

Binderless Molecular Sieve Catalyst and a Preparation Method Thereof

Technical field

- 5 The present invention relates to a binderless molecular sieve catalyst and a process for preparing the same.

Background art

- 10 Due to the uniform and regular porous structure, greater specific surface area and higher thermal stability, better shape-selective catalytic performance and adsorption performance, zeolite molecular sieves are widely applied in the fields such as petrochemical industry and the like. When molecular sieves are used for industrial catalysis, 100% molecular sieves generally cannot be made into the catalyst for the industrial process.
- 15 Because of worse binding property and too small particle size, molecular sieves still have a strength of lower than 20 Newtons even if press-molded, so that they cannot be molded to form the catalyst directly applied in the industrial process. In addition, the manufacturing cost of molecular sieves is generally higher. If 100% molecular sieves are used as the industrial
- 20 catalyst, the operation cost of the industrial process increases. The industrial process generally requests that the catalyst has a certain shape and strength so as to be adapted to the industrial reactor. As for a fixed-bed reactor, the catalyst does not need to be moved after installation, but the catalyst shall have a certain anti-crush strength to avoid breakage
- 25 due to impact during the loading process and to prevent the catalyst loaded in the lower part from breakage under pressure. The breakage and pulverization of the catalyst may result in an increase of the pressure drop in the device, abnormal reaction behavior, or product composition change, which are disadvantageous to the target reaction process. As for a
- 30 fixed-bed reactor, because of circular flow and turbulent motion of the catalyst *per se* in the reactor, friction and collision between the catalyst particles, between the catalyst and the reactor wall, between the catalyst and the regenerator wall, between the catalyst and the heater wall, between the catalyst and the flow pipe wall all will grind and damage the catalyst
- 35 so as to escape from the reaction system in a fine powder form. Such fine powder will pollute the environment, and increase the use-cost of the

catalyst. Thus, no matter whether the molecular sieves are applied in a fixed-bed reactor or a fluidized-bed reactor, a binder is necessary for a catalyst composition formed by molecular sieves and carrier materials. Such molecular sieve composition has the catalytic activity, selectivity, stability, shape and strength, and meets the requirements on the catalyst during the industrial process.

Since a binder shall be added for forming the molecular sieves, and the binder wraps the molecular sieves in the molded catalyst, the effective availability of molecular sieves decreases, so as to result in a lower specific surface area and a lower activity of the catalyst. Random porous structure of the binder causes the difficulty of the dispersion of the reaction materials and product in the catalyst, and carbon deposit easily occurs, so as to have effect on the service life of the catalyst. The conversion of the binder in the catalyst into the effective component molecular sieve can overcome said problems and improve the activity and diffusivity of the catalyst.

The binderless molecular sieve catalyst involves converting the binder added during the molding of the zeolite molecular sieve catalyst into the effective component of the molecular sieve, making the whole catalyst containing no binder component and maintaining a better strength of the catalyst. In the binderless molecular sieve catalyst, the binder is completely converted to the molecular sieve component, which increases the molecular sieve content in a unit volume of the catalyst, so as to improve the activity and handling capacity of the catalyst. Meanwhile, since the catalyst contains no binder, it solves the problems that the effective availability of the molecular sieve is reduced because the binder wraps the molecular sieves, and that the binder blocks up the pore channel of the molecular sieves, so as to greatly increase the effective availability and carbon deposit resistance thereof.

Generally, a binderless molecular sieve catalyst means that the binder content in the catalyst is less than 10%.

US6509290 discloses a process for preparing a molecular sieve catalyst,

which contains molecular sieve-containing attrition particles and virgin molecular sieve, the attrition particles having been recycled from a catalyst manufacture process or from a reaction system. Such process comprises mixing together molecular sieves, virgin binder and filler, spray-dried attrition particles or agglomerates, and non-virgin attrition particles from a reaction system, drying the mixture to form an end product catalyst particles. In order to increase the strength of the catalyst particles, the attrition particles substantially contain no coke.

10 US6153552 studies a process for preparing a molecular sieve catalyst, comprising mixing together molecular sieves and an alumina sol which is prepared in a solution and maintains a pH value of 2-10, spray-drying and calcining such mixture at high temperature, to form a catalyst resistant to attrition.

15 CN1791463 discloses a process for preparing a molecular sieve catalyst, comprising mixing together molecular sieve, liquid, and an effective hardening amount of a dried molecular sieve catalyst to form a slurry, drying the slurry and then calcining to form a catalyst resistant to attrition.

20 Although some patents have involved the process for preparing a fluidized-bed catalyst, the abrasion resistance thereof is lower and needs to be further improved.

25 Generally, molecular sieves are prepared by the hydrothermal synthesis, showing a powder form, having no strength, and being easy to lose. Even if they are molded by compression, the strength thereof is also less than 20 Newton, so that they cannot be applied directly. The molecular sieves shall be extruded or spray-molded by adding a binder during the industrial or laboratory application. During the molding process of the conventional molecular sieve catalyst, the weight of the binder to be added is not less than 40% of the total weight of the catalyst. Although the molded catalyst has a certain strength, it has a reduced effective availability and worse activity and diffusivity.

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Contents of the invention

The first problem to be solved by the present invention is to provide a novel binderless molecular sieve catalyst, which has the advantages of higher activity, greater pore volume, larger average pore diameter and porosity, and better diffusivity.

The second problem to be solved by the present invention is to provide a novel preparation process for the binderless molecular sieve fixed-bed catalyst as mentioned in the above first technical problem to be solved. Such process has the advantages of simple preparation, lower cost and environmental protection.

The third problem to be solved by the present invention is to provide a novel preparation process for the binderless molecular sieve fluidized-bed catalyst as mentioned in the above first technical problem to be solved. Such process has the advantages of simple preparation, lower cost and environmental protection.

In a first aspect of the present invention, in order to solve the first problem above, the present invention comprises a binderless molecular sieve catalyst, comprising, based on the weight of the catalyst, 90-100 wt.% of a molecular sieve, 0-10 wt.% of a binder, and 0-10 wt.% of an anti-wear agent, wherein said catalyst has a pore volume of 0.10-0.52 ml/g, an average pore diameter of 50-100 nm, and a porosity of 20-40%; the anti-wear agent is selected from the rod or needle-like inorganic materials having a length/diameter ratio of 2-20.

In one preferred embodiment, the content of the binder in the binderless-type catalyst may be less than 5 wt.%, preferably less than 2 wt.%, more preferably less than 1 wt.%, based on the weight of the catalyst.

In one preferred embodiment, the catalyst has a pore volume of 0.15-0.3 ml/g, an average pore diameter of 50-70 nm, a porosity of 20-30%. In another preferred embodiment, the catalyst has a pore volume of 0.31-0.5 ml/g, an average pore diameter of 71-100 nm, a porosity of 31-40%.

In one preferred embodiment, the molecular sieve in the binderless molecular sieve catalyst comprises at least one selected from the group consisting of ZSM-5, ZSM-23, ZSM-11, mordenite, Y zeolite, β zeolite, MCM-22, MCM-49, MCM-56, ZSM-5/mordenite, β zeolite/mordenite, ZSM-5/ β zeolite, ZSM-5/Y, MCM-22/mordenite, ZSM-5/Magadiite, ZSM-5/ β zeolite/mordenite, ZSM-5/ β zeolite/Y zeolite and ZSM-5/Y zeolite/mordenite.

In one preferred embodiment, the anti-wear agent is at least one inorganic material selected from the group consisting of asbestos, ceramic fiber, glass fiber, and wollastonite mineral, wherein the anti-wear agent has a length of 1-100 μm and a length/diameter ratio of 3-10 and is in an amount 2-10 wt.% based on the weight of the calcined end product of the catalyst.

In one preferred embodiment, the binder is at least one selected from the group consisting of silica sol and aluminum sol.

