

Catalyst Composition and Preparation therefor and Use thereof

TECHNICAL FIELD

The present invention relates to the technical field of catalysts, specifically
5 to a catalyst composition and the preparation therefor and the use thereof for the alkylation of an aromatic hydrocarbon and an olefin.

BACKGROUND TECHNOLOGY

An aromatic hydrocarbon is important basic organic raw materials with
10 very extensive uses and play an important role in the development of the national economy. In particular, ethylbenzene is mainly used downstream for the production of styrene which is further used as a raw material monomer for the synthesis of the polymers such as polystyrene, styrene-butadiene rubber, ABS and SBS, and is widely used in the fields such as the urban construction,
15 the electronic equipment, and the aerospace.

Ethylbenzene is mainly produced by the alkylation reaction of benzene and ethylene under the action of an acidic molecular sieve catalyst. In the actual catalytic reaction process, the alkylation of benzene and ethylene is a complex reaction system wherein series and parallel side reactions coexist. In addition to
20 the generation of the target product of ethylbenzene, by-products such as diethylbenzene, triethylbenzene, toluene, xylene, propylbenzene, ethyltoluene, butylbenzene and heavy components are also generated. In order to suppress the generation of the by-products, in the actual industrial production, an excess of raw material of benzene needs to be added to the reaction system, and the molar
25 ratio of benzene to ethylene is much higher than the stoichiometric ratio of 1:1. The excess raw material benzene circulates in the reaction system, which undoubtedly increases the energy consumption of the reaction unit. Therefore,

the development of alkylation catalysts with the characteristics of a high efficiency and a low benzene-to-olefin ratio is particularly important for reducing the benzene-to-olefin ratio in the actual reaction process and for the energy saving and the consumption reduction of the unit.

5 In addition, in the actual industrial production, the following three problems are frequently encountered: first, the industrial raw material of benzene or ethylene contains impurity water. If the catalyst does not have an excellent water resistance, water molecules will easily undergo a competitive adsorption with benzene or ethylene molecules at the acidic active centers of the
10 catalyst during the reaction process, resulting in a decreased catalytic performance. Second, the industrial raw material of benzene or ethylene carries alkaline substances, which very easily undergo an acid-base neutralization reaction with the acidic active centers of the catalyst during the reaction process, resulting in the rapid alkaline poisoning and deactivation of the catalyst. Third,
15 in the liquid-phase reaction process route, the reaction temperature is relatively low, the diffusion rate of reaction molecules is slow, and heavy components are easily generated during the reaction process, blocking the pore channels of the molecular sieve and resulting in the decreased catalyst activity and the shortened lifetime. Therefore, a catalyst with a good water resistance and a good alkaline
20 impurity resistance is needed in the industrial production, and heavy components are generated in a small amount, with an excellent long-term stability performance.

CN201911019842.0 discloses a liquid-phase alkylation catalyst and a preparation method and application thereof, as well as a method for the liquid-
25 phase alkylation reaction of benzene with ethylene. Therein, the liquid-phase alkylation catalyst comprises a molecular sieve having an MWW topological structure and a binder. Based on the total weight of the liquid-phase alkylation catalyst, the mass content of the molecular sieve having an MWW topological

structure is 50%-90%, and the mass content of the binder is 10%-50%. The external surface pore volume of the catalyst is 0.45-0.65 cm³/g. The use of the catalyst is beneficial for improving the ethylene conversion and the ethyl selectivity. However, under the applicable process conditions, the ethylene conversion is still lower than 99.8%, and the ethyl selectivity is lower than 99.7%. Likewise, the problem of solving the catalyst's water resistance and alkaline impurity resistance capability as well as the problem of the long-term stability of the catalyst are not mentioned.

CN201610440729.X discloses a method for producing alkylbenzenes. The catalyst used in the method is a binder-free molecular sieve catalyst, particularly a binder-free MWW structural molecular sieve catalyst or a binder-free Beta molecular sieve catalyst, with the compressive strength controlled within 60-120 N/cm, which can effectively improve the conversion of benzene and olefins in the liquid-phase alkylation reaction to produce alkylbenzenes. However, this method does not address the anti-impurity performance and the long-term stability performance of the catalyst, nor does it mention solving the problem of the selectivity of the catalyst.

CN201910992918.1, CN201710119230.3, and CN201510655644.9 disclose the use of the mixed loading of different types of the molecular sieve catalysts to improve the reaction performance of the liquid-phase alkylation of benzene and ethylene to produce ethylbenzene, but all fail to maximize the technical effects brought about by the mixed loading.

CONTENTS OF THE INVENTION

The present invention provides a catalyst composition, a preparation method therefor and a use thereof for the alkylation of an aromatic hydrocarbon and an olefin. The catalyst composition has high activity, selectivity, stability and impurity resistance when used in the reaction for preparing an alkyl

aromatic hydrocarbon by the alkylation of the aromatic hydrocarbon and the olefin, and is simultaneously applicable to a feed condition with a lower molar ratio of the aromatic hydrocarbon to the olefin.

In a first aspect, the present invention provides a catalyst composition, in particular a catalyst composition for the alkylation of an aromatic hydrocarbon and an olefin, comprising:

(a) a first catalyst, which is a molecular sieve catalyst having a static water initial contact angle θ_1 of 10-15°, for example 11° or 12°, and a static water adsorption amount of 220-280 mg/g, for example 247 mg/g, 256 mg/g, or 270 mg/g; and

(b) a second catalyst, which is a molecular sieve catalyst having a static water initial contact angle θ_2 of 140-165°, for example 152° or 158°, and a static water adsorption amount of 130-170 mg/g, for example 140 mg/g, 154 mg/g, or 160 mg/g.

In one embodiment of the above technical solutions, in the catalyst composition, the ratio of the static water initial contact angle θ_1 of the first catalyst to the static water initial contact angle θ_2 of the second catalyst is 1:(9.3-16), for example 1:(10-14).

In one embodiment of the above technical solutions, the mass ratio of the first catalyst to the second catalyst is 85-97:3-15, preferably 88-95:5-12.

In one embodiment of the above technical solutions, in the XRD pattern of the catalyst composition, the peak intensity ratio of the peak at a 2θ angle of 7.1° ($\pm 0.1^\circ$) to the peak at a 2θ angle of 7.4° ($\pm 0.1^\circ$) is 2.0-3.0, preferably 2.2-2.9; and/or the peak intensity ratio of the peak at a 2θ angle of 22.6° ($\pm 0.1^\circ$) to the peak at a 2θ angle of 26.0° ($\pm 0.1^\circ$) is 0.63-0.85, preferably 0.63-0.80.

In one embodiment of the above technical solutions, the alkaline substance breakthrough tolerance coefficient of the catalyst composition is 0.30-0.60. Therein the alkaline substance breakthrough tolerance coefficient of the catalyst

composition is defined as the ratio of the alkaline substance breakthrough time of the first catalyst to the alkaline substance breakthrough time of the second catalyst. The alkaline substance breakthrough time of the catalyst is determined under the conditions of a temperature of 180°C, a pressure of 3.5 MPa, an ethylene weight hourly space velocity of 2 h⁻¹, and a benzene-to-ethylene molar ratio of 2.5, the used benzene containing 20 ppm of pyridine. The time from the start of the reaction until the ethylene conversion drops to 50% is recorded as the alkaline substance breakthrough time of the catalyst.

In one embodiment of the above technical solutions, the ratio of the series reaction occurrence descriptor values of the catalyst composition is 0.40-0.65. Therein the series reaction occurrence descriptor value is defined as the ratio of the total mass of diethylbenzene and triethylbenzene to the total mass of ethylbenzene, diethylbenzene, and triethylbenzene in the alkylation liquid after the end of the reaction. The ratio of the series reaction occurrence descriptor values is defined as the ratio of the series reaction occurrence descriptor value of the first catalyst to the series reaction occurrence descriptor value of the second catalyst. The series reaction occurrence descriptor value of the catalyst is determined under the conditions of a temperature of 180°C, a pressure of 3.5 MPa, an ethylene weight hourly space velocity of 1 h⁻¹, and a benzene-to-ethylene molar ratio of 2.8.

In one embodiment of the above technical solutions, the ratio of the complex side reaction occurrence descriptor values of the catalyst composition is 0.20-0.35. Therein the complex side reaction occurrence descriptor value is defined as the ratio of the mass of the components having a boiling point higher than that of triethylbenzene to the mass of ethylbenzene in the alkylation liquid after the end of the reaction. The ratio of the complex side reaction occurrence descriptor values is defined as the ratio of the complex side reaction occurrence descriptor value of the first catalyst to the complex side reaction occurrence

descriptor value of the second catalyst. The complex side reaction occurrence descriptor value is determined under the conditions of a temperature of 180°C, a pressure of 3.5 MPa, an ethylene weight hourly space velocity of 1 h⁻¹, and a benzene-to-ethylene molar ratio of 2.8.

5 In one embodiment of the above technical solution, the first catalyst is a binder-free molecular sieve catalyst; preferably, based on the mass of the catalyst, the mass content of the molecular sieve is 98%-100%.

In the above technical solutions, the first catalyst is preferably a silicoaluminate molecular sieve catalyst having a twelve-membered ring pore
10 structure, more preferably an MWW-type molecular sieve, and still more preferably an MCM-22, MCM-49, or MCM-56 molecular sieve catalyst.

In the above technical solutions, preferably, the aluminum at a total of 5 T sites of T1, T3, T4, T5 and T8 located in the intralayer ten-membered ring pore channel in the MWW-type molecular sieve (for example, the MCM-22
15 molecular sieve) accounts for ≤45%, preferably 10%-45%, more preferably 20%-45%, of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7 and T8; and/or the aluminum at the T2 site accounts for ≥23%, preferably 23%-40%, more preferably 23%-35%, of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7 and T8. In a further embodiment, the aluminum at a total
20 of 5 T sites of T1, T3, T4, T5 and T8 located in the intralayer ten-membered ring pore channel of the molecular sieve accounts for 30%-42%, for example 32%, 36%, 38%, 40%, of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7 and T8, and/or the aluminum at the T2 site accounts for 24%-35%, for example 26%, 27%, of the aluminum at a total of 8 T sites of T1, T2, T3, T4,
25 T5, T6, T7 and T8.

In the above technical solutions, preferably, the MCM-22 molecular sieve in the MCM-22 molecular sieve catalyst has a sheet-like morphology, the c-axis sheet thickness La is 2.5-5.5 nm, the dimension Lb perpendicular to the c-axis

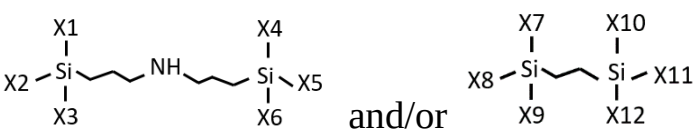
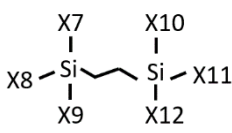
crystal plane is 50-500 nm, and Lb/La = 20-100.

