VIB, IA and IIA; a ranges from 0.01-0.5; b ranges from 0.01-0.5; c
30 ranges from 0.01-0.5; and X is the total number of oxygen atoms satisfying the requirements on the valence of each of the

elements in the catalyst. Said molecular sieves are optionally at least one selected from the group consisting of ZSM-5, Y zeolite, β zeolite, MCM-22, SAPO-34 and mordenite; said composite molecular sieves are the composite co-grown by at least two molecular sieves selected from the group consisting of ZSM-5, Y zeolite, β zeolite, MCM-22, SAPO-34 and mordenite. The molecular sieves in the catalyst are in an amount of 0-60% by weight of the catalyst.

In the technical solution above, a preferably ranges from 0.01-0.3; b preferably ranges from 0.01-0.3; c preferably ranges from 0.01-0.3. The preferred rare earth element is at least one selected from the group consisting of La and Ce; the preferred VIII group element is at least one selected from the group consisting of Fe, Co and Ni; the preferred IB is at least one selected from the group consisting of Cu and Ag; the preferred IIB is Zn; the preferred VIIB is Mn; the preferred VIB is selected from the group consisting of Cr, Mo and mixtures thereof; the preferred IA is at least one selected from the group consisting of Li, Na and K; and the preferred IIA is at least one selected from the group consisting of Ma, Ca, Ba and Sr. The preferred molecular sift is at least one selected from the group consisting of ZSM-5, Y zeolite, mordenit and β zeolite; and the composite molecular sift is at least one selected from the group consisting of ZSM-5/mordenit, ZSM-5/Y zeolite and ZSM-5/ β zeolite. The silica alumina molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of molecular sieves and composite molecular sieves preferably ranges from 10-500, more preferably 20-300. In the catalyst, the molecular sieves are in an amount of 10-60% by weight, preferably 20-50% by weight of the catalyst.

The catalyst for catalytic cracking fluidized-bed of the present invention is used to catalytically crack heavy oil, light

diesel oil, light gasoline, catalytically cracked gasoline, gas oil, condensate oil, C4 olefin or C5 olefin.

During the preparation of the catalyst for catalytic cracking fluidized-bed of the present invention, the elements A in the raw materials are the corresponding nitrates, oxalates or oxides; the elements B are the corresponding nitrates, oxalates, acetates or soluble halides; and the phosphorus element used therein is derived from phosphoric acid, triammonium phosphate, diammonium phosphate and ammonium dihydrogen phosphate.

In the preparation of the catalyst, active elements may be impregnated onto the molecular sieves, or homogeneously mixed with molecular sieves for moulding. The preparation of the moulding form of the catalyst comprises heating and reflowing the slurry added with various ingredient elements and supports in a water bath having a temperature of 70-80°C for 5 hours and spray-drying. The resulted powder is then calcined in the muffle furnace at a temperature of 600-750°C for 3-10 hours.

Since at least one selected from the group of SiO_2 , Al_2O_3 , molecular sieves or composite molecular sieves having acidity, shape selectivity and high specific surface area is used as the cracking auxiliary agent, it is advantageous to cracking olefin materials according to the carbonium ion mechanism, producing low carbon olefins, and obtaining the synergistic effects when being compounded with active ingredients having oxidation reduction. At a relatively low temperature (580-650°C), it achieves better catalytically cracking effects, obtains relatively high ethylene-propylene yield and better technical effects.

In order to evaluate the activity of the catalyst of the present invention, naphtha is used as the raw material (see Table 1 for specific indexes). The reaction is carried out at a

temperature of 580-650 °C , a catalyst loading of 0.5-2 g naphtha/g catalyst · h, and a water/naphtha weight ratio of 0.5-3:1. The fluidized-bed reactor has an inner diameter of 39 mm and a reaction pressure of 0-0.2 MPa.

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Table 1 Indexes of naphtha raw material

Items	Data
Density (20°C) kg/m ³	704.6
Distillation range, initial distillation range, °C	40
Final distillation range, °C	60
Saturated steam pressure (20°C) kpa	50.2
Alkane% (by weight)	65.2
Normal Alkane%	32.5
Cyclane%	28.4
Olefin% (by weight)	0.17
Arene% (by weight)	6.2

The present invention is further elucidated via the following examples.