In a second aspect of the present invention, in order to solve the second problem above, the present invention comprises a process for preparing a binderless molecular sieve catalyst, comprising the steps of

a) based on the weight of the molded and calcined catalyst, mixing 10-80 wt.% of a molecular sieve, 0.1-20 wt.% of an induction material, 0-20 wt.% of an aluminum compound and 10-80 wt.% of silica, molding and drying to obtain a molded catalyst precursor mix I, wherein the weight percent of the aluminum compound in the mix I is less than that of silica;

b) crystallizing the mix I at 100-200°C in water vapor or template vapor for 10-300 h, to obtain a binderless molecular sieve catalyst precursor;

c) drying the catalyst precursor, and calcining at 400-700°C for 1-10 h to obtain a binderless molecular sieve catalyst; wherein the induction material is at least one selected from the group consisting of i) oxides or hydroxides of the elements of Group IA or IIA of the Periodic Table of Elements, or salts of weak acids thereof, ii) at least one selected from the group consisting of carbonates, bicarbonates, oxalates, citrates and ammonium salts of the elements of Group IA or IIA

of the Periodic Table of Elements; the aluminum compound is at least one selected from the group consisting of aluminum salts, aluminum oxides, hydrous oxides of aluminum and hydroxides of aluminum.

- 5 In one preferred embodiment, the molecular sieve is at least one selected from the group consisting of ZSM-5, ZSM-23, ZSM-11, mordenite, Y zeolite, β zeolite, MCM-22, MCM-49, MCM-56, ZSM-5/mordenite, ZSM-5/ β zeolite, ZSM-5/Y, MCM-22/mordenite, ZSM-5/Magadiite, ZSM-5/ β zeolite/mordenite, ZSM-5/ β zeolite/Y zeolite and ZSM-5/Y
10 zeolite/mordenite.

- In one preferred embodiment, the template is at least one selected from the group consisting of ammonia, ethylene diamine, triethylamine, n-butylamine, hexanediamine, tetrapropylammonium bromide or
15 tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetraethylammonium bromide and hexamethyleneimine, and is in an amount of 5-200 wt.% based on the weight of the mix I.

- In one preferred embodiment, the element of Group IA is at least one
20 selected from the group consisting of sodium and potassium.

In one preferred embodiment, the element of Group IIA is at least one selected from the group consisting of magnesium and calcium.

- 25 In one preferred embodiment, the salt of weak acids is at least one selected from the group consisting of bisulfate, sulfite, hydrosulfite, phosphate and biphosphate.

- In one preferred embodiment, the ammonium salt is at least one selected
30 from the group consisting of ammonium carbonate, ammonium bicarbonate, ammonium citrate, ammonium oxalate, ammonium sulphate, ammonium bisulphate, ammonium sulphite, ammonium bisulphite, ammonium phosphate, ammonium hydrogen phosphate and diammonium phosphate.

- 35 In one preferred embodiment, the molecular sieve in step a) is in an

amount of 20-70 wt.%, based on the weight of the molded and calcined catalyst.

5 In one preferred embodiment, the induction material in step a) is in an amount of 0.5-10 wt.%, based on the weight of the molded and calcined catalyst.

10 In one preferred embodiment, the aluminum compound in step a) is in an amount of 1-15 wt.%, based on the weight of the molded and calcined catalyst.

In one preferred embodiment, silica in step a) is in an amount of 30-70 wt.%, based on the weight of the molded and calcined catalyst.

15 In one preferred embodiment, the crystallization is carried out at 120-200°C for 20-100 h.

20 In one preferred embodiment, during the molding process of step a), at least one pore-expanding agent selected from the group consisting of methyl cellulose, polyvinyl alcohol, sesbania powder, dissolvable starch and carbon nano-tube is added in an amount of 0.1-2 wt.%, based on the weight of the molded and calcined catalyst.

25 In one preferred embodiment, the catalyst prepared according to the aforesaid aspect has a strength of 60-200 newton, preferably 100-180 newton.

30 The binderless catalyst prepared according to the aforesaid aspect is preferably useful in the reactions of preparing low carbon olefins by catalytic cracking of naphtha and by methanol dehydration.

35 Upon extrusion, the catalyst precursor mix I is present in a form of a long strip solid having a tangential plane in a cylindrical form and a diameter of 0.5-2 mm, and is dried and crushed into short cylindrical catalyst strips having a length of 5 mm per particle for convenience of crystal conversion treatment and evaluation. The mechanical strength of the catalyst in the

present invention is measured and calculated according to such shape. In addition, the catalyst precursor mix I can also be made as required into a cellular form, a clover form, a hollow tubular or a spherical form, and the strength standard is extra.

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Among the characterizing means of the binderless catalyst, XRD is used to determine the phase contained therein, and the content of each phase; the scanning electron microscope is used to observe the crystal conversion of the binder and the morphology of the produced molecular sieve. Upon
10 crystal conversion, the binder content is determined by the XRD phase quantification and the binder content in the scanning electron photomicroscope. The Si-Al ratio in the catalyst is determined by the chemical analysis method. The strength of the catalyst is determined by measuring the crushing strength of the calcined catalyst on the
15 compression testing machine. The catalyst to be measured has a particle diameter of 1.5 mm and a length of 5 mm. The catalyst is horizontally disposed on the testing machine to determine the maximum pressure suffered when the catalyst is crushed. The crushing strength of 10 particles of the catalyst is measured to take the average. The pore volume, average
20 pore diameter and porosity of the catalyst are determined by the mercury injection method.

In a third aspect of the present invention, in order to solve the third problem above, the present invention comprises a process for preparing a
25 binderless molecular sieve catalyst, comprising the steps of

(a) homogeneously mixing a molecular sieve, a binder, a dispersant having the induction action, a liquid medium, an optional pore-expanding agent, an optional substrate material, and an optional anti-wear agent to form a suspension, wherein the dispersant is selected from the group
30 consisting of i) salts of weak acids of the elements of Group IA or IIA of the Periodic Table of Elements, or ii) carbonates, bicarbonate, oxalates and citrates of ammonium;

(b) high velocity (*e.g.* 6,000-30,000 rpm) shearing and diffusing to control the particle size of the materials in the suspension within 0.1-5 μm ;

35 (c) spray-drying said suspension to form a microsphere catalyst precursor I;

(d) calcining such microsphere catalyst precursor I at 300-700°C for 1-10 h to obtain a catalyst precursor II;

(e) crystallizing the catalyst precursor II at 100-300°C in water vapor or template vapor for 10-240 h, to obtain a catalyst precursor III; and

(f) calcining such microsphere catalyst precursor III at 400-700°C for 1-10 h to obtain an end product of the catalyst.

In one preferred embodiment, the molecular sieve is at least one selected from the group consisting of ZSM-5, ZSM-23, ZSM-11, mordenite, Y zeolite, β zeolite, MCM-22, MCM-49, MCM-56, ZSM-5/mordenite, ZSM-5/ β zeolite, ZSM-5/ β zeolite, ZSM-5/Y, MCM-22/mordenite, ZSM-5/Magadiite, ZSM-5/ β zeolite/mordenite, ZSM-5/ β zeolite/Y zeolite and ZSM-5/Y zeolite/mordenite, and is in an amount of 20-80 wt.% based on the weight of the calcined end product catalyst.

In one preferred embodiment, the binder is at least one selected from silicasol and aluminum sol, and is in an amount of preferably 2-50 wt.% based on the weight of the calcined end product of the catalyst.

In one preferred embodiment, the substrate material is at least one selected from the group consisting of kaolin, calcined kaolin, diatomite, bentonite, argil and clay, and is in an amount of 0-50 wt.% based on the weight of the calcined end product of the catalyst.

In one preferred embodiment, the pore-expanding agent is at least one selected from the group consisting of methyl cellulose, polyvinyl alcohol, sesbania powder, dissolvable starch and carbon nano-tube, and is in an amount 0.1-5 wt.% based on the weight of the molecular sieve in the calcined end product of the catalyst.

In one preferred embodiment, the salt of weak acids is at least one selected from the group consisting of bisulphate, sulphite, hydrosulfite, phosphate and biphosphate.

In one preferred embodiment, the dispersant is at least one selected from the group consisting of tri-ammonium citrate, ammonium oxalate,

ammonium carbonate and ammonium bicarbonate, and is in an amount 0.01-5 wt.% based on the weight of the molecular sieve in the calcined end product of the catalyst.

- 5 In one preferred embodiment, the anti-wear agent is at least one inorganic material selected from the group consisting of asbestos, ceramic fiber, glass fiber, and wollastonite mineral, wherein the anti-wear agent has a length of 1-100 μm and a length/diameter ratio of 3-10 and is in an amount 2-10 wt.% based on the weight of the calcined end product of the catalyst.

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In one preferred embodiment, the liquid medium is distilled water.

In one preferred embodiment, the solids content of the suspension in step (a) is preferably 10-50%.

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In one preferred embodiment, the particle size of the materials is controlled to be 0.1-2 μm by using a high velocity shearing or cyclic emulsification method.