In the above technical solutions, preferably, the SiO₂/Al₂O₃ molar ratio of the first catalyst is 15-60, for example 30.

In the above technical solutions, preferably, the specific surface area of the first catalyst is 480-550 m²/g, for example 500 m²/g, 520 m²/g.

In the above technical solutions, preferably, the micropore volume of the first catalyst is 0.19-0.21 cm³/g, for example 0.20 cm³/g.

In one embodiment of the above technical solutions, the second catalyst is a binder-free molecular sieve catalyst comprising a Beta molecular sieve connected with a bis-silyl group; preferably, the structural formula of the bis-

silyl group is  and/or , wherein X1-X12 represent the positions where the bis-silyl group is connected to the Beta molecular sieve, and the bis-silyl group is connected to the Beta molecular sieve by one or more of the positions X1-X12.

In the above technical solutions, in the second catalyst, preferably, based on the mass of the catalyst, the mass content of the molecular sieve is 95%-98%, for example 97%, and/or, based on the mass of the catalyst, the mass content of the bis-silyl group calculated as silica is 2%-5%.

In the above technical solutions, the molecular sieve in the second catalyst is preferably a silicoaluminate molecular sieve having a twelve-membered ring pore structure, more preferably a Beta molecular sieve.

In the above technical solutions, preferably, the Beta molecular sieve in the Beta molecular sieve catalyst has a granular morphology with a grain size of 5-20 nm.

In the above technical solutions, preferably, the SiO₂/Al₂O₃ molar ratio of the molecular sieve in the second catalyst is 16-50, for example 20-40, more

specifically for example 25.

In the above technical solutions, preferably, the specific surface area of the second catalyst is 550-650 m²/g, for example 600-630 m²/g.

In the above technical solutions, preferably, the micropore volume of the
5 second catalyst is 0.18-0.21 cm³/g, for example 0.20 cm³/g.

In a second aspect, the present invention provides a preparation method of the above catalyst composition, comprising the following step:

subjecting the first catalyst and the second catalyst to physical mixing to obtain the catalyst composition.

10 In the above technical solutions, preferably, the mass ratio of the first catalyst to the second catalyst is 85-97:3-15, preferably 88-95:5-12.

In one embodiment of the above technical solutions, the preparation method of the first catalyst comprises the following steps:

1) mixing a first molecular sieve raw powder, a first silicon source, a first
15 silica sol, a first aluminum source and an additive, molding, and drying to obtain a first catalyst preform;

2) contacting the first catalyst preform with an organic base solution to obtain a first mixture;

3) treating the first mixture to obtain the first catalyst, wherein the treating
20 may comprise sealed heating, calcination, and ammonium exchange,

wherein the additive is a mixture of at least two quaternary ammonium salts, for example a mixture of two quaternary ammonium salts.

In the above technical solutions, preferably, the molar ratio of one quaternary ammonium salt (also referred to as "first quaternary ammonium salt")
25 to another quaternary ammonium salt (also referred to as "second quaternary ammonium salt") is 1:(0.03-0.12), more preferably 1:(0.05-0.1), for example 1:0.075.

In the above technical solutions, preferably, the structural formula of the

first quaternary ammonium salt is $\begin{array}{c} \text{H}_3\text{C} \\ \diagup \\ \text{N}^+ \\ \diagdown \\ \text{H}_3\text{C} \end{array} \begin{array}{c} \diagup \\ \text{R1} \\ \diagdown \\ \text{CH}_3 \end{array} \text{X}^-$, wherein R1 is selected from C12-C20 alkyl, preferably C16-C18 alkyl, and X is selected from halogen atoms, preferably Cl or Br atoms. The first quaternary ammonium salt is for example selected from at least one of cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, octadecyltrimethylammonium bromide, and octadecyltrimethylammonium chloride.

In the above technical solutions, preferably, the structural formula of the

second quaternary ammonium salt is $\begin{array}{c} \text{R2} \\ \diagup \\ \text{N}^+ \\ \diagdown \\ \text{H}_3\text{C} \end{array} \begin{array}{c} \diagup \\ \text{CH}_3 \\ \diagdown \end{array} \text{CH}_2\text{CH}_2\text{CH}_2\text{S}(=\text{O})_2\text{O}^-$, wherein R2 is selected from C1-C18 alkyl, preferably C2-C14 alkyl. The second quaternary ammonium salt is for example selected from at least one of dimethylethyl(3-sulfopropyl)ammonium salt, 3-sulfopropyltetradecyldimethylammonium, 3-sulfopropyldodecyldimethylbetaine, 3-(decyldimethylammonio)propane-1-sulfonate inner salt, and 3-(N,N-dimethyloctylammonio)propane-1-sulfonate inner salt.

In the above technical solutions, preferably, step 1) has at least one of the following characteristics:

the molecular sieve in the first molecular sieve raw powder is a silicoaluminate molecular sieve having a twelve-membered ring pore structure, more preferably an MWW-type molecular sieve, and still more preferably an MCM-22, MCM-49 or MCM-56 molecular sieve;

the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the first molecular sieve raw powder is 15-60, for example 30;

the first aluminum source is selected from at least one of aluminum chloride, aluminum nitrate, aluminum sulfate, aluminum isopropoxide, pseudo-boehmite, aluminum hydroxide, and sodium metaaluminate;

the first silicon source is selected from silicon powder, i.e., silica powder,

the particle size of the silicon powder being preferably 10 nm-1000 nm, for example 100 nm;

the first silica sol is an alkaline silica sol, such as an sodium-type silica sol and/or an ammonium-type silica sol;

5 in the first silica sol, the mass content of silica is 30%-60%, for example 40%, 50%;

the first molecular sieve raw powder, the first silicon source, and the first silica sol are all calculated as SiO_2 , the first aluminum source is calculated as Al_2O_3 , and the molar ratio of the first molecular sieve raw powder, the first silicon source, the first silica sol, the first aluminum source, and the additive is (0.2-1.0):1:(1.5-3.0):(0.04-0.27):(0.1-0.2), for example (0.3-0.7):1:(2.0-2.6):(0.1-0.2):(0.12-0.16), and the molar ratio of the total SiO_2 in the first silicon source and the first silica sol to the Al_2O_3 in the first aluminum source is preferably 15-60:1, for example 30:1.

15 In the above technical solutions, there is no strict limitation on the specific manner of the molding in step 1), and any conventional catalyst molding method in the art may be used. For example, the extrusion molding may be employed;

In the above technical solutions, in step 1), the first catalyst preform may be made into various shapes as needed. For example, it may be made into a strip shape, the cross-section of which may be circular, gear-shaped, clover-shaped, four-leaf clover-shaped, honeycomb-shaped, or the like. In a preferred embodiment, the diameter of the first catalyst preform is 1.0-3.0 mm, for example 1.6 mm, 2.0 mm, for example 3-8 mm, and the length is 2-10 mm;

25 In the above technical solutions, in step 1), the drying may be carried out by a conventional method. For example, the drying may adopt conditions of: a drying temperature of 100-150°C and drying time of 5-10 hours.

In the above technical solution, preferably, step 2) has one or more of the following characteristics:

the organic base solution is selected from at least one of hexamethyleneimine aqueous solution, piperidine aqueous solution, piperazine aqueous solution, trimethylcyclohexylammonium hydroxide aqueous solution, and dimethylethylcyclohexylammonium hydroxide aqueous solution;

5 the mass concentration of the organic base solution is 8%-12%, for example 10%;

in the above technical solutions, preferably, the mass ratio of the first catalyst preform to the organic base solution is 1:(1.7-3), for example 1:2.

In the above technical solutions, preferably, the sealed heating treatment in
10 step 3) comprises subjecting the first mixture to standing or stirring in a sealed space at 130-180°C for 24-72 hours, for example standing or stirring at 140-160°C for 30-50 hours. In step 3), after the sealed heating treatment and before the calcination, conventional steps such as washing and drying may be included. The washing may be carried out by a conventional method, for example,
15 washing with deionized water until the pH of the solution is 7-7.5. The drying may be carried out by a conventional method. For example, the drying may adopt conditions of: a drying temperature of 100-150°C and drying time of 5-10 hours. The calcination may be carried out by a conventional method. For example, the calcination conditions may be as follows: a calcination temperature
20 of 520-580°C and calcination time of 4-8 hours. The ammonium exchange may be carried out by a conventional method. For example, the ammonium exchange conditions may be as follows: a temperature of 20-70°C, time of 1-5 hours. The ammonium salt may be at least one of ammonium chloride, ammonium sulfate, ammonium oxalate, or ammonium nitrate, and the mass concentration of the
25 ammonium salt solution may be 1%-10%.

In one embodiment of the above technical solution, the preparation method of the second catalyst comprises the following steps:

a) contacting a second molecular sieve raw powder with a first aromatic

hydrocarbon and a first modifier, and drying to obtain a modified second molecular sieve raw powder;

b) mixing the modified second molecular sieve raw powder with a second silicon source, a second aluminum source, and a second silica sol, molding, and
5 drying to obtain a second catalyst preform;

c) contacting the second catalyst preform with a structure-directing agent solution to obtain a second mixture;

d) treating the second mixture to obtain a second catalyst precursor, wherein the treating may comprise sealed heating, calcination, and ammonium
10 exchange;

e) contacting the second catalyst precursor with a pore-forming liquid, and treating to obtain a modified second catalyst precursor, wherein the treating may comprise sealed heating and calcination;

f) contacting the modified second catalyst precursor with a second aromatic
15 hydrocarbon and a second modifier, and treating to obtain the second catalyst, wherein the treating may comprise sealed heating, washing, and drying,
wherein the first modifier and the second modifier are different.

In the above technical solutions, preferably, step a) has one or more of the following characteristics:

20 the second molecular sieve raw powder is a silicoaluminate molecular sieve having a twelve-membered ring pore structure, preferably a Beta molecular sieve;

the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the second molecular sieve raw powder is 16-50, for example 20-40, more specifically for example 25;

25 the first aromatic hydrocarbon is selected from at least one of benzene, ethylbenzene, and toluene;

the first modifier is a silazane, the silazane being preferably selected from at least one of hexamethyldisilazane, hexamethyldisilurea, N,O-

bistrimethoxyalkylacetamide, and tetramethyldivinylidisilazane;

the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier is 1:(1.5-10):(0.05-0.2), for example 1:(3-8):(0.07-0.15);

5 the contacting comprises mixing and stirring the first aromatic hydrocarbon and the first modifier at 10-40°C for 5-30 minutes, then adding the second molecular sieve raw powder, and standing or stirring at 90-130°C for 60-120 minutes.

In the above technical solutions, in step a), the drying may be carried out
10 by a conventional method. For example, the drying conditions may be as follows: a drying temperature of 100-150°C and drying time of 5-10 hours.