10

Mode of carrying out the invention

[Example 1]

2 g of ammonium nitrate was dissolved into 100 ml of
 15 water, and 20 g of ZSM-5 molecular sieves row powder (having a silica alumina molar ratio SiO₂/Al₂O₃ of 400) was added therein. After the exchange for 2 hours at 90°C, the filtration was carried out to obtain the filter cake.

16.2 g of ferric nitrate, 7.86 g of cobalt nitrate, 12.23 g of
 20 chromic nitrate and 2.4 g of lanthanum nitrate were dissolved into 250 ml of water to obtain the solution A. 4.65 g of

diammonium phosphate was dissolved into 100 ml of water and then added into the solution A, to obtain the slurry B after homogeneous stirring.

The slurry B was heated in a water bath having a temperature of 70-80°C, and 15 g of molecular sieves after exchange and 5 g of silicon dioxide were added therein. After refluxing for 5 hours, the slurry was dried and moulded by a spray-drying apparatus.

The dried powder was heated in the muffle furnace at a temperature of 740°C and ignited for 5 hours, to obtain a catalyst after cooling. The catalyst was then passed through the sift having 100 meshes.

The chemical formula of the catalyst, $\text{Fe}_{0.11}\text{Co}_{0.08}\text{Cr}_{0.08}\text{La}_{0.04}\text{P}_{0.05}\text{O}_x$ + Support 31.57 wt.%, was obtained.

The catalyst activity was evaluated under the following conditions: a fluidized-bed reactor having 39 mm inner diameter, a reaction temperature of 650°C and a pressure of 0.15 MPa. The water/naphtha weight ratio was 3:1; the catalyst loading amount was 20 g; and the loading was 1 g of naphtha/g catalyst·hour. The gaseous product was collected to carry out the gas phase chromatographic analysis, wherein the product distribution and the ethylene+propylene yield were shown in Table 2.

Table 2 Gas phase product distribution and ethylene+propylene yield

Products	Content (vol% for H ₂ , and wt% for the balance)
H ₂ (vol%)	15.5
Methane	17.08
Ethane	1.62

Ethylene	42.23
Propane	0.41
Propylene	14.72
C ₄	7.98
the balance	15.96
Conversion rate	76.37
Ethylene yield	32.25
Propylene yield	11.24
Ethylene+propylene yield	43.49

[Example 2]

2 g of ammonium nitrate was dissolved into 100 ml of water, and 20 g of Y molecular sieves raw powder (having a silica alumina molar ratio SiO₂/Al₂O₃ of 20) was added therein. After the exchange for 2 hours at 90°C, the filtration was carried out to obtain the filter cake.

7.27 g of nickel nitrate, 8.48 g of chromic nitrate and 5.44 g of cerous nitrate were dissolved into 250 ml of water to obtain the solution A. 6.54 g of diammonium phosphate was dissolved into 100 ml of water and then added into the solution A, to obtain the slurry B after homogeneous stirring.

15 g of molecular sieves after exchange, 5 g of silicon dioxide and 2 g of alumina were added into the slurry B. The remaining was the same as Example 1 to obtain the chemical formula of the catalyst, Ni_{0.07}Cr_{0.06}Ce_{0.09}P_{0.08}O_x + Support 44.9 wt.%.

The catalyst evaluation was the same as Example 1, and the cracked product distribution and the ethylene+propylene yield were shown in Table 3.

Table 3 Gas phase product distribution and ethylene+propylene yield

Products	Content (vol% for H ₂ , and wt% for the balance)
H ₂ (vol%)	15.52
Methane	20.46
Ethane	2.40
Ethylene	44.00
Propane	0.37
Propylene	14.28
C ₄	5.60
the balance	12.89
Conversion rate	75.26
Ethylene yield	33.11
Propylene yield	10.75
Ethylene+propylene yield	43.86

[Example 3]

5.49 g of cobalt nitrate, 5.60 g of zinc nitrate, 5.44 g of cerous nitrate, 6.30 g of copper nitrate were dissolved into 250 ml of water to obtain the solution A. 6.54 g of diammonium phosphate was dissolved into 100 ml of water and then added into the solution A, to obtain the slurry B after homogeneous stirring.