- 20 In one preferred embodiment, the spray-drying is conducted under the conditions of an inlet temperature of 180-350°C, an outlet temperature of 100-180°C, a centrifugal rotational speed of 5,000-15,000 rpm, and a cyclone pressure difference of 0.5-1.0 KPa at the outlet.

- 25 In one preferred embodiment, after the spray-dried catalyst is calcined at high temperature, the particles of the catalyst precursor II have an average particle size of 50-90 μm , a specific surface area of 100-300 m^2/g , an average pore diameter of 1-20 nm, a density of 0.6-1.2 g/ml and an abrasion index of 0.005-1.2 wt.%/h (when an anti-wear agent is added, the
30 abrasion index may reach 0.001 wt.%/h).

- In one preferred embodiment, the template is at least one selected from the group consisting of ammonia, ethylene diamine, triethylamine, n-butylamine, hexanediamine, tetrapropylammonium bromide or
35 tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetraethylammonium bromide and hexamethyleneimine, and is in an

amount of 5-200 wt.% based on the weight of the molded and calcined catalyst precursor II.

In one preferred embodiment, the crystallization is carried out at 120-200°C for 20-200 h.

Among the characterizing means of the binderless catalyst, XRD is used to determine the phase contained therein, and the content of each phase; the scanning electron microscope is used to observe the crystal conversion of the binder and the morphology of the produced molecular sieve. Upon crystal conversion, the binder content is determined by the XRD phase quantification and the binder content in the scanning electron photomicroscope. The Si-Al ratio in the catalyst is determined by the chemical analysis method. The abrasion index of the catalyst is determined by the solid granular catalyst abrasion tester, wherein nitrogen gas is used as the carrier gas. The pore volume, average pore diameter and porosity of the catalyst are determined by the mercury injection method. The specific surface areas of the catalyst precursor II and end product catalyst are determined by the nitrogen temperature programmed desorption.

In the second aspect of the present invention, the environment and material proportion adapted to the growth of molecular sieves are controlled by using as the crystal seed the molecular sieves added into the molded catalyst, so as to nucleate the binder and to make it grow under the common induction of the crystal seed and induction materials and only in an environment of water vapor. As a result, the binder is converted into the effective component of molecular sieves, so as to obtain a binderless molecular sieve catalyst and to achieve the object of simplicity and environmental protection. In the produced binderless molecular sieve catalyst, the binder may be in an amount of less than 2 wt.%, preferably less than 1 wt.%, or even there is no binder (*i.e.* the catalyst merely contains molecular sieves and an optional anti-wear agent). Since the molecular sieve content in the catalyst per unit volume is higher, the active site number in the catalyst per unit volume is greater, so that the binderless molecular sieve catalyst has a higher activity. Since the crystal grains of the binderless catalyst molecular sieves obtained by crystal conversion are

interlaced with each other, and closely integrated with each other, the catalyst strength may reach 120-200 newton per grain, preferably higher than 180 newton per grain. Since a template can be omitted during the crystal conversion, the technological process of crystal conversion is simple and environmentally friendly. Some salts of weak acids, carbonates, oxalates, citrates or ammonium salts are added during the preparation of the binderless molecular sieve catalyst, so as to have the induction action during the crystal conversion and to produce some macropores due to decomposition of the salts and thus have the function of the pore-expanding agent. Thus the produced catalyst has the advantages of higher pore volume, greater average pore diameter and porosity and better diffusivity. The fixed-bed catalyst produced according to the present invention can be used in the reaction for producing propylene by catalytic cracking of naphtha. The yield of dienes of ethylene and propylene is preferably higher than 53%, more preferably higher than 55%.

In the third aspect of the present invention, at least one selected from the group consisting of, *e.g.* tri-ammonium citrate, ammonium oxalate, ammonium carbonate and ammonium bicarbonate is added to make the components in the catalyst being homogeneously dispersed and difficult to agglomerate. By high velocity emulsification and shearing, the suspension is not easy to stratify or precipitate, and the prepared catalyst has a smooth surface and a high sphericity. When heated, these salts of weak acids are easy to decompose so as to produce gases, which is advantageous to increasing the porosity, average particle diameter and surface area of molecular sieves. When the dispersant is selected from the salts of weak acids of the elements of Group IA or IIA, such dispersant has a certain low acidity. Even if heated and decomposed, the dispersant may produce certain basic oxides. The presence of these basic oxides is advantageous to convert the binder and substrate components into the molecular sieve components. Without template or molecular sieves, these suitable ingredients may be converted into molecular sieve components in a water vapor environment.

In a preferred embodiment, the catalyst has a better diffusivity and a higher activity due to the addition of at least one pore-expanding agent

selected from the group consisting of methyl cellulose, polyvinyl alcohol, sesbania powder, dissolvable starch and carbon nano-tube during the preparation of the catalyst. Since the formulated slurry is homogeneous, and the substances can closely bind to each other, the phases of the prepared catalyst are closely integrated with each other, so that the end product catalyst obtained thereby has a higher abrasion strength. Since the formulated slurry is homogeneous, the components and substances in the catalyst can closely bind to each other by adding slender crystal anti-wear agents having a higher strength in the preferred embodiment, so that the end product catalyst obtained thereby has a higher abrasion strength and an abrasion index as high as 0.001 wt.%/h (e.g. 0.001-0.01 wt%/h), and achieves a better technical effect. The fluidized-bed catalyst produced according to the present invention can be used in the reaction for producing propylene by catalytic cracking of naphtha. The yield of dienes of ethylene and propylene may be higher than 50%.

Unless otherwise noted, the percent in the present invention refers to the weight percent.

Description of the drawings

Fig.1 shows the XRD spectrum of the binderless ZSM-5 catalyst prepared according to Example 1.

Fig.2 shows the scanning electron microscope graph of the binderless ZSM-5 catalyst prepared according to Example 1.

Fig.3 shows the scanning electron microscope graph of the binderless catalyst prepared according to Example 2.

Fig.4 shows the scanning electron microscope graph of the catalyst prepared according to Example 50.

Fig.5 shows the scanning electron microscope graph of the binderless ZSM-5 catalyst prepared according to Example 61.

Embodiments

The present invention is further illustrated by the following examples, but is not limited to the examples.

Example 1

5 60 g of ZSM-5 molecular sieve having a Si-Al ratio (molecular ratio, hereinafter inclusive) of 30 was added to 40 g of 40 wt.% of a silicasol, homogeneously mixed and stirred. 10 ml of 1 mol/l of sodium hydroxide solution was then added, homogeneously mixed and stirred, and extrusion-molded. The molded catalyst was dried at 80°C for 3 h, fed into
10 an autoclave the inner bottom of which contains water. The catalyst was not brought in contact with liquid water, then sealed in the autoclave and disposed in an oven, crystallized at 170°C for 60 h, taken out, water-washed twice, oven-dried at 120°C in an oven for 3 h, calcined in a muffle furnace at 400°C for 2 h and at 550°C for 3 h, to obtain a binderless
15 ZSM-5 catalyst. The results of the prepared catalyst are shown in Table 3, wherein the XRD spectrum thereof shown in Fig.1 which shows a pure ZSM-5 phase. The scanning electron microscope graph of the prepared catalyst is shown in Fig.2 which shows pure ZSM-5 crystal grains, almost without any amorphous binder. The amount of amorphous binder was
20 determined to be 0.2%, and the crushing-resistant strength of the catalyst sample was determined to be 150 newton per grain.

Example 2

According to the method in Example 1 of CN101428233A, a mixed crystal
25 molecular sieve of ZSM-5/ β zeolite having a Si-Al ratio of 40 was prepared. 60 g of ZSM-5/ β zeolite was added to 40 g of 40 wt.% of a silicasol, homogeneously mixed and stirred. Then 2 g of potassium oxide was added, homogeneously mixed and stirred, and extrusion-molded. The molded catalyst was dried at 80°C for 3 h, fed into an autoclave the inner
30 bottom of which contains water. The catalyst was not brought in contact with liquid water, then sealed in the autoclave and disposed in an oven, crystallized at 165°C for 80 h, taken out, water-washed twice, oven-dried at 120°C in an oven for 3 h, calcined in a muffle furnace at 400°C for 2 h and at 550°C for 3 h, to obtain a binderless ZSM-5/ β zeolite catalyst,
35 wherein the results are shown in Table 3. The XRD spectrum of the prepared catalyst shows a symbiotic phase of ZSM-5 and β zeolite. The

scanning electron microscope graph of the prepared catalyst shows a cubical shaped ZSM-5 molecular sieve phase, a spherical β zeolite phase, almost without any amorphous binder, as shown in Fig.3. The amorphous binder was in an amount of 0.5%, and the crushing-resistant strength of the catalyst sample was determined to be 160 newton per grain.