In the above technical solution, preferably, step b) has one or more of the following characteristics:

the second aluminum source is selected from at least one of aluminum
15 chloride, aluminum nitrate, aluminum sulfate, aluminum isopropoxide, pseudo-boehmite, aluminum hydroxide, and sodium metaaluminate;

the second silicon source is selected from silicon powder, i.e., silica powder, preferably having a particle size of 10 nm-2000 nm, for example 200 nm;

the second silica sol is an alkaline silica sol, preferably a sodium-type silica
20 sol and/or an ammonium-type silica sol;

in the second silica sol, the mass content of silica is 35%-60%, for example 40% or 50%;

the modified second molecular sieve raw powder, the second silicon source, and the second silica sol are all calculated as SiO_2 , the second aluminum source
25 is calculated as Al_2O_3 , and the molar ratio of the modified second molecular sieve raw powder, the second silicon source, the second silica sol, and the second aluminum source is (0.1-0.5):1:(1.0-2.5):(0.04-0.22), for example (0.2-0.4):1:(1.3-2.0):(0.08-0.20), and the molar ratio of the total SiO_2 in the second

silicon source and the second silica sol to the Al_2O_3 in the second aluminum source is preferably 16-50:1.

In the above technical solutions, there is no strict limitation on the specific manner of the molding in step b), and any conventional catalyst molding method
5 in the art may be used. For example, the extrusion molding may be employed;

In the above technical solutions, in step b), the second catalyst preform may be made into various shapes as needed. For example, it may be made into a strip shape, the cross-section of which may be circular, gear-shaped, clover-shaped, four-leaf clover-shaped, honeycomb-shaped, or the like. In a preferred
10 embodiment, the diameter of the second catalyst preform is 1.0-3.0 mm and the length is 2-10 mm.

In the above technical solutions, in step b), the drying may be carried out by a conventional method. For example, the drying conditions may be as follows: a drying temperature of 100-150°C and drying time of 5-10 hours. In the above
15 technical solutions, preferably, step c) has one or more of the following characteristics:

In the above technical solutions, preferably, the structure-directing agent solution is selected from at least one of tetraethylammonium hydroxide aqueous solution, tetraethylammonium bromide aqueous solution,
20 trimethylcyclohexylammonium hydroxide aqueous solution, and dimethylethylcyclohexylammonium hydroxide aqueous solution;

In the above technical solutions, preferably, the mass concentration of the structure-directing agent solution is 6%-15%, for example 10% or 12%;

In the above technical solutions, preferably, the mass ratio of the second
25 catalyst preform to the structure-directing agent solution is 1:(1-1.5), for example 1:1.2.

In the above technical solutions, preferably, in step d), the sealed heating treatment comprises subjecting the second mixture to standing or stirring in a

sealed space at 140-170°C for 36-96 hours. In step d), after the sealed heating treatment and before the calcination, conventional steps such as washing and drying may be included. The washing and drying may be carried out by conventional methods. For example, the washing conditions may be as follows:
5 washing with deionized water until the pH of the solution is 7-7.5; the drying conditions may be as follows: a drying temperature of 100-150°C and drying time of 5-10 hours. The calcination may be carried out by a conventional method. For example, the calcination conditions may be as follows: a calcination temperature of 520-580°C and calcination time of 4-8 hours. The ammonium
10 exchange may be carried out by a conventional method. For example, the ammonium exchange conditions may be as follows: a temperature of 20-70°C, time of 1-5 hours. The ammonium salt may be at least one of ammonium chloride, ammonium sulfate, ammonium oxalate, or ammonium nitrate, and the mass concentration of the ammonium salt solution may be 1%-10%.

15 In the above technical solutions, preferably, step e) has one or more of the following characteristics:

the pore-forming liquid is a tetraethylammonium hydroxide aqueous solution or a mixed aqueous solution of tetraethylammonium hydroxide and tetraethylammonium bromide, and the mass concentration of the pore-forming
20 liquid is preferably 5%-15%;

the mass ratio of the second catalyst precursor to the pore-forming liquid is 1:(1.5-2), for example 1:1.7.

In the above technical solutions, preferably, the sealed heating treatment in the step e) comprises subjecting the second catalyst precursor and the pore-
25 forming liquid to standing or stirring at 160-180°C for 24-96 hours. In step e), after the sealed heating treatment and before the calcination, conventional steps such as washing and drying may be included. The washing and drying may be carried out by conventional methods. For example, the washing conditions may

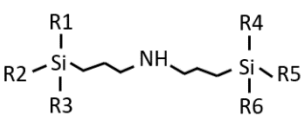
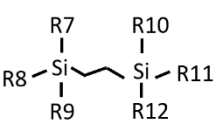
be as follows: washing with deionized water until the pH of the solution is 7-7.5; the drying conditions may be as follows: a drying temperature of 100-150°C and drying time of 5-10 hours. The calcination may be carried out by a conventional method. For example, the calcination conditions may be as follows:

5 a calcination temperature of 520-580°C and calcination time of 4-8 hours.

In the above technical solutions, preferably, step f) has one or more of the following characteristics:

the second aromatic hydrocarbon is selected from at least one of benzene, ethylbenzene, and toluene;

10 the second modifier is a bis-silane, the structural formula of which is

preferably  and/or , wherein R1-R12 are each independently selected from C1-C6 alkoxy and C1-C6 alkoxy-C1-C6 alkyl, preferably each independently methoxy, ethoxy, or 3-methoxypropyl; preferably, the second modifier includes but is not limited to at least one of 15 bis[(3-triethoxysilyl)propyl]amine, bis[(3-trimethoxysilyl)propyl]amine, and 1,2-bis(triethoxysilyl)ethane;

the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier is 1:(1.5-5.0):(0.1-0.5), for example 1:(2-4.0):(0.2-0.4).

20 In the above technical solutions, preferably, the sealed heating treatment in step f) comprises mixing and stirring the second aromatic hydrocarbon and the second modifier at 20-80°C for 10-30 minutes, then adding the modified second catalyst precursor, and standing or stirring at 100-140°C for 30-60 minutes, followed by washing and drying. The washing and drying may be carried out by 25 conventional methods. For example, the washing conditions may be as follows: repeatedly washing with a large amount of ethanol; the drying conditions may

be as follows: a drying temperature of 100-150°C and drying time of 5-10 hours.

In a third aspect, the present invention provides a method for the alkylation of an aromatic hydrocarbon and an olefin, wherein the reaction raw materials of the aromatic hydrocarbon and the olefin are contacted with the above catalyst composition to carry out an alkylation reaction to obtain an alkyl aromatic hydrocarbon.

In the above technical solutions, preferably, the aromatic hydrocarbon is selected from at least one of benzene and alkylbenzene, preferably selected from at least one of benzene, toluene, ethylbenzene, propylbenzene, and butylbenzene; the olefin is selected from C2-C6 olefins, preferably selected from at least one of ethylene, propylene, and butylene, wherein the olefin may be a pure olefin or a mixture with other non-olefin gases, and the volume concentration of the olefin is preferably 10%-100%.

In the above technical solutions, preferably, the conditions of the alkylation reaction comprise: a reaction temperature of 120-250°C, a reaction pressure of 2.0-5.0 MPa, an olefin mass hourly space velocity of 0.5-3.0 h⁻¹, and an aromatic hydrocarbon-to-olefin molar ratio of 1.0-3.0.

Compared with the prior art, the present invention has the following beneficial effects:

1. The inventors of the present invention have found through research that when the catalyst composition comprises a first catalyst and a second catalyst, the first catalyst has a static water initial contact angle θ_1 of 10-15° and a static water adsorption amount of 220-280 mg/g, and the second catalyst has a static water initial contact angle θ_2 of 140-165° and a static water adsorption amount of 130-170 mg/g, the catalyst composition is particularly suitable for the liquid-phase alkylation reaction of an aromatic hydrocarbon and an olefin, and has high activity, selectivity, stability, and impurity resistance, and is simultaneously applicable to feed conditions with a lower molar ratio of the aromatic

hydrocarbon to the olefin through the mutual cooperation of the two catalysts with specific contact angles and static water adsorption amounts.

2. The inventors of the present invention have further found through research that when the alkaline substance breakthrough tolerance coefficient of the catalyst composition is controlled to be 0.30-0.60, and/or the ratio of the series reaction occurrence descriptor values is 0.40-0.65, and/or the ratio of the complex side reaction occurrence descriptor values is 0.20-0.35, the activity, selectivity, and stability of the catalyst can be further improved when used in the liquid-phase alkylation reaction of an aromatic hydrocarbon and an olefin.

3. The inventors of the present invention have further found through research that when the molecular sieve in the first catalyst is preferably an MCM-22 molecular sieve, the molecular sieve in the second catalyst is preferably a Beta molecular sieve, and the XRD pattern of the catalyst composition has specific 2θ angle characteristics in the catalyst composition, the catalyst has the advantages of the excellent diffusion performance and the good accessibility of active centers. In particular, in the liquid-phase alkylation reaction of an aromatic hydrocarbon and an olefin, the catalyst can effectively improve the olefin conversion, suppress side reactions, reduce the generation amount of heavy components, improve the selectivity, extend the service life of the catalyst, and reduce the molar ratio of the aromatic hydrocarbon to the olefin in the feed during the reaction process, which is very beneficial for the energy saving and the consumption reduction.

3. The catalyst composition of the present invention is particularly suitable for the olefin having a volume concentration of 10-100%. Taking ethylene raw material as an example, the raw material may be pure ethylene, or may be off-gas with a low ethylene concentration from FCC or DCC units, or mixed C_2 with a high ethylene concentration, which fully expands the sources of ethylene raw materials and creates more economic benefits.

DESCRIPTION OF THE DRAWINGS

Figure 1 is an XRD pattern of the first catalyst prepared in Example 1 of the present invention;

5 Figure 2 is a static water contact angle test photograph of the first catalyst prepared in Example 1 of the present invention;

Figure 3 is an ^{27}Al MAS NMR spectrum of the first catalyst prepared in Example 1 of the present invention;

10 Figure 4 is an SEM photograph of the first catalyst prepared in Example 1 of the present invention;

Figure 5 is a TEM photograph of the first catalyst prepared in Example 1 of the present invention;

Figure 6 is an XRD pattern of the second catalyst prepared in Example 1 of the present invention;

15 Figure 7 is a static water contact angle test photograph of the second catalyst prepared in Example 1 of the present invention;

Figure 8 is a TEM photograph of the second catalyst prepared in Example 1 of the present invention;

20 Figure 9 is an XRD pattern of the catalyst composition prepared in Example 1 of the present invention.

MODE OF CARRYING OUT THE INVENTION

The present invention is described in detail below in combination with specific embodiments, but it should be understood that the protection scope of
25 the present invention is not limited by the specific embodiments.

In the present invention, an XRD pattern of the catalyst is obtained using a D8 ADVANCE X-ray powder diffractometer from Bruker, Germany. The voltage is selected as 40 kV, the current is selected as 40 mA, and the scanning

speed is $0.3^{\circ}\cdot\text{min}^{-1}$.