10 g of hydrogen-type ZSM-5 molecular sieves having a silica alumina ratio of 120, 5 g of hydrogen-type β zeolite having a silica alumina ratio of 30 and 5 g of silicon dioxide were added into the slurry B. The remaining was the same as Example 1 to obtain the chemical formula of the catalyst, $\text{Co}_{0.06}\text{Zn}_{0.06}\text{Cu}_{0.08}\text{Ce}_{0.09}\text{P}_{0.08}\text{O}_x$ + Support 40.5 wt.%.

15 The product yield was shown in Table 4.

[Example 4]

7.62 g of ferric nitrate, 5.60 g of zinc nitrate, 5.44 g of cerous nitrate, 5.18 g of calcium nitrate were dissolved into 250 ml of water to obtain the solution A. 6.54 g of diammonium phosphate was dissolved into 100 ml of water and then added into the solution A, to obtain the slurry B after homogeneous stirring.

5 g of hydrogen-type mordenite having a silica alumina ratio of 20, 5 g of hydrogen-type MCM-22 having a silica alumina ratio of 40, 22.5 g of hydrogen-type β zeolite having a silica alumina ratio of 30 and 5 g of silicon dioxide were added to the solution. The remaining was the same as Example 1 to obtain the chemical formula of the catalyst, $\text{Fe}_{0.05}\text{Zn}_{0.06}\text{Ce}_{0.09}\text{Ca}_{0.04}\text{P}_{0.08}\text{O}_x$ + Support 39.7 wt.%.

The product yield was shown in Table 4.

[Example 5]

5.49 g of cobalt nitrate, 10.81 g of 50% manganous nitrate solution and 5.44 g of cerous nitrate were dissolved into 250 ml of water to obtain the solution A. 6.54 g of diammonium phosphate was dissolved into 100 ml of water and then added into the solution A, to obtain the slurry B after homogeneous stirring.

20 g of alumina was added to the slurry B, and the remaining was the same as Example 1 to obtain the chemical formula of the catalyst, $\text{Mn}_{0.08}\text{Co}_{0.06}\text{Ce}_{0.09}\text{P}_{0.08}\text{O}_x$ + Support 46.6 wt.%.

The product yield was shown in Table 4.

[Example 6]

5.49 g of cobalt nitrate, 10.81 g of 50% manganous nitrate

solution and 5.44 g of cerous nitrate were dissolved into 250 ml of water to obtain the solution A. 6.54 g of diammonium phosphate was dissolved into 100 ml of water and then added into the solution A, to obtain the slurry B after homogeneous stirring.

20 g of silicon dioxide was added to the slurry B, and the remaining was the same as Example 1 to obtain the chemical formula of the catalyst, $\text{Mn}_{0.08}\text{Co}_{0.06}\text{Ce}_{0.09}\text{P}_{0.08}\text{O}_x$ + Support 46.6 wt.%.

The product yield was shown in Table 4.

[Example 7]

5.49 g of cobalt nitrate, 8.48 g of chromic nitrate, 5.44 g of cerous nitrate and 1.1 g of potassium nitrate were dissolved into 250 ml of water to obtain the solution A. 6.54 g of diammonium phosphate was dissolved into 100 ml of water and then added into the solution A, to obtain the slurry B after homogeneous stirring.

15 g of silica and 5 g of alumina as the support were added to the slurry B, and the remaining was the same as Example 1 to obtain the chemical formula of the catalyst, $\text{Co}_{0.06}\text{Cr}_{0.06}\text{Ce}_{0.09}\text{K}_{0.02}\text{P}_{0.08}\text{O}_x$ + 45.1 wt.% Support (containing no molecular sieves).

The product yield was shown in Table 4.