Examples 3-16

Mordenite having a Si-Al ratio of 20, 60 g of Y zeolite having a Si-Al ratio of 10, MCM-22 having a Si-Al ratio of 40, ZSM-5/mordenite symbiotic molecular sieve having a Si-Al ratio of 20, ZSM-5/ β zeolite/Y zeolite symbiotic molecular sieve having a Si-Al ratio of 40, ZSM-5/Yzeolite/mordenite symbiotic molecular sieve having a Si-Al ratio of 20, ZSM-23 having a Si-Al ratio of 20, ZSM-11 having a Si-Al ratio of 30 , MCM-49 having a Si-Al ratio of 40, MCM-56 having a Si-Al ratio of 60, ZSM-5/Y zeolite symbiotic molecular sieve having a Si-Al ratio of 20, MCM-22/mordenite having a Si-Al ratio of 40, ZSM-5/Magadiite having a Si-Al ratio of 200 and ZSM-5/ β zeolite/mordenite having a Si-Al ratio of 30 were respectively taken (the feedstock proportion is shown in Table 1) to prepare a binderless mordenite catalyst according to the method in Example 1, as shown in Table 3.

Examples 17-22

The molecular sieves used in Examples 3-8 were respectively used. During the molding, the pore-expanding agents selected from the group consisting of sesbania powder, methyl cellulose, dissolvable starch and polyvinyl alcohol were added, wherein the feedstock proportion is shown in Table 2, and other conditions are stated in Example 1, to prepare a binderless zeolite catalyst. The results are shown in Table 3.

Example 23

The binderless catalyst prepared according to Example 1 was exchanged with 5% of an ammonium nitrate solution three times at 90°C in a solid:liquid (catalyst:ammonium nitrate solution) ratio of 1:10, and then calcined at 550°C for 3 h, to obtain a hydrogen-type binderless ZSM-5/ β zeolite symbiotic molecular sieve catalyst. The activity of the catalyst was

evaluated by using the raw material C₄-C₁₀ light oils produced by Sinopec Shanghai Gaoqiao Company and a fixed-bed reactor having a diameter of 12 mm under the conditions of a reaction temperature of 650°C, a reaction pressure of 0.02 MPa, a weight hourly space velocity of 1 h⁻¹, a water/feedstock oil weight ratio of 1:1. The product distribution after half an hour is shown in Table 5; the ethylene weight yield is 28%; the propylene weight yield is 27%; the diene weight total yield is 55% (see Table 6 for results).

Example 24

The binderless catalyst prepared according to Example 8 was exchanged with 5% of an ammonium nitrate solution three times at 90°C in a solid:liquid (catalyst:ammonium nitrate solution) ratio of 1:10, and then calcined at 550°C for 3 h, to obtain a hydrogen-type binderless molecular sieve catalyst. The catalyst was evaluated by using methanol as the raw material and a fixed-bed reactor having a diameter of 12 mm under the conditions of 450°C, a weight hourly space velocity of 1 h⁻¹, a water/methanol weight ratio of 1:1, a pressure of 0.02 MPa, to obtain the ethylene weight yield of 25%, and the propylene weight yield of 45%.

Comparative Example 1

The catalyst was prepared according to the same method as Example 1, except that sodium hydroxide was not used. The results of the prepared catalyst are shown in Table 3. According to the method of Example 23 above, a hydrogen-type molecular sieve was prepared and evaluated by the same method, and the results are shown in Table 6 below.

Table 1

Examples	Feedstocks								Crystallization temperature (°C)	Crystallization time (h)
	Molecular sieves		Aluminum compounds		Silica (g)	Induction materials		Water		
	Type	Amount (g)	Type	Amount (g)		Type	Amount (g)	Amount (g)		
Example 3	Mordenite	30	aluminium sulphate	5	20	sodium hydroxide	2	20	170	80
Example 4	Y zeolite	50	sodium aluminate	10	10	potassium hydroxide	14	4	180	10
Example 5	MCM-22	50			19	magnesium hydroxide	7	10	150	150
Example 6	ZSM-5/mordenite	80	aluminium chloride	10	15	calcium oxide	20	4	160	200
Example 7	ZSM-5/ β zeolite/Y zeolite	80	pseudo-boehmite	1	80	potassium oxide	0.5	40	165	80
Example 8	ZSM-5/Y zeolite/mordenite	80	aluminium nitrate	5	20	potassium hydroxide	0.1	20	180	60
Example 9	ZSM-23	10	aluminium sulphate	10	80	potassium hydroxide	20	40	170	240
Example 10	ZSM-11	70	sodium aluminate	10	25	sodium hydroxide	10	20	100	200
Example 11	MCM-49	10	sodium aluminate	10	15	sodium hydroxide	5	4	150	80
Example 12	MCM-56	70	sodium aluminate	5	20	potassium hydroxide	5	20	150	200
Example 13	ZSM-5/Y zeolite	40	sodium aluminate	5	10	sodium hydroxide + potassium hydroxide	5 for each	20	160	40
Example 14	MCM-22/mordenite	80	aluminium nitrate	5	20	potassium hydroxide	0.1	20	180	60
Example 15	ZSM-5/Magadiite	10	aluminium sulphate	10	80	potassium hydroxide	20	40	170	240
Example 16	ZSM-5/ β zeolite/mordenite	70	sodium aluminate	10	25	sodium hydroxide	10	20	100	200

0.1	aluminium sulphate	10	80	potassium phosphate	20	190	240
2	sodium aluminate	10	25	potassium hydrogen phosphate	10	100	10
1	sodium aluminate	10	15	potassium phosphate + sodium bisulphate	5 for each	150	60
0.6	sodium aluminate	5	20	potassium dihydrogen phosphate	5	150	300

Table 3

Examples	Zeolite content (wt.%) in the resultant binderless catalyst	Binder content (wt.%) in the resultant catalyst	Strength of the resultant catalyst (newton per grain)	Pore volume (ml/g)	Average pore diameter (nm)	Porosity (vol.%)
Example 1	99.8	0.2	150	0.34	62	32
Example 2	99.5	0.5	160	0.31	51	29
Example 3	99.4	0.6	170	0.21	60	25
Example 4	98.8	1.2	150	0.28	65	27
Example 5	97.9	2.1	150	0.26	64	26
Example 6	100	0	190	0.3	53	22
Example 7	98.5	1.5	175	0.29	58	24
Example 8	98.6	1.4	175	0.29	56	24
Example 9	95.0	5.0	80	0.31	71	30
Example 10	98.4	1.6	160	0.24	54	26
Example 11	99.9	0.1	200	0.15	50	20
Example 12	95.5	4.5	110	0.26	65	28
Example 13	96.1	3.9	90	0.32	69	29
Example 14	98.5	1.5	175	0.19	54	27
Example 15	98.6	1.4	175	0.17	53	26
Example 16	95.0	5.0	80	0.32	70	30
Example 17	98.4	1.6	160	0.17	55	28
Example 18	99.9	0.1	200	0.10	49	20
Example 19	98.5	1.5	175	0.14	52	26
Example 20	98.6	1.4	175	0.16	53	27
Example 21	95.0	5.0	80	0.27	70	31
Example 22	98.4	1.6	160	0.19	56	26
Com.Exp. 1	62.1	37.9	70	0.08	20	11

Table 4

Items	Data
Density (20°C) kg/m ³	704.6
Distillation range	
Initial distillation range (°C)	40
Distillation range	
Final distillation range (°C)	160
Saturated vapor pressure (20°C) kpa	50.2
Alkane% (wt.%)	65.2
Cyclane% (wt.%)	28.4
Alkene% (wt.%)	0.2
Arene% (wt.%)	6.2

Product distribution	Product weight yield (%)
Methane	5.2
Ethane	6.1
Ethylene	28.0
Propane	6.5
Propylene	27.0
Butane	8.7
Butene	7.6
Fractions having more than 5 carbons	8.8
Others	2.1

Table 6

Examples	Catalyst intensity (Newton/grain)	Ethylene yield (wt.%)	Propylene yield (wt.%)	Diene yield (wt.%)
Example 23	150	28	27	55
Com.Exp. 1	70	24	23	47