In the present invention, the static water initial contact angle of the molecular sieve is measured using a JY-82C video contact angle measuring instrument from Chengde Dingsheng. An appropriate amount of the ground powder sample is placed in a tableting machine and pressed into a sheet, which is then placed on a contact angle test platform (ambient temperature 25°C). An automatic titration system of the equipment is used to drop a water droplet ($5\text{ }\mu\text{L}$ volume of deionized water), a test photograph is taken, and then the contact angle is measured using an angle measuring method.

In the present invention, the static water adsorption amount is measured using a BSD-VVS multi-station gravimetric gas vapor adsorption instrument from BSD Instrument Technology (Beijing) Co., Ltd. Before testing, activation is carried out under vacuum at 200°C for 6 hours. The cumulative water adsorption amount of the sample at a relative pressure P/P_0 of 0.90 is taken as the final static water adsorption amount.

In the present invention, an SEM photograph is taken using a Hitachi S-4800 cold field emission high-resolution scanning electron microscope produced by Hitachi, Ltd.

In the present invention, a TEM photograph is taken using a Tecnai G220 S-TWIN transmission electron microscope.

In the present invention, the nitrogen adsorption-desorption isotherm of the catalyst is measured at liquid nitrogen temperature using a BEL-MAX specific surface area and pore size analyzer produced by BELSORP, Japan. The specific surface area is calculated using the BET equation, and the micropore volume is calculated using the t-plot method.

In the present invention, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is obtained by ICP testing that is performed using a Model S-35 ICP-AES analyzer from Kontron to obtain data of the silica-alumina ratio.

In the present invention, the aluminum distribution at T sites of the molecular sieve is obtained by ^{27}Al MAS NMR testing. The testing is performed on a JEOL 500 MHz (11.7 T) spectrometer using a 3.2 mm HX MAS NMR probe at a spinning rate of 18 kHz. The spectrum is acquired at a resonance frequency of 130.3 MHz, with the chemical shift referenced to a 1 mol/L $\text{Al}(\text{NO}_3)_3$ solution ($\delta = 0$ ppm). The aluminum at δ of 56 ppm in the spectrum corresponds to the aluminum distribution at 5 T sites (T1, T3, T4, T5, and T8) in the intralayer ten-membered ring pore channel; the aluminum at δ of 61 ppm corresponds to the aluminum distribution at the T site (T2) in the surface half-supercage; and the aluminum at δ of 50 ppm, 56 ppm, and 61 ppm corresponds to the aluminum distribution at 8 T sites (T1, T2, T3, T4, T5, T6, T7, and T8). Therein the percentage of aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel relative to the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8 is calculated as the percentage of the peak area at δ of 56 ppm relative to the peak area at δ of 50 ppm, 56 ppm, and 61 ppm; the percentage of aluminum at the T2 site in the surface half-supercage relative to the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8 is calculated as the percentage of the peak area at δ of 61 ppm relative to the peak area at δ of 50 ppm, 56 ppm, and 61 ppm.

[Example 1]

The example is used for preparing a molecular sieve catalyst composition for the alkylation of the aromatic hydrocarbon and the olefin. The specific preparation process is as follows:

1. Preparation of the first catalyst

30 g of MCM-22 molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 30), 60 g of silicon powder (particle size of 100 nm), 240 g of sodium-type silica sol aqueous

solution with a mass content of 50%, 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%), 50.9 g of cetyltrimethylammonium bromide, and 2.0 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and the first additive was 0.5:1:2:0.1:0.15, and the molar ratio of cetyltrimethylammonium bromide to dimethylethyl(3-sulfopropyl)ammonium salt was 1:0.075; and then, a strip-shaped first catalyst preform A1 with a diameter of 2.0 mm, a length of 3-8 mm, and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A1 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a first mixture B1. The first mixture B1 was allowed to stand in a sealed space at 160°C for 48 hours, then washed with deionized water until the pH of the solution was 7, dried at 130°C for 7 hours, calcined at 550°C for 5 hours, and finally subjected to exchange with an ammonium chloride solution having a mass concentration of 5% at 50°C for 3 hours to obtain a first catalyst C1.

2. Preparation of the second catalyst

500 g of toluene and 10 g of N,O-bis(trimethoxyalkyl)acetamide were mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25) and allowed to stand at 110°C for 80 minutes, then dried at 140°C for 6 hours to obtain a modified second molecular sieve raw powder D1, wherein the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:5:0.1. Then, 18 g of the modified second molecular sieve raw powder D1, 60 g of silicon powder (particle size of 200 nm), 225 g of sodium-type silica sol aqueous solution with a mass content of 40%, and 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular sieve raw powder, the second silicon powder, the second silica

sol, and the second aluminum source was 0.3:1:1.5:0.1. Then, a strip-shaped second catalyst preform E1 with a diameter of 1.5 mm, a length of 3-8 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Subsequently, 100 g of the second catalyst preform E1 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a second mixture F1. The second mixture F1 was allowed to stand in a sealed space at 150°C for 50 hours, then washed with deionized water until the pH of the solution was 7.5, dried at 120°C for 8 hours, calcined at 560°C for 6 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 7% at 55°C for 2 hours to obtain a second catalyst precursor G1. 100 g of the second catalyst precursor G1 and 170 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) were uniformly mixed, allowed to stand at 170°C for 48 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 150°C for 6 hours, and calcined at 550°C for 5 hours to obtain a modified second catalyst precursor H1. 300 g of ethylbenzene and 30 g of bis[(3-triethoxysilyl)propyl]amine were mixed and stirred at 60°C for 15 minutes, added with 100 g of the modified second catalyst precursor H1 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:3:0.3, then repeatedly washed with a large amount of ethanol, and dried at 140°C for 7 hours to obtain a second catalyst I1.

3. 92 g of the first catalyst C1 and 8 g of the second catalyst I1 were subjected to physical mixing to obtain a final molecular sieve catalyst composition J1 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C1 are as follows: the XRD pattern is shown in Figure 1, having characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test photograph

is shown in Figure 2, with a value of 12°; the molecular sieve content is 100%; the static water adsorption amount is 247 mg/g; the SiO₂/Al₂O₃ molar ratio is 30; the specific surface area is 516 m²/g, and the micropore volume is 0.20 cm³/g. The ²⁷Al MAS NMR spectrum is shown in Figure 3, wherein the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 38% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 24% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph is shown in Figure 4, wherein the MCM-22 molecular sieve has a sheet-like morphology, and the TEM photograph is shown in Figure 5, wherein the c-axis sheet thickness is 5.3-5.4 nm.

The characterization test results of the second catalyst I1 are as follows: the XRD pattern is shown in Figure 6, having characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test photograph is shown in Figure 7, with a value of 152°; the molecular sieve content is 97%; the static water adsorption amount is 154 mg/g; the SiO₂/Al₂O₃ molar ratio is 25; the specific surface area is 602 m²/g, and the micropore volume is 0.19 cm³/g. The TEM photograph is shown in Figure 8, wherein the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

In the catalyst composition J1, the mass content of the first catalyst C1 is 92%, and the mass content of the second catalyst I1 is 8%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J1 is 0.40, the ratio of the series reaction occurrence descriptor values is 0.62, and the ratio of the complex side reaction occurrence descriptor values is 0.32.

The XRD pattern of the catalyst composition J1 is shown in Figure 9,

wherein the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.72; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak at a 2θ angle of 26.0° in the XRD pattern is 0.65.

5 **[Example 2]**

The example is used for preparing a molecular sieve catalyst composition for the alkylation of the aromatic hydrocarbon and the olefin. The specific preparation process is as follows:

1. Preparation of the first catalyst

10 60 g of MCM-22 molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 15), 60 g of silicon powder (particle size of 100 nm), 300 g of ammonium-type silica sol aqueous solution with a mass content of 60%, 68.9 g of sodium metaaluminate (Al_2O_3 mass content of 40%), 66.2 g of cetyltrimethylammonium bromide, and 3.6 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, 15 wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and the additive was 1:1:3:0.27:0.2, and the molar ratio of cetyltrimethylammonium bromide to dimethylethyl(3-sulfopropyl)ammonium salt was 1:0.1; and then, a strip-shaped first catalyst preform A2 with a diameter of 1.6 mm, a length of 2-10 mm, and 20 a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A2 was immersed in 300 g of piperidine aqueous solution (mass concentration of 8%) to obtain a first mixture B2. The first mixture B2 was allowed to stand in a sealed space at 180°C for 24 hours, then washed with deionized water until the pH of the solution was 7, 25 dried at 150°C for 5 hours, calcined at 580°C for 4 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 10% at 70°C for 1 hour to obtain a first catalyst C2.

2. Preparation of the second catalyst

1000 g of toluene and 20 g of tetramethyldivinylidisilazane were mixed and stirred at 40°C for 5 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 16) and allowed to stand at 130°C for 60 minutes, then dried at 150°C for 5 hours to obtain a modified second molecular sieve raw powder D2, wherein the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:10:0.2. Then, 30 g of the modified second molecular sieve raw powder D2, 60 g of silicon powder (particle size of 200 nm), 250 g of ammonium-type silica sol aqueous solution with a mass content of 60%, and 56.1 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 0.5:1:2.5:0.22, and then, a strip-shaped second catalyst preform E2 with a diameter of 3 mm, a length of 2-10 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the second catalyst preform E2 was immersed in 150 g of a mixed aqueous solution of tetraethylammonium hydroxide and tetraethylammonium bromide (mass concentration of 15%, containing 15 g of tetraethylammonium hydroxide and 7.5 g of tetraethylammonium bromide in the solution) to obtain a second mixture F2. The second mixture F2 was allowed to stand in a sealed space at 170°C for 36 hours, then washed with deionized water until the pH of the solution was 7, dried at 150°C for 5 hours, calcined at 580°C for 4 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 10% at 70°C for 1 hour to obtain a second catalyst precursor G2. 100 g of the second catalyst precursor G2 and 200 g of a mixed aqueous solution of tetraethylammonium hydroxide and tetraethylammonium bromide (mass concentration of 15%, containing 15 g of tetraethylammonium hydroxide and 15 g of tetraethylammonium bromide in the solution) were uniformly mixed,

allowed to stand at 180°C for 24 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 150°C for 10 hours, and calcined at 580°C for 4 hours to obtain a modified second catalyst precursor H2. 500 g of benzene and 50 g of 1,2-bis(triethoxysilyl)ethane were mixed and stirred at
5 80°C for 10 minutes, added with 100 g of the modified second catalyst precursor H2 and allowed to stand at 140°C for 30 minutes, wherein the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:5:0.5, then repeatedly washed with a large amount of ethanol, and dried at 150°C for 5 hours to obtain a second catalyst I2.