Table 4 Product yield of different supports

Examples	Ethylene yield	Propylene yield	Ethylene+propylene yield
Example 3	36.0%	5.47%	41.47%
Example 4	25.37%	15.35%	40.72%
Example 5	30.71%	9.33%	40.04%

Example 6	26.98%	12.49%	39.47%
Example 7	27.12%	12.33%	39.45%

[Example 8]

The slurry B was prepared according to the process in Example 1. The same ZSM-5 molecular sieves and silicon dioxide were added directly without any loading process. After homogeneous stirring, the slurry B was directly moulded by spraying. The composition of the catalyst was the same as that in Example 1. Then the evaluation was carried out according to the process of Example 1, and the results were shown in Table 5.

[Example 9]

284 g of sodium metasilicate was dissolved into 300 g of distilled water to obtain the solution A. 33.3 g of aluminium sulphate and 100 g of distilled water were prepared into the solution B. The solution B was slowly poured into the solution A and strongly stirred. Then 24.4 g of ethylene diamine was added, and the pH thereof was adjusted to 11.5 with weak sulphuric acid after stirring for a period of time. The molar proportion of the sol was controlled to be Si:Al:ethylene diamine:H₂O=1:0.1:0.4:40. The mixed solutions were fed into the autoclave, thermally insulated at 180°C for 40 hours, taken out, washed with water, dried and calcined to obtain composite molecular sieves of ZSM-5 and mordenite. Said composite molecular sieves were exchanged twice at 70°C with 5% ammonium nitrate solution and then calcined. Said process was repeated twice to obtain the hydrogen-type ZSM-5/mordenite composite molecular sieves.

The slurry B was prepared according to the process in

Example 1. ZSM-5/mordenite composite molecular sieves having a silica alumina ratio of 20 and silicon dioxide in the same amount were added therein, and the same process was used to prepare a catalyst. Then the evaluation was carried out according to the process of Example 1, and the results were shown in Table 5.

[Example 10]

284 g of sodium metasilicate was dissolved into 300 g of distilled water to obtain the solution A. 33.3 g of aluminium sulphate and 100 g of distilled water were prepared into the solution B. The solution B was slowly poured into the solution A and strongly stirred. Then 24.4 g of ethylene diamine was added, and the pH thereof was adjusted to 11 with weak sulphuric acid after stirring for a period of time. 5 g of Y zeolite crystal seeds were added therein, and the molar proportion of the sol was controlled to be Si:Al:ethylene diamine:H₂O=1:0.1:0.4:40. The mixed solutions were fed into the autoclave, thermally insulated at 170°C for 36 hours, taken out, washed with water, dried and calcined to obtain composite molecular sieves of ZSM-5 and Y zeolite. Said composite molecular sieves were exchanged twice at 70°C with 5% ammonium nitrate solution and then calcined. Said process was repeated twice to obtain the hydrogen-type ZSM-5/Y zeolite composite molecular sieves.

The slurry B was prepared according to the process in Example 1. ZSM-5/Y zeolite composite molecular sieves having a silica alumina ratio of 20 and silicon dioxide in the same amount were added therein, and the same process was used to prepare a catalyst. Then the evaluation was carried out according to the process of Example 1, and the results were

shown in Table 5.

[Example 11]

284 g of sodium metasilicate was dissolved into 300 g of
5 distilled water to obtain the solution A. 33.3 g of aluminium
sulphate and 100 g of distilled water were prepared into the
solution B. The solution B was slowly poured into the solution
A and strongly stirred. Then 24.4 g of ethylene diamine and 10
g of tetraethyl ammonium hydroxide were added, and the pH
10 thereof was adjusted to 12 with weak sulphuric acid after
stirring for a period of time. 5 g of β zeolite crystal seeds were
added, and the molar proportion of the sol was controlled to be
Si:Al:ethylene diamine:H₂O=1:0.1:0.4:40. The mixed solutions
were fed into the autoclave, thermally insulated at 160°C for 40
15 hours, taken out, washed with water, dried and calcined to
obtain composite molecular sieves of mordenite and β zeolite.
Said composite molecular sieves were exchanged twice at 70°C
with 5% ammonium nitrate solution and then calcined. Said
process was repeated twice to obtain the hydrogen-type
20 mordenite/ β zeolite composite molecular sieves.