Example 25

- 5 60 g of ZSM-5 molecular sieve having a Si-Al ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molecular molar ratio, hereinafter inclusive) of 30, and 3.2 g of sesbania powder were homogeneously mixed and stirred. 40 g of 40 wt.% of a silicasol was added, homogeneously mixed and stirred. 10 ml of 1 mol/l of sodium bicarbonate solution was then added, homogeneously mixed and stirred,
- 10 and extrusion-molded. The molded catalyst was dried at 80°C for 3 h, fed into an autoclave the inner bottom of which contains water. The catalyst was not brought in contact with liquid water, then sealed in the autoclave and disposed in an oven, crystallized at 180°C for 60 h, taken out, water-washed twice, oven-dried at 120°C in an oven for 3 h, calcined in a
- 15 muffle furnace at 400°C for 2 h and at 550°C for 3 h, to obtain a binderless ZSM-5 catalyst. The XRD spectrum of the prepared catalyst shows a pure ZSM-5 phase. The scanning electron microscope graph thereof shows pure ZSM-5 crystal grains, almost without any amorphous binder. The amorphous binder was in an amount of 0.2%, and the crushing-resistant
- 20 strength of the catalyst sample was determined to be 145 newtons per grain. By the mercury-injection method, the pore volume is determined to be 0.38 ml/g; the average pore diameter thereof is 82 nm; and the porosity thereof is 36%, as shown in Table 9.

Example 26

According to the method in Example 1 of CN101428233A, a mixed crystal molecular sieve of ZSM-5/ β zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molecular molar ratio of 40 was prepared. 60 g of ZSM-5/ β zeolite was added to 40 g of 40 wt.% of a silicasol, homogeneously mixed and stirred. Then 20 ml of 1 mol/l of ammonium citrate was added, homogeneously mixed and stirred, and extrusion-molded. The molded catalyst was dried at 80°C for 3 h, fed into an autoclave the inner bottom of which contains water. The catalyst was not brought in contact with liquid water, then sealed in the autoclave and disposed in an oven, crystallized at 165°C for 80 h, taken out, water-washed twice, oven-dried at 120°C in an oven for 3 h, calcined in a muffle furnace at 400°C for 2 h and at 550°C for 3 h, to obtain a binderless ZSM-5/ β zeolite catalyst are shown in Table 9. The crushing-resistant strength of the catalyst sample was determined to be 160 newtons per grain, and the amorphous binder was in an amount of 0.6%. By the mercury-injection method, the pore volume is determined to be 0.37 ml/g; the average pore diameter thereof is 80 nm; and the porosity thereof is 35%.

Examples 27-40

Mordenite having a Si-Al ratio of 20, 60 g of Y zeolite having a Si-Al ratio of 10, MCM-22 having a Si-Al ratio of 40, ZSM-5/mordenite symbiotic molecular sieve having a Si-Al ratio of 20, ZSM-5/ β zeolite/Y zeolite symbiotic molecular sieve having a Si-Al ratio of 40, ZSM-5/Y zeolite/mordenite symbiotic molecular sieve having a Si-Al ratio of 20, ZSM-23 having a Si-Al ratio of 20, ZSM-11 having a Si-Al ratio of 30, MCM-49 having a Si-Al ratio of 40, MCM-56 having a Si-Al ratio of 60, ZSM-5/Y zeolite symbiotic molecular sieve having a Si-Al ratio of 20, MCM-22/mordenite having a Si-Al ratio of 40, ZSM-5/Magadiite having a Si-Al ratio of 200 and ZSM-5/ β zeolite/mordenite having a Si-Al ratio of 30 were respectively taken (the feedstock proportion is shown in Table 7) to prepare a binderless mordenite catalyst according to the method in Example 25, as shown in Table 9.

Examples 41-46

The molecular sieves used in Examples 27-32 were respectively used. During the molding, the pore-expanding agents selected from the group consisting of sesbania powder, methyl cellulose, dissolvable starch and polyvinyl alcohol were added, wherein the feedstock proportion is shown in Table 8, and other conditions are stated in Example 25, to prepare a binderless zeolite catalyst. The results are shown in Table 9.

Example 47

The binderless catalyst prepared according to Example 25 was exchanged with 5% of an ammonium nitrate solution three times at 90°C in a solid:liquid (catalyst:ammonium nitrate solution) ratio of 1:10, and then calcined at 550°C for 3 h, to obtain a hydrogen-type binderless ZSM-5/ β zeolite symbiotic molecular sieve catalyst. The activity of the catalyst was evaluated by using the raw material C₄-C₁₀ light oils produced by Sinopec Shanghai Gaoqiao Company (see Table 4 for the physical property indexes of the raw materials) and a fixed-bed reactor having a diameter of 12 mm under the conditions of a reaction temperature of 650°C, a reaction pressure of 0.02 MPa, a weight hourly space velocity of 1 h⁻¹, a water/feedstock oil weight ratio of 1:1. The product distribution after half an hour is shown in Table 10; the ethylene weight yield is 28%; the propylene weight yield is 28%; the diene weight total yield is 56%.

Example 48

The binderless catalyst prepared according to Example 32 was exchanged with 5% of an ammonium nitrate solution three times at 90°C in a solid:liquid (catalyst:ammonium nitrate solution) ratio of 1:10, and then calcined at 550°C for 3 h, to obtain a hydrogen-type binderless molecular sieve catalyst. The catalyst was evaluated by using methanol as the raw material and a fixed-bed reactor having a diameter of 12 mm under the conditions of 450°C, a weight hourly space velocity of 1 h⁻¹, a water/methanol weight ratio of 1:1, a pressure of 0.02 MPa, to obtain the ethylene weight yield of 24%, and the propylene weight yield of 47%.

Comparative Example 2

The catalyst was prepared according to the same method as Example 25,

except for that sodium bicarbonate was not used. The results of the prepared catalyst are shown in Table 9. According to the method of Example 47 of the present invention, a hydrogen-type molecular sieve was prepared and evaluated by the same method, and the results are shown in

5 Table 11 below.

				carbonate				
0	aluminium sulphate	10	80	potassium citrate	20	40	170	240
0	sodium aluminate	10	25	sodium oxalate	10	20	100	200
0	sodium aluminate	10	15	ammonium oxalate	5	4	150	80
0	sodium aluminate	5	20	potassium bicarbonate	5	20	150	200
0	sodium aluminate	5	10	sodium carbonate + potassium carbonate	5 for each	20	160	40
0	aluminium nitrate	5	20	ammonium bisulfate	0.1	20	180	60
0	aluminium sulphate	10	80	ammonium bisulphite	20	40	170	240
0	sodium aluminate	10	25	ammonium phosphate	10	20	100	200

		sulphate						
	2	sodium aluminate	10	25	ammonium hydrogen phosphate	10	100	10
	1	sodium aluminate	10	15	ammonium phosphate + ammonium bisulphite	5 for each	150	60
	0.6	sodium aluminate	5	20	ammonium dihydrogen phosphate	5	150	300

Table 9

Examples	Zeolite content (wt.%) in the resultant binderless catalyst	Binder content (wt.%) in the resultant catalyst	Strength of the resultant catalyst (newton per grain)	Pore volume (ml/g)	Average pore diameter (nm)	Porosity (vol.%)
Example 25	99.8	0.2	145	0.38	82	36
Example 26	99.4	0.6	160	0.37	80	35
Example 27	99.2	0.8	170	0.31	80	35
Example 28	98.3	1.7	150	0.38	85	37
Example 29	98.9	1.1	150	0.36	84	36
Example 30	100	0	180	0.35	73	32
Example 31	98.5	1.5	175	0.3	78	34
Example 32	98.4	1.6	175	0.31	76	34
Example 33	95.5	4.5	80	0.51	100	30
Example 34	98.3	1.7	160	0.34	94	36
Example 35	99.8	0.2	185	0.35	80	30
Example 36	95.6	4.4	110	0.36	95	38
Example 37	96.5	3.5	90	0.42	99	39
Example 38	98.3	1.7	175	0.39	84	37
Example 39	98.0	2.0	175	0.37	83	36
Example 40	95.4	4.6	80	0.52	90	40
Example 41	98.7	1.3	160	0.37	85	38
Example 42	99.9	0.1	180	0.31	89	31
Example 43	98.6	1.4	175	0.34	92	36
Example 44	98.5	1.5	175	0.36	93	37
Example 45	96.0	4.0	80	0.47	100	40
Example 46	98.3	1.7	160	0.39	96	36
Com.Exp. 2	63.0	37.0	60	0.08	20	10