10 3. 88 g of the first catalyst C2 and 12 g of the second catalyst I2 were subjected to physical mixing to obtain a final molecular sieve catalyst composition J2 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C2 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22
15 molecular sieve; the static water contact angle test value is 10°; the molecular sieve content is 100%; the static water adsorption amount is 280 mg/g; the SiO₂/Al₂O₃ molar ratio is 15; the specific surface area is 550 m²/g, and the micropore volume is 0.21 cm³/g. The ²⁷Al MAS NMR spectrum shows that the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer
20 ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 32% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 35% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve
25 has a sheet-like morphology, and the TEM photograph shows that the c-axis sheet thickness is 2.5-2.7 nm.

The characterization test results of the second catalyst I2 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular

sieve; the static water contact angle test value is 160° ; the molecular sieve content is 95%; the static water adsorption amount is 130 mg/g; the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is 16; the specific surface area is $648 \text{ m}^2/\text{g}$, and the micropore volume is $0.21 \text{ cm}^3/\text{g}$. The TEM photograph shows that the Beta molecular sieve
5 has a granular morphology with a grain size of 5-12 nm.

In the catalyst composition J2, the mass content of the first catalyst C2 is 88%, and the mass content of the second catalyst I2 is 12%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J2 is 0.60, the ratio of the series reaction occurrence descriptor
10 values is 0.42, and the ratio of the complex side reaction occurrence descriptor values is 0.21.

The XRD pattern of the catalyst composition J2 shows that the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.73; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak
15 at a 2θ angle of 26.0° in the XRD pattern is 0.64.

[Example 3]

The example is used for preparing a molecular sieve catalyst composition for the alkylation of the aromatic hydrocarbon and the olefin. The specific preparation process is as follows:

20 1. Preparation of the first catalyst

12 g of MCM-22 molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 60), 60 g of silicon powder (particle size of 100 nm), 180 g of ammonium-type silica sol aqueous solution with a mass content of 50%, 10.7 g of sodium metaaluminate (Al_2O_3 mass content of 40%), 34.7 g of cetyltrimethylammonium bromide, and
25 0.93 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and the additive was 0.2:1:1.5:0.042:0.1, and the molar ratio of cetyltrimethylammonium bromide to

dimethylethyl(3-sulfopropyl)ammonium salt was 1:0.05, and then, a strip-shaped first catalyst preform A3 with a diameter of 3.0 mm, a length of 2-10 mm, and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A3 was immersed in 170 g of a mixed aqueous solution of hexamethyleneimine and dimethylethylcyclohexylammonium hydroxide (mass concentration of 12%, containing 18 g of hexamethyleneimine and 2.4 g of dimethylethylcyclohexylammonium hydroxide in the solution) to obtain a first mixture B3. The first mixture B3 was allowed to stand in a sealed space at 130°C for 72 hours, then washed with deionized water until the pH of the solution was 7, dried at 100°C for 10 hours, calcined at 520°C for 8 hours, and finally subjected to exchange with an ammonium oxalate solution having a mass concentration of 1% at 20°C for 5 hours to obtain a first catalyst C3.

2. Preparation of the second catalyst

150 g of toluene and 5 g of hexamethyldisilurea were mixed and stirred at 10°C for 30 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 50) and allowed to stand at 90°C for 120 minutes, then dried at 100°C for 10 hours to obtain a modified second molecular sieve raw powder D3, wherein the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:1.5:0.05. Then, 6 g of the modified second molecular sieve raw powder D3, 60 g of silicon powder (particle size of 200 nm), 120 g of sodium-type silica sol aqueous solution with a mass content of 50%, and 10.2 g of sodium aluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 0.1:1:1:0.04. Then, a strip-shaped second catalyst preform E3 with a diameter of 2 mm, a length of 2-10 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and

drying steps. Then, 100 g of the second catalyst preform E3 was immersed in 100 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 6%) to obtain a second mixture F3. The second mixture F3 was allowed to stand in a sealed space at 140°C for 96 hours, then washed with deionized water until the pH of the solution was 7, dried at 100°C for 10 hours, calcined at 520°C for 8 hours, and finally subjected to exchange with an ammonium nitrate solution having a mass concentration of 1% at 20°C for 5 hours to obtain a second catalyst precursor G3. 100 g of the second catalyst precursor G3 and 150 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 5%) were uniformly mixed, allowed to stand at 160°C for 96 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 100°C for 10 hours, and calcined at 520°C for 8 hours to obtain a modified second catalyst precursor H3. 150 g of toluene and 10 g of bis[(3-trimethoxysilyl)propyl]amine were mixed and stirred at 20°C for 30 minutes, then added with 100 g of the modified second catalyst precursor H3 and allowed to stand at 100°C for 60 minutes, wherein the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:1.5:0.1, then repeatedly washed with a large amount of ethanol, and dried at 100°C for 10 hours to obtain a second catalyst I3.

3. 95 g of the first catalyst C3 and 5 g of the second catalyst I3 were subjected to physical mixing to obtain a final molecular sieve catalyst composition J3 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C3 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test value is 15°; the molecular sieve content is 100%; the static water adsorption amount is 220 mg/g; the SiO₂/Al₂O₃ molar ratio is 60; the specific surface area is 480 m²/g, and the micropore volume is 0.19 cm³/g. The ²⁷Al MAS NMR spectrum shows that the

aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 40% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 27% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve has a sheet-like morphology, and the TEM photograph shows that the c-axis sheet thickness is 5.4-5.5 nm.

The characterization test results of the second catalyst I3 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 140° ; the molecular sieve content is 98%; the static water adsorption amount is 170 mg/g; the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is 50; the specific surface area is $551 \text{ m}^2/\text{g}$, and the micropore volume is $0.18 \text{ cm}^3/\text{g}$. The TEM photograph shows that the Beta molecular sieve has a granular morphology with a grain size of 16-20 nm.

In the catalyst composition J3, the mass content of the first catalyst C3 is 95%, and the mass content of the second catalyst I3 is 5%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J3 is 0.57, the ratio of the series reaction occurrence descriptor values is 0.58, and the ratio of the complex side reaction occurrence descriptor values is 0.26.

The XRD pattern of the catalyst composition J3 shows that the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.71; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak at a 2θ angle of 26.0° in the XRD pattern is 0.66.

[Example 4]

The example is used for preparing a molecular sieve catalyst composition

for the alkylation of the aromatic hydrocarbon and the olefin. The specific preparation process is as follows:

1. Preparation of the first catalyst

30 g of MCM-22 molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 30), 60 g of silicon powder (particle size of 100 nm), 240 g of sodium-type silica sol aqueous solution with a mass content of 50%, 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%), 48.6 g of octadecyltrimethylammonium chloride, and 3.8 g of 3-sulfopropyltetradecyldimethylammonium were uniformly mixed, wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and the first additive was 0.5:1:2:0.1:0.15, and the molar ratio of octadecyltrimethylammonium chloride to 3-sulfopropyltetradecyldimethylammonium was 1:0.075, and then, a strip-shaped first catalyst preform A4 with a diameter of 2.0 mm, a length of 3-8 mm, and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A4 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a first mixture B4. The first mixture B4 was allowed to stand in a sealed space at 160°C for 48 hours, then washed with deionized water until the pH of the solution was 7, dried at 130°C for 7 hours, calcined at 550°C for 5 hours, and finally subjected to exchange with an ammonium chloride solution having a mass concentration of 5% at 50°C for 3 hours to obtain a first catalyst C4.

2. Preparation of the second catalyst

500 g of toluene and 10 g of N,O-bis(trimethoxyalkyl)acetamide were mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25) and allowed to stand at 110°C for 80 minutes, then dried at 140°C for 6 hours to obtain a modified second molecular sieve raw powder D4, wherein the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:5:0.1. Then, 18 g of

the modified second molecular sieve raw powder D4, 60 g of silicon powder (particle size of 200 nm), 225 g of sodium-type silica sol aqueous solution with a mass content of 40%, and 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 0.3:1:1.5:0.1. Then, a strip-shaped second catalyst preform E4 with a diameter of 1.5 mm, a length of 3-8 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the second catalyst preform E4 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a second mixture F4. The second mixture F4 was allowed to stand in a sealed space at 150°C for 50 hours, then washed with deionized water until the pH of the solution was 7.5, dried at 120°C for 8 hours, calcined at 560°C for 6 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 7% at 55°C for 2 hours to obtain a second catalyst precursor G4. 100 g of the second catalyst precursor G4 and 170 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) were uniformly mixed, allowed to stand at 170°C for 48 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 150°C for 6 hours, and calcined at 550°C for 5 hours to obtain a modified second catalyst precursor H4. 300 g of ethylbenzene and 30 g of bis[(3-triethoxysilyl)propyl]amine were mixed and stirred at 60°C for 15 minutes, then added with 100 g of the modified second catalyst precursor H4 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:3:0.3, then repeatedly washed with a large amount of ethanol, and dried at 140°C for 7 hours to obtain a second catalyst I4.

3. 92 g of the first catalyst C4 and 8 g of the second catalyst I4 were

subjected to physical mixing to obtain a final molecular sieve catalyst composition J4 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C4 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test value is 11°; the molecular sieve content is 100%; the static water adsorption amount is 256 mg/g; the SiO₂/Al₂O₃ molar ratio is 30; the specific surface area is 501 m²/g, and the micropore volume is 0.21 cm³/g. The ²⁷Al MAS NMR spectrum shows that the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 36% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 26% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve has a sheet-like morphology, and the TEM photograph shows that the c-axis sheet thickness is 5.2-5.4 nm.

The characterization test results of the second catalyst I4 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 152°; the molecular sieve content is 97%; the static water adsorption amount is 154 mg/g; the SiO₂/Al₂O₃ molar ratio is 25; the specific surface area is 602 m²/g, and the micropore volume is 0.19 cm³/g. The TEM photograph shows that the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

In the catalyst composition J4, the mass content of the first catalyst C4 is 92%, and the mass content of the second catalyst I4 is 8%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J4 is 0.42, the ratio of the series reaction occurrence descriptor values is 0.59, and the ratio of the complex side reaction occurrence descriptor

values is 0.30.

The XRD pattern of the catalyst composition J4 is shown in Figure 9, wherein the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.74; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak at a 2θ angle of 26.0° in the XRD pattern is 0.64.

[Comparative Example 1]

The example merely differs from Example 1 in that: in the process of preparing the first catalyst, dimethylethyl(3-sulfopropyl)ammonium salt was not added, and an equal molar weight of cetyltrimethylammonium bromide was used to replace dimethylethyl(3-sulfopropyl)ammonium salt. The specific preparation process of the comparative catalyst composition is as follows:

1. Preparation of the first catalyst

30 g of MCM-22 molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 30), 60 g of silicon powder (particle size of 100 nm), 240 g of sodium-type silica sol aqueous solution with a mass content of 50%, 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%), and 54.6 g of cetyltrimethylammonium bromide were uniformly mixed, wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and cetyltrimethylammonium bromide was 0.5:1:2:0.1:0.15, and then, a strip-shaped first catalyst preform A5 with a diameter of 2.0 mm, a length of 3-8 mm, and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A5 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a first mixture B5. The first mixture B5 was allowed to stand in a sealed space at 160°C for 48 hours, then washed with deionized water until the pH of the solution was 7, dried at 130°C for 7 hours, calcined at 550°C for 5 hours, and finally subjected to exchange with an ammonium chloride solution having a

mass concentration of 5% at 50°C for 3 hours to obtain a first catalyst C5.