The slurry B was prepared according to the process in
Example 1. β zeolite/mordenite composite molecular sieves
having a silica alumina ratio of 20 and silicon dioxide in the
same amount were added therein, and the same process was
25 used to prepare a catalyst. Then the evaluation was carried out
according to the process of Example 1, and the results were
shown in Table 5.

[Example 12]

30 The slurry B was prepared according to the process in
Example 1. 5 g of the hydrogen type ZSM-5 having a silica

alumina ratio of 120, 10 g of ZSM-5/mordenite composite molecular sieves having a silica alumina ratio of 20, 5 g of silicon dioxide were added therein, and the same process was used to prepare a catalyst. Then the evaluation was carried out according to the process of Example 1, and the results were shown in Table 5.

[Example 13]

The slurry B was prepared according to the process in Example 1. 12 g of the hydrogen type ZSM-5 having a silica alumina ratio of 150 as a support was added therein to obtain a catalyst having the composition chemical formula of $\text{Fe}_{0.11}\text{Co}_{0.08}\text{Cr}_{0.08}\text{La}_{0.04}\text{P}_{0.05}\text{O}_x$ + Support 21.32 wt.%. Then the evaluation was carried out according to the process of Example 1, and the results were shown in Table 5.

[Example 14]

The slurry B was prepared according to the process in Example 1. 20 g of the hydrogen type ZSM-5/mordenite having a silica alumina ratio of 30 as a support was added therein to obtain a catalyst having the composition chemical formula of $\text{Fe}_{0.11}\text{Co}_{0.08}\text{Cr}_{0.08}\text{La}_{0.04}\text{P}_{0.05}\text{O}_x$ + Support 31.6 wt.%. Then the evaluation was carried out according to the process of Example 1, and the results were shown in Table 5.

Table 5

Examples	Ethylene yield	Propylene yield	Ethylene+propylene yield
Example 8	32.36%	11.17%	43.53%
Example 9	33.76%	11.45%	45.21%
Example 10	33.42%	10.83%	44.25%
Example 11	32.72%	10.87%	43.59%
Example 12	33.47%	11.21%	44.68%

Example 13	34.52%	12.07%	46.59%
Example 14	35.02%	12.53%	47.55%

[Example 15]

Under the same conditions as those in Example 1, the evaluation was carried out by using the catalyst prepared according to Example 1 and the light diesel oil having a boiling point of lower than 350°C as the reaction materials, and the results were shown in Table 6.

[Example 16]

Under the same conditions of 550°C, a water/oil ratio of 3:1 and a space velocity of 1 as those in Example 1, the evaluation was carried out by using the catalyst prepared according to Example 1 and the mixed C4 (alkane:olefin=1:1) as the reaction materials, and the results were shown in Table 6.

Table 6

Examples	Ethylene yield	Propylene yield	Ethylene+propylene yield
Example 15	28.47%	9.25%	37.72%
Example 16	12.21%	38.63%	50.84%

[Example 17]

According to the process in Example 1, a catalyst was prepared by using the hydrogen type ZSM-5/mordenite as the support prepared in Example 9, and introduced into the fixed-bed reactor having an inner diameter of 12 mm. The reaction was carried out under the conditions of a reaction temperature of 650°C, a mass space velocity of 2 hour⁻¹ and a water/raw oil mass ratio of 1.5, and the results were shown in Table 7.

[Example 18]

According to the process in Example 1, a catalyst was prepared by using the hydrogen type ZSM-5/Y zeolite as the support prepared in Example 10. The evaluation was carried out according to Example 17, and the results were shown in Table 7.

5 **[Example 19]**

According to the process in Example 1, a catalyst was prepared by using the hydrogen type β zeolite/mordenite as the support prepared in Example 11. The evaluation was carried out according to Example 17, and the results were shown in Table 7.