Table 10

Product distribution	Product weight yield (%)
Methane	5.2
Ethane	6.1
Ethylene	28.0
Propane	6.5
Propylene	27.0
Butane	8.7
Butene	7.6
Fractions having more than 5 carbons	8.8
Others	2.1

Table 11

Examples	Catalyst intensity (n/grain)	Ethylene yield (wt.%)	Propylene yield (wt.%)	Diene yield (wt.%)
Example 47	145	28	28	56
Com.Exp.2	80	23	22	45

Example 49

- 5 500 g of kaolin and 2 g of sesbania powder were homogeneously mixed. 2,000 g of distilled water was then added. The mixture was high velocity-sheared with a high velocity shearing machine at a rotating speed of 14,000 rpm for 30 minutes. 400 g of ZSM-5 molecular sieve having a Si-Al molecular ratio of 30 was added, and a high velocity shearing was
- 10 then conducted for another 30 minutes. 500 g of aluminum sol containing 20 wt.% of alumina was added, and a high velocity shearing continued to be conducted for another 30 minutes. 1 g of triammonium citrate was added, and a high velocity shearing continued to be conducted for another 30 minutes. A laser particle size analyzer was used to determine the
- 15 particle size of the suspension, wherein the average particle size was 2 μm . A spray-drier was used for spray-molding under the conditions of an inlet temperature of 240°C, an outlet temperature of 120°C, a centrifugal rotational speed of 10,000 rpm, a cyclone pressure difference of 0.7 KPa at the outlet, a feeding rate of 1 kg/h, to obtain a microsphere catalyst
- 20 precursor I. The catalyst precursor I was calcined by the temperature programming method at 400°C for 3 h, and at 650°C for 3 h, to obtain a calcined, molded catalyst precursor II. A laser particle size analyzer was used to determine the particle size of the calcined catalyst precursor II, wherein the average particle size was 70 μm ; the nitrogen adsorption and
- 25 desorption method was used to determine the specific surface area, which was 310 m^2/g ; the average pore diameter was 3.5 nm; the density of the catalyst was 0.8 g/ml; an abrader was used to determine the abrasion index, which is 0.02 wt.%/h.
- 30 200 g of a calcined, molded catalyst precursor II was disposed inside the autoclave, the bottom of which contained 50 g of water and 50 g of ethylene diamine and was separated by a screen. The catalyst was disposed onto the screen to keep the catalyst from liquid water. The catalyst was sealed in the

autoclave and placed in an oven, crystallized at 180°C for 80 h, taken out, water-washed twice, oven-dried at 120°C in an oven for 3 h, calcined in a muffle furnace at 400°C for 2 h and at 550°C for 3 h, to obtain a binderless ZSM-5 fluidized-bed catalyst. The XRD spectrum of the prepared catalyst shows a pure ZSM-5 phase. The scanning electron microscope graph thereof shows pure ZSM-5 crystal grains, almost without any amorphous binder. The amorphous binder is in an amount of 0.2%, and other results are listed in Table 14.

Example 50

The same method according to Example 49 was used, except for that the template ethylene diamine was not used. The scanning electron microscope of the prepared catalyst shows a part of the binder is present, as shown in Fig.4, wherein the amorphous binder is in a content of about 5%, and other results are listed in Table 14.

Examples 51-59

The ingredients in Table 12 and preparation conditions in Table 13 were used, wherein silicasol contained 40 wt.% of silica, to prepare the fluidized-bed catalysts according to the method in Example 49. The properties of the prepared catalysts are shown in Table 13; and the results of the prepared catalysts are shown in Table 14.

Example 60

200 g of the fluidized-bed ZSM-5 catalyst prepared according to the method in Example 48 was disposed in a fluidized-bed reactor having an inner diameter of 50 mm. The activity of the catalyst was evaluated by using as the raw material C₄-C₁₀ light oils produced by Sinopec Shanghai Gaoqiao Company (see Table 4 for the physical property indexes of the raw materials) under the conditions of a reaction temperature of 680°C, a reaction pressure of 0.02 MPa, a weight hourly space velocity of 1 h⁻¹, a water/methanol weight ratio of 1:1. The product distribution is shown in Table 15, wherein the ethylene weight yield is 28%; the propylene weight yield is 22%; and the diene weight total yield is 50%.

Comparative Example 3

The catalyst was prepared according to the same method as Example 50, with the difference of using no dispersant. The results of the prepared catalyst are shown in Table 14. The method in Example 60 was used to evaluate. The obtained ethylene weight yield is 22.5%, the propylene weight yield of 20.3% and the diene weight total yield of 42.8%.

Table 12

Examples	Molecular sieve		Substrate		Binder		Pore-expanding agent		Dispersant		Template	
	Type	Amount (g)	Type	Amount (g)	Type	Amount (g)	Type	Amount (g)	Type	Amount (g)	Type	Amount (g)
Example 51	ZSM-5	400	kaolin	500	Aluminum sol	500	cellulose	2	triammonium citrate	1	Tetrapropyl-ammonium bromide	30
Example 52	mordenite	200	Calcined kaolin	700	Aluminum sol	500	polyvinyl alcohol	10	ammonium bicarbonate	0.1	tetrapropyl-ammonium hydroxide	20
Example 53	Y zeolite	500	diatomite	400	Aluminum sol	500	sesbania powder	1	ammonium carbonate	10	ethylene diamine	20
Example 54	β zeolite	200	bentonite	500	Aluminum sol	1500	dissolvable starch	3	ammonium oxalate	30	triethylamine	10
Example 55	MCM-22	400	argil	400	Aluminum sol	1000	carbon nano-tube	5	triammonium citrate	50	Hexamethyleneimine	30
Example 56	ZSM-5/mordenite	100	Clay	700	Aluminum sol	1000	dissolvable starch	1	triammonium citrate	0.5	hexanediamine	20
Example 57	ZSM-5/Y zeolite	600	kaolin	200	Silica sol	1000	-	-	triammonium citrate	2	ammonia	40
Example 58	ZSM-5/ β zeolite	300	kaolin	500	Silica sol	1000	dissolvable starch	20	triammonium citrate	10	tetraethyl-ammonium hydroxide	20
Example 59	ZSM-5 + β zeolite	200 for each	Kaolin + bentonite	200 for each	Aluminum sol + Silica sol	1000 for each	dissolvable starch + sesbania powder	5 for each	triammonium citrate + ammonium oxalate	2 for each	ethylene diamine and n-butylamine	20 for each

Table 13

Examples	Solids content (wt.%)	Particle size of suspension (μm)	Conditions for spray-molding			Average particle size of the catalyst precursor II (μm)	Specific surface area of the catalyst precursor II (m^2/g)	Average pore diameter of the catalyst precursor II (nm)	Density of the catalyst precursor II (g/ml)	Abrasion index of the catalyst precursor II (wt.%/h)
			centrifugal rotational speed (rpm)	cyclone pressure difference (Kpa)	Feeding speed (kg/h)					
Example 51	20	2.5	10000	0.6	2	72	295	1	0.8	0.01
Example 52	30	3.2	6000	0.7	1	80	290	3	1.1	1.0
Example 53	10	4.6	5000	0.5	2.5	100	240	5	1.2	1.2
Example 54	40	5.1	12000	0.4	3	65	270	3.5	0.9	1.0
Example 55	25	2.4	14000	0.6	4	60	260	2.8	0.8	0.5
Example 56	30	0.5	15000	0.8	5	58	280	10	0.6	0.2
Example 57	20	0.1	8000	0.9	2	76	260	15	1.2	0.02
Example 58	30	1.0	12000	0.6	1	70	180	10	0.7	0.02
Example 59	30	2.8	10000	0.5	0.5	66	100	5.4	0.8	0.08

Table 14

Examples	Zeolite content (wt.%) in the resultant binderless catalyst	Binder content (wt.%) in the resultant catalyst	Pore volume (ml/g)	Average pore diameter (nm)	Porosity (vol.%)
Example 50	95.0	5.0	0.30	80	26
Example 51	96.1	3.9	0.26	83	30
Example 52	96.5	3.5	0.31	82	32
Example 53	95.4	4.6	0.32	80	31
Example 54	98.5	1.5	0.33	72	32
Example 55	96.4	3.6	0.30	75	30
Example 56	98.0	2.0	0.28	71	28
Example 57	95.0	5.0	0.40	95	26
Example 58	98.1	1.9	0.29	92	29
Example 59	99.0	1.0	0.32	75	26
Com.Exp.3	96.7	3.3	0.32	82	30