2. Preparation of the second catalyst

500 g of toluene and 10 g of N,O-bis(trimethoxyalkyl)acetamide were mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve (SiO₂/Al₂O₃ molar ratio of 25) and allowed to stand at 110°C for 80 minutes, then dried at 140°C for 6 hours to obtain a modified second molecular sieve raw powder D5, wherein the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier is 1:5:0.1. Then, 18 g of the modified second molecular sieve raw powder D5, 60 g of silicon powder (particle size of 200 nm), 225 g of sodium-type silica sol aqueous solution with a mass content of 40%, and 25.5 g of sodium metaaluminate (Al₂O₃ mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 0.3:1:1.5:0.1, and then, a strip-shaped second catalyst preform E5 with a diameter of 1.5 mm, a length of 3-8 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the second catalyst preform E5 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a second mixture F5. The second mixture F5 was allowed to stand in a sealed space at 150°C for 50 hours, then washed with deionized water until the pH of the solution was 7.5, dried at 120°C for 8 hours, calcined at 560°C for 6 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 7% at 55°C for 2 hours to obtain a second catalyst precursor G5. 100 g of the second catalyst precursor G5 and 170 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) were uniformly mixed, allowed to stand at 170°C for 48 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 150°C for 6 hours, and calcined at 550°C for 5 hours to obtain a

modified second catalyst precursor H5. 300 g of ethylbenzene and 30 g of bis[(3-triethoxysilyl)propyl]amine were mixed and stirred at 60°C for 15 minutes, then added with 100 g of the modified second catalyst precursor H5 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:3:0.3, then repeatedly washed with a large amount of ethanol, and dried at 140°C for 7 hours to obtain a second catalyst I4.

3. 92 g of the first catalyst C5 and 8 g of the second catalyst I5 were subjected to physical mixing to obtain a final molecular sieve catalyst composition J5 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C5 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test value is 23°; the molecular sieve content is 100%; the static water adsorption amount is 205 mg/g; the SiO₂/Al₂O₃ molar ratio is 30; the specific surface area is 465 m²/g, and the micropore volume is 0.20 cm³/g. The ²⁷Al MAS NMR spectrum shows that the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 52% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 17% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve has a sheet-like morphology, and the TEM photograph shows that the c-axis sheet thickness is 10.6-16.2 nm.

The characterization test results of the second catalyst I5 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 152°; the molecular sieve content is 97%; the static water adsorption amount is 154 mg/g; the SiO₂/Al₂O₃

molar ratio is 25; the specific surface area is 602 m²/g, and the micropore volume is 0.19 cm³/g. The TEM photograph shows that the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

In the catalyst composition J5, the mass content of the first catalyst C5 is 92%, and the mass content of the second catalyst I5 is 8%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J5 is 0.26, the ratio of the series reaction occurrence descriptor values is 0.75, and the ratio of the complex side reaction occurrence descriptor values is 0.38.

The XRD pattern of the catalyst composition J5 shows that the peak intensity ratio of the peak at a 2 θ angle of 7.1° to the peak at a 2 θ angle of 7.4° is 2.79; and the peak intensity ratio of the peak at a 2 θ angle of 22.6° to the peak at a 2 θ angle of 26.0° in the XRD pattern is 0.64.

[Comparative Example 2]

The example merely differs from Example 1 in that: in the process of preparing the second catalyst, the first modifier of N,O-bis(trimethoxyalkyl)acetamide was not added. The specific preparation process of the catalyst composition is as follows:

1. Preparation of the first catalyst

30 g of MCM-22 molecular sieve (SiO₂/Al₂O₃ molar ratio of 30), 60 g of silicon powder (particle size of 100 nm), 240 g of sodium-type silica sol aqueous solution with a mass content of 50%, 25.5 g of sodium metaaluminate (Al₂O₃ mass content of 40%), 50.9 g of cetyltrimethylammonium bromide, and 2.0 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and the additive was 0.5:1:2:0.1:0.15, and the molar ratio of cetyltrimethylammonium bromide to

dimethylethyl(3-sulfopropyl)ammonium salt was 1:0.075, and then, a strip-shaped first catalyst preform A6 with a diameter of 2.0 mm, a length of 3-8 mm, and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A6 was immersed in 200 g of
5 hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a first mixture B6. The first mixture B6 was allowed to stand in a sealed space at 160°C for 48 hours, then washed with deionized water until the pH of the solution was 7, dried at 130°C for 7 hours, calcined at 550°C for 5 hours, and finally subjected to exchange with an ammonium chloride solution having a
10 mass concentration of 5% at 50°C for 3 hours to obtain a first catalyst C5.

2. Preparation of the second catalyst

500 g of toluene was mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25) and allowed to stand at 110°C for 80 minutes, then dried at 140°C for 6 hours to obtain a
15 modified second molecular sieve raw powder D6. Then, 18 g of the modified second molecular sieve raw powder D6, 60 g of silicon powder (particle size of 200 nm), 225 g of sodium-type silica sol aqueous solution with a mass content of 40%, and 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular
20 sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 0.3:1:1.5:0.1, and then, a strip-shaped second catalyst preform E6 with a diameter of 1.5 mm, a length of 3-8 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the second catalyst preform E6 was immersed in
25 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a second mixture F6. The second mixture F6 was allowed to stand in a sealed space at 150°C for 50 hours, then washed with deionized water until the pH of the solution was 7.5, dried at 120°C for 8 hours, calcined at

560°C for 6 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 7% at 55°C for 2 hours to obtain a second catalyst precursor G6. 100 g of the second catalyst precursor G5 and 170 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) were uniformly mixed, allowed to stand at 170°C for 48 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 150°C for 6 hours, and calcined at 550°C for 5 hours to obtain a modified second catalyst precursor H6. 300 g of ethylbenzene and 30 g of bis[(3-triethoxysilyl)propyl]amine were mixed and stirred at 60°C for 15 minutes, then added with 100 g of the modified second catalyst precursor H6 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:3:0.3, then repeatedly washed with a large amount of ethanol, and dried at 140°C for 7 hours to obtain a second catalyst I6.

3. 92 g of the first catalyst C6 and 8 g of the second catalyst I6 were subjected to physical mixing to obtain a final molecular sieve catalyst composition J6 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C6 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test value is 12°; the molecular sieve content is 100%; the static water adsorption amount is 247 mg/g; the SiO₂/Al₂O₃ molar ratio is 30; the specific surface area is 516 m²/g, and the micropore volume is 0.20 cm³/g. The ²⁷Al MAS NMR spectrum shows that the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 38% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 24% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5,

T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve has a sheet-like morphology, and the TEM photograph shows that the c-axis sheet thickness is 5.3-5.4 nm.

The characterization test results of the second catalyst I6 are as follows: the
5 XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 131°; the molecular sieve content is 97.5%; the static water adsorption amount is 184 mg/g; the SiO₂/Al₂O₃ molar ratio is 25; the specific surface area is 508 m²/g, and the micropore volume is 0.20 cm³/g. The TEM photograph shows that the Beta
10 molecular sieve has a granular morphology with a grain size of 36-55 nm.

In the catalyst composition J6, the mass content of the first catalyst C6 is 92%, and the mass content of the second catalyst I6 is 8%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J6 is 0.67, the ratio of the series reaction occurrence descriptor
15 values is 0.32, and the ratio of the complex side reaction occurrence descriptor values is 0.16.

The XRD pattern of the catalyst composition J6 shows that the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.56; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak
20 at a 2θ angle of 26.0° in the XRD pattern is 0.73.

[Comparative Example 3]

The example merely differs from Example 1 in that: in the process of preparing the second catalyst, the second modifier of bis[(3-
25 triethoxysilyl)propyl]amine was not added. The specific preparation process of the catalyst composition is as follows:

1. Preparation of the first catalyst

30 g of MCM-22 molecular sieve (SiO₂/Al₂O₃ molar ratio of 30), 60 g of

silicon powder (particle size of 100 nm), 240 g of sodium-type silica sol aqueous solution with a mass content of 50%, 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%), 50.9 g of cetyltrimethylammonium bromide, and 2.0 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, wherein
5 the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and the additive was 0.5:1:2:0.1:0.15, and the molar ratio of cetyltrimethylammonium bromide to dimethylethyl(3-sulfopropyl)ammonium salt was 1:0.075, and then, a strip-shaped first catalyst preform A7 with a diameter of 2.0 mm, a length of 3-8 mm,
10 and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A7 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a first mixture B7. The first mixture B7 was allowed to stand in a sealed space at 160°C for 48 hours, then washed with deionized water until the pH of the
15 solution was 7, dried at 130°C for 7 hours, calcined at 550°C for 5 hours, and finally subjected to exchange with an ammonium chloride solution having a mass concentration of 5% at 50°C for 3 hours to obtain a first catalyst C7.

2. Preparation of the second catalyst

500 g of toluene and 10 g of N,O-bis(trimethoxyalkyl)acetamide were mixed
20 and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25) and allowed to stand at 110°C for 80 minutes, then dried at 140°C for 6 hours to obtain a modified second molecular sieve raw powder D7, wherein the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:5:0.1. Then, 18 g of
25 the modified second molecular sieve raw powder D7, 60 g of silicon powder (particle size of 200 nm), 225 g of sodium-type silica sol aqueous solution with a mass content of 40%, and 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified

second molecular sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 0.3:1:1.5:0.1, and then, a strip-shaped second catalyst preform E7 with a diameter of 1.5 mm, a length of 3-8 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the second catalyst preform E7 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a second mixture F7. The second mixture F6 was allowed to stand in a sealed space at 150°C for 50 hours, then washed with deionized water until the pH of the solution was 7.5, dried at 120°C for 8 hours, calcined at 560°C for 6 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 7% at 55°C for 2 hours to obtain a second catalyst precursor G7. 100 g of the second catalyst precursor G7 and 170 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) were uniformly mixed, allowed to stand at 170°C for 48 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 150°C for 6 hours, and calcined at 550°C for 5 hours to obtain a modified second catalyst precursor H7. 300 g of ethylbenzene was stirred at 60°C for 15 minutes, then added with 100 g of the modified second catalyst precursor H7 and allowed to stand at 120°C for 50 minutes, then repeatedly washed with a large amount of ethanol, and dried at 140°C for 7 hours to obtain a second catalyst I7.

3. 92 g of the first catalyst C7 and 8 g of the second catalyst I7 were subjected to physical mixing to obtain a final molecular sieve catalyst composition J7 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C7 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test value is 12°; the molecular sieve content is 100%; the static water adsorption amount is 247

mg/g; the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the molecular sieve is 30; the specific surface area is $516 \text{ m}^2/\text{g}$, and the micropore volume is $0.20 \text{ cm}^3/\text{g}$. The ^{27}Al MAS NMR spectrum shows that the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 38% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 24% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve has a sheet-like morphology, and the TEM photograph shows that the c-axis sheet thickness is 5.3-5.4 nm.