10 **[Example 20]**

284 g of sodium metasilicate was dissolved into 300 g of distilled water to obtain the solution A. 16.7 g of aluminium sulphate and 100 g of distilled water were prepared into the solution B. The solution B was slowly poured into the solution
15 A and strongly stirred. Then 12.2 g of ethylene diamine and 29.4 g of tetraethyl ammonium hydroxide (the mixed template agent was labeled as M) were added, and the pH thereof was adjusted to 11 with weak sulphuric acid after stirring for a period of time. The molar proportion of the sol was controlled
20 to be Si:Al:M:H₂O=1:0.05:0.4:40, and 2.8 g of β zeolite crystal seeds were added. The mixed solutions were fed into the autoclave, thermally insulated at 160°C for 40 hours, taken out, washed with water, dried and calcined to obtain intergrowth molecular sieves of ZSM-5/ β zeolite. Said composite molecular
25 sieves were exchanged twice at 70°C with 5% ammonium nitrate solution and then calcined. Said process was repeated twice to obtain the hydrogen-type ZSM-5/ β zeolite intergrowth molecular sieves.

According to the process in Example 1, a catalyst was
30 prepared by using as the support the hydrogen type ZSM-5/ β zeolite prepared above. The evaluation was carried out

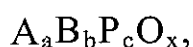
according to Example 17, and the results were shown in Table 7.

Table 7

Examples	Ethylene yield (wt.%)	Propylene yield (wt.%)	Ethylene+propylene yield (wt.%)
Example 17	32.01	30.94	62.95
Example 18	28.1	33.35	61.45
Example 19	29.06	32.12	61.18
Example 20	31.15	31.08	62.23

Claims

1. A catalyst for catalytic cracking fluidized-bed, comprising at least one support selected from the group consisting of SiO₂, Al₂O₃ and composite molecular sieves, and a composition having the following chemical formula, which is on the basis of atom ratio:



wherein A therein is at least one selected from the group consisting of rare earth elements;

B is at least one element selected from the group consisting of VIII, IB, IIB, VIIB, VIB, IA and IIA;

a ranges from 0.01-0.5;

b ranges from 0.01-0.5;

c ranges from 0.01-0.5; and

X is the total number of oxygen atoms satisfying the requirements on the valence of each of the elements in the catalyst;

said composite molecular sieves are the composite co-grown by at least two molecular sieves selected from the group consisting of ZSM-5, Y zeolite, β zeolite, MCM-22, SAPO-34 and mordenite, wherein the molecular sieves in the catalyst are in an amount of 0-60% by weight of the catalyst.

2. The catalyst for catalytic cracking fluidized-bed according to claim 1, characterized in that a ranges from 0.01-0.3; b ranges from 0.01-0.3; and c ranges from 0.01-0.3.

3. The catalyst for catalytic cracking fluidized-bed according to claim 1, characterized in that the rare earth element is at least one selected from the group consisting of La and Ce.

4. The catalyst for catalytic cracking fluidized-bed

according to claim 1, characterized in that the VIII group element is at least one selected from the group consisting of Fe, Co and Ni; the IB element is at least one selected from the group consisting of Cu and Ag; the IIB element is Zn; the VIIB element is Mn; the VIB element is at least one selected from the group consisting of Cr and Mo; the IA element is at least one selected from the group consisting of Li, Na and K; and the IIA element is at least one selected from the group consisting of Mg, Ca, Ba and Sr.

10 5. The catalyst for catalytic cracking fluidized-bed according to claim 1, characterized in that the composite molecular sieve is at least one selected from the group consisting of ZSM-5/mordenite, ZSM-5/Y zeolite and ZSM-5/ β zeolite.

15 6. The catalyst for catalytic cracking fluidized-bed according to claim 1, characterized in that the silica alumina molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the composite molecular sieves ranges from 10 to 500.

20 7. The catalyst for catalytic cracking fluidized-bed according to claim 6, characterized in that the silica alumina molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the composite molecular sieves ranges from 20 to 300.

8. The catalyst for catalytic cracking fluidized-bed according to claim 1, characterized in that the molecular sieves are in an amount of 10-60% by weight of the catalyst.

25 9. The catalyst for catalytic cracking fluidized-bed according to claim 1, characterized in that the molecular sieves are in an amount of 20-50% by weight of the catalyst.

30 10. Use of the catalyst for catalytic cracking fluidized-bed according to claim 1 for catalytically cracking heavy oil, light diesel oil, light gasoline, catalytically cracked gasoline, gas oil, condensate oil, C4 olefin or C5 olefin.