Table 15

Product distribution	Product weight yield (%)
Methane	5.5
Ethane	7.6
Ethylene	28.0
Propane	7.1
Propylene	22.0
Butane	8.2
Butene	8.4
Fractions having more than 5 carbons	9.3
Others	3.9

5 Example 61

500 g of kaolin, 2 g of sesbania powder and 20 g of Wollastonite having a length-diameter ratio of 8 were homogeneously mixed. 2,000 g of distilled water was then added. The mixture was high velocity-sheared with a high velocity shearing machine for 30 minutes. 400 g of ZSM-5 molecular sieve having a Si-Al molecular ratio of 30 was added, and a high velocity shearing was then conducted for another 30 minutes. 500 g of aluminum sol containing 20 wt.% of alumina was added, and a high velocity shearing continued to be conducted for another 30 minutes. 1 g of triammonium citrate was added, and a high velocity shearing continued to be conducted for another 30 minutes. A laser particle size analyzer was used to

determine the particle size of the suspension which was 2 μm . A spray-drier was used for spray-molding under the conditions of an inlet temperature of 240°C, an outlet temperature of 120°C, a centrifugal rotational speed of 10,000 rpm, a cyclone pressure difference of 0.7 KPa at the outlet, a feeding rate of 1 kg/h. The spray-molded particles were calcined by the temperature programming method at 400°C for 3 h, and at 650°C for 3 h. A laser particle size analyzer was used to determine the calcined catalyst precursor II, wherein the average particle size was 68 μm ; the specific surface area was 305 m^2/g ; the average pore diameter was 3.2 nm; the density of the catalyst was 0.9 g/ml; an abrader was used to determine the abrasion index, which is 0.001 wt.%/h.

200 g of the calcined and molded catalyst above was disposed inside the autoclave, the bottom of which contained 50 g of water and 50 g of ethylene diamine and was separated by a screen. The catalyst was disposed onto the screen to keep the catalyst from liquid water. The catalyst was sealed in the autoclave and placed in an oven, crystallized at 180°C for 40 h, taken out, oven-dried at 120°C in an oven for 3 h, calcined in a muffle furnace at 400°C for 2 h and at 550°C for 3 h, to obtain a binderless ZSM-5 fluidized-bed catalyst. The XRD spectrum of the prepared catalyst shows a pure ZSM-5 phase. The scanning electron microscope graph thereof as shown in Fig.5 shows pure ZSM-5 crystal grains. The amorphous binder is in an amount of 0.3%, and other results are listed in Table 19.

Examples 62-70

The ingredients and preparation conditions in Tables 16-18 were used, wherein silicasol contained 40 wt.% of silica, to prepare the fluidized-bed catalysts according to the method in Example 61. The properties of the prepared catalysts are shown in Table 19.

Example 71

200 g of the fluidized-bed ZSM-5 catalyst prepared according to the method in Example 61 was disposed in a fluidized-bed reactor having an inner diameter of 50 mm. The activity of the catalyst was evaluated by using as the raw material C₄-C₁₀ light oils produced by Sinopec Shanghai

Gaoqiao Company (see Table 4 for the physical property indexes of the raw materials) under the conditions of a reaction temperature of 680°C, a reaction pressure of 0.02 MPa, a weight hourly space velocity of 1 h⁻¹, a water/feedstock oil weight ratio of 1:1, to obtain the ethylene weight yield of 27%, the propylene weight yield of 23% and the diene weight total yield of 50%.

argil	400	Aluminum sol	1000	carbon nano-tube	5	tri-ammonium citrate	50	wollastonite	2	5
Clay	700	Aluminum sol	1000	dissolvable starch	1	tri-ammonium citrate	0.5	glass fiber	10	3
kaolin	200	Silica sol	1000	-	-	tri-ammonium citrate	2	ceramic fiber	5	1
kaolin	500	Silica sol	1000	dissolvable starch	20	tri-ammonium citrate	10	wollastonite	8	2
kaolin + bentonite	200 for each	Aluminum sol +Silica sol	1000 for each	dissolvable starch+sessbania powder	5 for each	tri-ammonium citrate+ ammonium oxalate	2 for each	wollastonite +ceramic fiber	8 and10	5 for each

Table 17

Examples	Solids content (wt.%)	Particle size of suspension (μm)	Conditions for spray-molding					Average particle size of the catalyst precursor II (μm)	Specific surface area of the catalyst precursor II (m^2/g)	Average pore diameter of the catalyst precursor II (nm)	Density of the catalyst precursor II (g/ml)	Abrasion index of the catalyst precursor II (wt.%/h)
			Inlet temperature ($^{\circ}\text{C}$)	Outlet temperature ($^{\circ}\text{C}$)	centrifugal rotational speed (rpm)	cyclone pressure difference (Kpa)	Feeding speed (kg/h)					
Example 62	20	2.5	240	150	10000	0.6	2	72	295	1	0.9	0.001
Example 63	30	3.2	180	170	6000	0.7	1	80	290	3	1.2	0.8
Example 64	10	4.6	290	150	5000	0.5	2.5	100	240	5	1.3	0.5
Example 65	40	5.1	300	120	12000	0.4	3	65	270	3.5	1.0	0.3
Example 66	25	2.4	350	180	14000	0.6	4	60	260	2.8	0.9	0.005
Example 67	30	0.5	200	100	15000	0.8	5	58	280	10	0.7	0.1
Example 68	20	0.1	270	140	8000	0.9	2	76	270	15	1.3	0.005
Example 69	30	1.0	240	120	12000	0.6	1	70	180	10	0.8	0.002
Example 70	30	2.8	250	130	10000	0.5	0.5	66	100	5.4	0.9	0.02

Table 18

Examples	Template used therein		Crystallization temperature (°C)	Crystallization time (h)	Calcining temperature (°C)	Calcining time (h)
	Type	Amount (based on the weight percent of the molded and calcined catalyst precursor)				
Example 62	triethylamine	5	180	80	600	2
Example 63	ethylene diamine	50	300	10	500	4
Example 64	hexanediamine	30	150	150	550	3
Example 65	tetraethylammonium hydroxide	200	130	200	400	10
Example 66	hexamethyleneimine	150	170	80	700	1
Example 67	triethylamine	100	180	60	600	3
Example 68	tetrapropylammonium bromide	80	190	240	550	4
Example 69	hexanediamine	25	100	10	650	3
Example 70	tetrapropylammonium hydroxide	120	150	60	450	8

Table 19

Examples	Zeolite content (wt.%) in the resultant binderless catalyst	Binder content (wt.%) in the resultant catalyst	Pore volume (ml/g)	Average pore diameter (nm)	Porosity (vol.%)
Example 61	95.0	5.0	0.30	94	35
Example 62	96.0	4.0	0.36	95	34
Example 63	97.3	2.7	0.33	82	31
Example 64	96.0	4.0	0.34	81	30
Example 65	95.5	4.5	0.50	92	34
Example 66	98.2	1.8	0.32	84	35
Example 67	99.1	0.9	0.41	87	30
Example 68	98.2	1.8	0.30	91	31
Example 69	97.5	2.5	0.33	90	34
Example 70	98.5	1.5	0.34	83	31

Claims

1. A molecular sieve catalyst, comprising, based on the weight of the catalyst, 90-100 wt.% of a molecular sieve, 0-10 wt.% of a binder, and
5 0-10 wt.% of an anti-wear agent, wherein said catalyst has a pore volume of 0.10-0.52 ml/g, an average pore diameter of 50-100 nm, and a porosity of 20-40%; the anti-wear agent is selected from the rod or needle-like inorganic materials having a length/diameter ratio of 2-20.
- 10 2. The molecular sieve catalyst according to claim 1, characterized in that the catalyst has a pore volume of 0.15-0.3 ml/g, an average pore diameter of 50-70 nm, and a porosity of 20-30%.
3. The molecular sieve catalyst according to claim 1, characterized in that
15 the catalyst has a pore volume of 0.31-0.5 ml/g, an average pore diameter of 71-100 nm, and a porosity of 31-40%.
4. The molecular sieve catalyst according to claim 1, characterized in that the molecular sieve in the molecular sieve catalyst comprises at least one
20 selected from the group consisting of ZSM-5, ZSM-23, ZSM-11, mordenite, Y zeolite, β zeolite, MCM-22, MCM-49, MCM-56, ZSM-5/mordenite, β zeolite/mordenite, ZSM-5/ β zeolite, ZSM-5/Y, MCM-22/mordenite, ZSM-5/Magadiite, ZSM-5/ β zeolite/mordenite, ZSM-5/ β zeolite/Y zeolite and ZSM-5/Y zeolite/mordenite.
- 25 5. The molecular sieve catalyst according to claim 1, characterized in that the anti-wear agent is at least one inorganic material selected from the group consisting of asbestos, ceramic fiber, glass fiber, and wollastonite mineral, wherein the anti-wear agent has an average length of 1-100 μ m
30 and a length/diameter ratio of 3-10 and is in an amount 2-10 wt.% based on the weight of the calcined end product of the catalyst.
6. A process for preparing a molecular sieve catalyst according to claim 1, comprising the steps of
35 a) based on the weight of the molded and calcined catalyst, mixing