The characterization test results of the second catalyst I7 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 36° ; the molecular sieve content is 99%; the static water adsorption amount is 201 mg/g ; the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is 25; the specific surface area is $626 \text{ m}^2/\text{g}$, and the micropore volume is $0.20 \text{ cm}^3/\text{g}$. The TEM photograph shows that the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

In the catalyst composition J7, the mass content of the first catalyst C6 is 92%, and the mass content of the second catalyst I7 is 8%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J7 is 0.23, the ratio of the series reaction occurrence descriptor values is 0.28, and the ratio of the complex side reaction occurrence descriptor values is 0.15.

The XRD pattern of the catalyst composition J7 shows that the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.70; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak

at a 2 θ angle of 26.0° in the XRD pattern is 0.68.

[Comparative Example 4]

The example merely differs from Example 1 in that: in the process of preparing the second catalyst, an equal mass of the second modifier of bis[(3-triethoxysilyl)propyl]amine was used to replace the first modifier of N,O-bis(trimethoxyalkyl)acetamide. The specific preparation process of the catalyst composition is as follows:

1. Preparation of the first catalyst

30 g of MCM-22 molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 30), 60 g of silicon powder (particle size of 100 nm), 240 g of sodium-type silica sol aqueous solution with a mass content of 50%, 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%), 50.9 g of cetyltrimethylammonium bromide, and 2.0 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, the first aluminum source, and the additive was 0.5:1:2:0.1:0.15, and the molar ratio of cetyltrimethylammonium bromide to dimethylethyl(3-sulfopropyl)ammonium salt was 1:0.075, and then, a strip-shaped first catalyst preform A8 with a diameter of 2.0 mm, a length of 3-8 mm, and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A8 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a first mixture B8. The first mixture B8 was allowed to stand in a sealed space at 160°C for 48 hours, then washed with deionized water until the pH of the solution was 7, dried at 130°C for 7 hours, calcined at 550°C for 5 hours, and finally subjected to exchange with an ammonium chloride solution having a mass concentration of 5% at 50°C for 3 hours to obtain a first catalyst C8.

2. Preparation of the second catalyst

500 g of toluene and 10 g of bis[(3-triethoxysilyl)propyl]amine were mixed

and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25) and allowed to stand at 110°C for 80 minutes, then dried at 140°C for 6 hours to obtain a modified second molecular sieve raw powder D8. Then, 18 g of the modified second molecular sieve raw powder D8, 5 60 g of silicon powder (particle size of 200 nm), 225 g of sodium-type silica sol aqueous solution with a mass content of 40%, and 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 10 0.3:1:1.5:0.1, and then, a strip-shaped second catalyst preform E8 with a diameter of 1.5 mm, a length of 3-8 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the second catalyst preform E8 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) 15 to obtain a second mixture F8. The second mixture F8 was allowed to stand in a sealed space at 150°C for 50 hours, then washed with deionized water until the pH of the solution was 7.5, dried at 120°C for 8 hours, calcined at 560°C for 6 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 7% at 55°C for 2 hours to obtain a second 20 catalyst precursor G8. 100 g of the second catalyst precursor G8 and 170 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) were uniformly mixed, allowed to stand at 170°C for 48 hours, then washed with deionized water until the pH of the solution was 7.0, dried at 150°C for 6 hours, and calcined at 550°C for 5 hours to obtain a modified second catalyst 25 precursor H8. 300 g of ethylbenzene and 30 g of bis[(3-triethoxysilyl)propyl]amine were mixed and stirred at 60°C for 15 minutes, then added with 100 g of the modified second catalyst precursor H8 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified second

catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:3:0.3, then repeatedly washed with a large amount of ethanol, and dried at 140°C for 7 hours to obtain a second catalyst I8.

3. 92 g of the first catalyst C8 and 8 g of the second catalyst I8 were
5 subjected to physical mixing to obtain a final molecular sieve catalyst composition J8 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C8 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test value is 12°; the molecular
10 sieve content is 100%; the static water adsorption amount is 247 mg/g; the SiO₂/Al₂O₃ molar ratio of the molecular sieve is 30; the specific surface area is 516 m²/g, and the micropore volume is 0.20 cm³/g. The ²⁷Al MAS NMR spectrum shows that the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22
15 molecular sieve accounts for 38% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 24% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve has a sheet-like morphology, and the TEM
20 photograph shows that the c-axis sheet thickness is 5.3-5.4 nm.

The characterization test results of the second catalyst I8 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 134°; the molecular sieve content is 97.3%; the static water adsorption amount is 181 mg/g; the
25 SiO₂/Al₂O₃ molar ratio is 25; the specific surface area is 526 m²/g, and the micropore volume is 0.19 cm³/g. The TEM photograph shows that the Beta molecular sieve has a granular morphology with a grain size of 28-45 nm.

In the catalyst composition J8, the mass content of the first catalyst C8 is

92%, and the mass content of the second catalyst I8 is 8%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J8 is 0.64, the ratio of the series reaction occurrence descriptor values is 0.37, and the ratio of the complex side reaction occurrence descriptor values is 0.18.

The XRD pattern of the catalyst composition J8 shows that the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.61; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak at a 2θ angle of 26.0° in the XRD pattern is 0.69.

10 **[Comparative Example 5]**

The example merely differs from Example 1 in that: in the process of preparing the first catalyst, neither cetyltrimethylammonium bromide nor dimethylethyl(3-sulfopropyl)ammonium salt was added. The specific preparation process of this comparative catalyst composition is as follows:

15 1. Preparation of the first catalyst

30 g of MCM-22 molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 30), 60 g of silicon powder (particle size of 100 nm), 240 g of sodium-type silica sol aqueous solution with a mass content of 50%, and 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the first molecular sieve raw powder, the first silicon powder, the first silica sol, and the first aluminum source was 0.5:1:2:0.1, and then, a strip-shaped first catalyst preform A9 with a diameter of 2.0 mm, a length of 3-8 mm, and a circular cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the first catalyst preform A9 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a first mixture B9. The first mixture B9 was allowed to stand in a sealed space at 160°C for 48 hours, then washed with deionized water until the pH of the solution was 7, dried at 130°C for 7 hours, calcined at 550°C for 5 hours, and

finally subjected to exchange with an ammonium chloride solution having a mass concentration of 5% at 50°C for 3 hours to obtain a first catalyst C9.

2. Preparation of the second catalyst

500 g of toluene and 10 g of N,O-bis(trimethoxyalkyl)acetamide were mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25) and allowed to stand at 110°C for 80 minutes, then dried at 140°C for 6 hours to obtain a modified second molecular sieve raw powder D9, wherein the mass ratio of the second molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:5:0.1. Then, 18 g of the modified second molecular sieve raw powder D9, 60 g of silicon powder (particle size of 200 nm), 225 g of sodium-type silica sol aqueous solution with a mass content of 40%, and 25.5 g of sodium metaaluminate (Al_2O_3 mass content of 40%) were uniformly mixed, wherein the molar ratio of the modified second molecular sieve raw powder, the second silicon powder, the second silica sol, and the second aluminum source was 0.3:1:1.5:0.1, and then, a strip-shaped second catalyst preform E9 with a diameter of 1.5 mm, a length of 3-8 mm, and a four-leaf clover-shaped cross-section was obtained through extrusion molding and drying steps. Then, 100 g of the second catalyst preform E9 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a second mixture F9. The second mixture F9 was allowed to stand in a sealed space at 150°C for 50 hours, then washed with deionized water until the pH of the solution was 7.5, dried at 120°C for 8 hours, calcined at 560°C for 6 hours, and finally subjected to exchange with an ammonium sulfate solution having a mass concentration of 7% at 55°C for 2 hours to obtain a second catalyst precursor G9. 100 g of the second catalyst precursor G9 and 170 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) were uniformly mixed, allowed to stand at 170°C for 48 hours, then washed with deionized water until the pH of the solution was

7.0, dried at 150°C for 6 hours, and calcined at 550°C for 5 hours to obtain a modified second catalyst precursor H9. 300 g of ethylbenzene and 30 g of bis[(3-triethoxysilyl)propyl]amine were mixed and stirred at 60°C for 15 minutes, then added with 100 g of the modified second catalyst precursor H9 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified second catalyst precursor, the second aromatic hydrocarbon, and the second modifier was 1:3:0.3, then repeatedly washed with a large amount of ethanol, and dried at 140°C for 7 hours to obtain a second catalyst I9.

3. 92 g of the first catalyst C9 and 8 g of the second catalyst I9 were subjected to physical mixing to obtain a final molecular sieve catalyst composition J9 for the alkylation of the aromatic hydrocarbon and the olefin.

The characterization test results of the first catalyst C9 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; the static water contact angle test value is 30°; the molecular sieve content is 100%; the static water adsorption amount is 195 mg/g; the SiO₂/Al₂O₃ molar ratio is 30; the specific surface area is 412 m²/g, and the micropore volume is 0.18 cm³/g. The ²⁷Al MAS NMR spectrum shows that the aluminum at a total of 5 T sites of T1, T3, T4, T5, and T8 located in the intralayer ten-membered ring pore channel of the MCM-22 molecular sieve accounts for 55% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8, and the aluminum at the T2 site located in the surface half-supercage accounts for 12% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8. The SEM photograph shows that the MCM-22 molecular sieve has a sheet-like morphology, and the TEM photograph shows that the c-axis sheet thickness is 20.1-50.4 nm.

The characterization test results of the second catalyst I9 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 152°; the molecular sieve

content is 97%; the static water adsorption amount is 154 mg/g; the SiO₂/Al₂O₃ molar ratio is 25; the specific surface area is 602 m²/g, and the micropore volume is 0.19 cm³/g. The TEM photograph shows that the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

5 In the catalyst composition J9, the mass content of the first catalyst C9 is 92%, and the mass content of the second catalyst I9 is 8%.

The alkaline substance breakthrough tolerance coefficient of the catalyst composition J9 is 0.20, the ratio of the series reaction occurrence descriptor values is 0.81, and the ratio of the complex side reaction occurrence descriptor
10 values is 0.41.

The XRD pattern of the catalyst composition J9 shows that the peak intensity ratio of the peak at a 2θ angle of 7.1° to the peak at a 2θ angle of 7.4° is 2.77; and the peak intensity ratio of the peak at a 2θ angle of 22.6° to the peak at a 2θ angle of 26.0° in the XRD pattern is 0.63.