10-80 wt.% of a molecular sieve, 0.1-20 wt.% of an induction material, 0-20 wt.% of an aluminum compound and 10-80 wt.% of silica, molding and drying to obtain a molded catalyst precursor mix I, wherein the weight percent of the aluminum compound in the mix I is less than that of silica;

5 b) crystallizing the mix I at 100-200°C in water vapor or vapor of a template for 10-300 h, to obtain a molecular sieve catalyst precursor; and

 c) drying the catalyst precursor, and calcining at 400-700°C for 1-10 h to obtain a molecular sieve catalyst;

 wherein the induction material is at least one selected from the group
10 consisting of i) oxides or hydroxides of the elements of Group IA or IIA of the Periodic Table of Elements, or salts of weak acids thereof, ii) carbonates, bicarbonates, oxalates, or citrates of the elements of Group IA or IIA of the Periodic Table of Elements, and iii) at least one ammonium salts; the aluminum compound is at least one selected from the group
15 consisting of aluminum salts, aluminum oxides, hydrous oxides of aluminum and hydroxides of aluminum.

7. The process for preparing a molecular sieve catalyst according to claim 6, characterized in that the template is at least one selected from the group
20 consisting of ammonia, ethylene diamine, triethylamine, n-butylamine, hexanediamine, tetrapropylammonium bromide or tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetraethylammonium bromide and hexamethyleneimine, and is in an amount of 5-200 wt.% based on the weight of the mix I.

25 8. The process for preparing a molecular sieve catalyst according to claim 6, characterized in that the element of Group IA is at least one selected from the group consisting of sodium and potassium; the element of Group IIA is at least one selected from the group consisting of magnesium and
30 calcium.

9. The process for preparing a molecular sieve catalyst according to claim 6, characterized in that the salt of weak acids is at least one selected from the group consisting of bisulphate, sulphite, hydrosulfite, phosphate and
35 biphosphate.

10. The process for preparing a molecular sieve catalyst according to claim 6, characterized in that the ammonium salt is at least one selected from the group consisting of ammonium carbonate, ammonium bicarbonate, ammonium citrate, ammonium oxalate, ammonium sulphate, ammonium bisulphate, ammonium sulphite, ammonium bisulphite, ammonium phosphate, ammonium hydrogen phosphate and diammonium phosphate.

11. The process for preparing a molecular sieve catalyst according to claim 6, characterized in that, based on the weight of the molded and calcined catalyst, the molecular sieve in step a) is in an amount of 10-80 wt.%; the induction material is in an amount of 0.5-10 wt.%; the aluminum compound is in an amount of 1-15 wt.%; and silica is in an amount of 10-80 wt.%.

12. The process for preparing a molecular sieve catalyst according to claim 6, characterized in that the crystallization is carried out at 120-200°C for 20-200 h.

13. The process for preparing a molecular sieve catalyst according to claim 6, characterized in that, during the molding process of step a), at least one pore-expanding agent selected from the group consisting of methyl cellulose, polyvinyl alcohol, sesbania powder, dissolvable starch and carbon nano-tube is added in an amount 0.1-2 wt.% based on the weight of the molded and calcined catalyst.

14. A process for preparing a molecular sieve catalyst according to claim 1, comprising the steps of

(a) homogeneously mixing a molecular sieve, a binder, a dispersant having an induction action, a liquid medium, an optional pore-expanding agent, an optional substrate material, and an optional anti-wear agent to form a suspension, wherein the dispersant is selected from the group consisting of i) salts of weak acids of the elements of Group IA or IIA of the Periodic Table of Elements, and ii) carbonates, bicarbonate, oxalates and citrates of ammonium;

(b) high velocity shearing and diffusing to control the particle size of the materials in the suspension within 0.1-5 μm ;

(c) spray-drying said suspension to form a microsphere catalyst precursor I;

(d) calcining such microsphere catalyst precursor I at 300-700°C for 1-10 h to obtain a catalyst precursor II;

5 (e) crystallizing the catalyst precursor II at 100-300°C in water vapor or vapor of a template for 10-240 h, to obtain a catalyst precursor III; and

(f) calcining such microsphere catalyst precursor III at 400-700°C for 1-10 h to obtain a end product of the catalyst.

10 15. The process for preparing a molecular sieve catalyst according to claim 6 or 14, characterized in that the molecular sieve is at least one selected from the group consisting of ZSM-5, ZSM-23, ZSM-11, mordenite, Y zeolite, β zeolite, MCM-22, MCM-49, MCM-56, ZSM-5/mordenite, ZSM-5/ β zeolite, ZSM-5/Y, MCM-22/mordenite, ZSM-5/Magadiite,
15 ZSM-5/ β zeolite/mordenite, ZSM-5/ β zeolite/Y zeolite and ZSM-5/Y zeolite/mordenite, and is in an amount of 10-80 wt.% based on the weight of the molded and calcined catalyst.

16. The process for preparing a molecular sieve catalyst according to claim
20 14, characterized in that the binder is at least one selected from silicasol and aluminum sol, and is in an amount of 2-70 wt.% based on the weight of the calcined end product of the catalyst.

17. The process for preparing a molecular sieve catalyst according to claim
25 14, characterized in that the substrate material is at least one selected from the group consisting of kaolin, calcined kaolin, diatomite, bentonite, argil and clay, and is in an amount of 0-50 wt.% based on the weight of the calcined end product of the catalyst.

30 18. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the pore-expanding agent is at least one selected from the group consisting of methyl cellulose, polyvinyl alcohol, sesbania powder, dissolvable starch and carbon nano-tube, and is in an amount 0.1-5 wt.% based on the weight of the molecular sieve in the calcined end
35 product of the catalyst.

19. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the dispersant is at least one selected from the group consisting of tri-ammonium citrate, ammonium oxalate, ammonium carbonate and ammonium bicarbonate, and is in an amount 0.01-5 wt.% based on the weight of the molecular sieve in the calcined end product of the catalyst.

20. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the anti-wear agent is at least one inorganic material selected from the group consisting of asbestos, ceramic fiber, glass fiber, and wollastonite mineral, wherein the anti-wear agent has an average length of 1-100 μm and a length/diameter ratio of 3-10 and is in an amount 2-10 wt.% based on the weight of the calcined end product of the catalyst.

21. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the content of the suspension solids in step (a) ranges from 10-50 wt.%.

22. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the particle size of the materials in step (b) is controlled to be 0.1-2 μm by using the high velocity shearing or cyclic emulsification method.

23. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the spray-drying in step (c) is conducted under the conditions of an inlet temperature of 180-350°C, an outlet temperature of 100-180°C, a centrifugal rotational speed of 5,000-15,000 rpm, a cyclone pressure difference of 0.5-1.0 KPa at the outlet.

24. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that, after the spray-dried catalyst is calcined at high temperature, the particles of the catalyst precursor II have an average particle size of 50-100 μm , a specific surface area of 100-310 m^2/g , an average pore diameter of 1-20 nm, a density of 0.6-1.2 g/ml and an abrasion index of 0.01-1.2 wt.%/h.

25. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the template is at least one selected from the group consisting of ammonia, ethylene diamine, triethylamine, n-butylamine, hexanediamine, tetrapropylammonium bromide or tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetraethylammonium bromide and hexamethyleneimine, and is in an amount of 5-200 wt.% based on the weight of the molded and calcined catalyst precursor II.

26. The process for preparing a molecular sieve catalyst according to claim 14, characterized in that the crystallization is carried out at 120-200°C for 20-200 h.