15

[Test Example 1]

The catalyst compositions J1-J9 prepared in Examples 1-4 and Comparative Examples 1-5 were respectively applied to the alkylation reaction of benzene and ethylene to produce ethylbenzene. Under the conditions of a
20 reaction temperature of 170°C, a pressure of 3.6 MPa, an ethylene mass hourly space velocity of 1.5 h⁻¹, and a benzene-to-ethylene molar ratio of 2.0, the ethylene conversion, the ethyl selectivity in the alkylation product, and the weight ratio of the heavy components having a boiling point higher than triethylbenzene to ethylbenzene in the product were tested. The ethylene
25 conversion (calculated on a molar basis) and the ethyl selectivity (calculated on a molar basis) were calculated according to the following formulas, and the test results are shown in Table 1.

ethylene conversion % = (inlet ethylene content - outlet ethylene content)

/ inlet ethylene content $\times 100\%$.

ethyl selectivity % = (moles of ethylbenzene + moles of diethylbenzene $\times 2$ + moles of triethylbenzene $\times 3$) / moles of ethylene consumed in the reaction $\times 100\%$.

5

Table 1 Test Results of Alkylation Reaction of Benzene and Ethylene to Produce Ethylbenzene

catalyst composition No.	ethylene conversion, %	ethyl selectivity, %	weight ratio of heavy components having a boiling point higher than triethylbenzene to ethylbenzene, mg/kg
J1	100.0	99.9	768
J2	100.0	99.9	650
J3	100.0	99.8	981
J4	100.0	99.8	928
J5	99.4	99.3	3043
J6	99.5	99.5	3258
J7	100.0	99.2	4680
J8	99.7	99.5	2758
J9	95.2	96.4	5479

It can be seen from Table 1 that the catalyst compositions J1-J4 of Examples 1-4 of the present invention are significantly superior to the catalyst compositions J5-J9 of the comparative examples in terms of the ethylene conversion, the ethyl selectivity, and the weight ratio of heavy components having a boiling point higher than triethylbenzene to ethylbenzene.

15

[Test Example 2]

The catalyst compositions J1-J9 prepared in Examples 1-4 and Comparative Examples 1-5 were respectively tested for their single-pass lifetime in the alkylation reaction of benzene and ethylene to produce ethylbenzene under reaction conditions with overproof alkaline impurities.

5 Tests were conducted under the conditions of a reaction temperature of 190°C, a pressure of 3.6 MPa, an ethylene mass hourly space velocity of 1.5 h⁻¹, a benzene-to-ethylene molar ratio of 2.0, and a mass content of alkaline impurities in the material of 3 ppm. The single-pass lifetime refers to the time taken from the start of the reaction until the ethylene conversion decreases to 40% of the
10 initial conversion. The test results are shown in Table 2 below, wherein the single-pass lifetime of the catalyst compositions J1-J4 is significantly longer than that of the catalyst compositions J5-J9.

Table 2 Test Results of Single-Pass Lifetime of Catalyst Compositions
15 under Reaction Conditions with Overproof Alkaline Impurities

catalyst composition No.	single-pass lifetime, h
J1	780
J2	854
J3	732
J4	744
J5	429
J6	318
J7	405
J8	347
J9	227

[Test Example 3]

The catalyst compositions J1-J9 prepared in Examples 1-4 and Comparative Examples 1-5 were respectively tested for their single-pass

lifetime in the alkylation reaction of benzene and ethylene to produce ethylbenzene under reaction conditions with overproof water impurities. Tests were conducted under the conditions of a reaction temperature of 190°C, a pressure of 3.6 MPa, an ethylene mass hourly space velocity of 1.5 h⁻¹, a benzene-to-ethylene molar ratio of 2.0, and a mass content of water impurities in the material of 1000 ppm. The single-pass lifetime refers to the time taken from the start of the reaction until the ethylene conversion decreases to 40% of the initial conversion. The test results are shown in Table 3 below, wherein the single-pass lifetime of the catalyst compositions J1-J4 is significantly longer than that of the catalyst compositions J5-J9.

Table 3 Test Results of Single-Pass Lifetime of Catalyst Compositions under Reaction Conditions with Overproof Water Impurities

catalyst composition No.	single-pass lifetime, h
J1	1076
J2	1148
J3	1021
J4	1034
J5	697
J6	503
J7	312
J8	522
J9	335

The specific embodiments of the present invention are described above in detail. However, the present invention is not limited thereto. Within the scope of the technical concept of the present invention, a variety of simple variations of the technical solutions of the present invention can be made, including combining various technical features in any other suitable manner.

These simple variations and combinations should also be considered as the contents of the present invention and all fall within the scope of protection of the present invention.

CLAIMS

1. A catalyst composition, comprising:

(a) a first catalyst, which is a molecular sieve catalyst having a static water
5 initial contact angle θ_1 of 10-15° and a static water adsorption amount of 220-
280 mg/g; and

(b) a second catalyst, which is a molecular sieve catalyst having a static
water initial contact angle θ_2 of 140-165° and a static water adsorption amount
of 130-170 mg/g.

10 2. The catalyst composition according to claim 1, characterized in that the
ratio of the static water initial contact angle θ_1 of the first catalyst to the static
water initial contact angle θ_2 of the second catalyst in the catalyst composition
is 1:(9.3-16).

3. The catalyst composition according to claim 1 or 2, characterized in that,
15 in an XRD pattern of the catalyst composition, a peak intensity ratio of a
peak at a 2θ angle of 7.1° ($\pm 0.1^\circ$) to a peak at a 2θ angle of 7.4° ($\pm 0.1^\circ$) is 2.0-
3.0, preferably 2.2-2.9; and/or

a peak intensity ratio of a peak at a 2θ angle of 22.6° ($\pm 0.1^\circ$) to a peak at a
 2θ angle of 26.0° ($\pm 0.1^\circ$) is 0.63-0.85, preferably 0.63-0.80; and/or

20 a mass ratio of the first catalyst to the second catalyst is 85-97:3-15,
preferably 88-95:5-12; and/or

a molecular sieve in the first catalyst is a silicoaluminate molecular sieve
having a twelve-membered ring pore structure, preferably an MWW-type
molecular sieve, more preferably an MCM-22, MCM-49, or MCM-56
25 molecular sieve; a molecular sieve in the second catalyst is a silicoaluminate
molecular sieve having a twelve-membered ring pore structure, preferably a
Beta molecular sieve.

4. The catalyst composition according to claim 3, characterized in that, in the first catalyst, aluminum at a total of 5 T sites of T1, T3, T4, T5 and T8 located in the intralayer ten-membered ring pore channel in the MWW-type molecular sieve (for example, the MCM-22 molecular sieve) accounts for $\leq 45\%$, preferably 10%-45%, more preferably 20%-45%, of aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7 and T8; and/or aluminum at T2 site accounts for $\geq 23\%$, preferably 23%-40%, more preferably 23%-35%, of aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7 and T8; preferably, the MCM-22 molecular sieve has a sheet-like morphology, c-axis sheet thickness L_a is 2.5-5.5 nm, dimension L_b perpendicular to c-axis crystal plane is 50-500 nm, and $L_b/L_a = 20-100$.

5. The catalyst composition according to any one of claims 1-4, characterized in that,

the first catalyst has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 15-60; and/or

the first catalyst has a specific surface area of 480-550 m^2/g ; and/or

the first catalyst has a micropore volume of 0.19-0.21 cm^3/g ; and/or

the second catalyst is a binder-free molecular sieve catalyst comprising a Beta molecular sieve connected with a bis-silyl group; preferably, the structural

formula of the bis-silyl group is

$$\begin{array}{c} \text{X1} \\ | \\ \text{X2}-\text{Si}-\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2-\text{Si}-\text{X5} \\ | \qquad \qquad | \\ \text{X3} \qquad \qquad \text{X4} \\ \qquad \qquad | \\ \qquad \qquad \text{X6} \end{array} \quad \text{and/or} \quad \begin{array}{c} \text{X7} \qquad \text{X10} \\ | \qquad | \\ \text{X8}-\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}-\text{X11} \\ | \qquad | \\ \text{X9} \qquad \text{X12} \end{array},$$

wherein X1-X12 represent the positions where the bis-silyl group is connected to the Beta molecular sieve; preferably, based on the mass of the catalyst, the mass content of the molecular sieve is 95%-98%, and/or, based on the mass of the catalyst, the mass content of the bis-silyl group calculated as silica is 2%-5%.

6. The catalyst composition according to any one of claims 3-5, characterized in that, the Beta molecular sieve in the second catalyst has a

granular morphology with a grain size of 5-20 nm; and/or

the molecular sieve in the second catalyst has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 16-50; and/or

the second catalyst has a specific surface area of 550-650 m^2/g ; and/or

5 the second catalyst has a micropore volume of 0.18-0.21 cm^3/g .

7. The catalyst composition according to any one of claims 1-6, characterized in that,

an alkaline substance breakthrough tolerance coefficient of the catalyst composition is 0.30-0.60; and/or

10 a ratio of series reaction occurrence descriptor values of the catalyst composition is 0.40-0.65; and/or

a ratio of complex side reaction occurrence descriptor values of the catalyst composition is 0.20-0.35.

8. A method for preparing the catalyst composition according to any one
15 of claims 1-7, comprising the following step:

subjecting the first catalyst and the second catalyst to physical mixing to obtain the catalyst composition.

9. The method according to claim 8, characterized in that the preparation method of the first catalyst comprises:

20 1) mixing a first molecular sieve raw powder, a first silicon source, a first silica sol, a first aluminum source and an additive, molding, and drying to obtain a first catalyst preform;

2) contacting the first catalyst preform with an organic base solution to obtain a first mixture;

25 3) treating the first mixture to obtain the first catalyst, wherein the treating may comprise sealed heating, calcination, and ammonium exchange,

wherein the additive is a mixture of at least two quaternary ammonium salts, for example a mixture of two quaternary ammonium salts.

10. The method according to claim 9, characterized in that the preparation method of the first catalyst comprises at least one of the following features:

(1) one quaternary ammonium salt (also referred to as "first quaternary

ammonium salt") has a structural formula of $\begin{array}{c} \text{H}_3\text{C} \quad \text{R1} \\ \diagdown \quad / \\ \text{N}^+ \\ / \quad \diagdown \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array} \text{X}^-$, wherein R1 is selected from C12-C20 alkyl, preferably C16-C18 alkyl, and X is selected from halogen atoms, preferably Cl or Br atoms, the first quaternary ammonium salt being for example selected from at least one of cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, octadecyltrimethylammonium bromide, and octadecyltrimethylammonium chloride;

(2) another quaternary ammonium salt (also referred to as "second

quaternary ammonium salt") has a structural formula of $\begin{array}{c} \text{R2} \\ \diagdown \\ \text{N}^+ \\ / \quad \diagdown \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array} \text{---} \text{CH}_2\text{CH}_2\text{CH}_2\text{---} \text{S}^-(\text{O})_2$, wherein R2 is selected from C1-C18 alkyl, preferably C2-C14 alkyl, the second quaternary ammonium salt being for example selected from at least one of dimethylethyl(3-sulfopropyl)ammonium salt, 3-sulfopropyltetradecyldimethylammonium, 3-sulfopropyldodecyldimethylbetaine, 3-(decyldimethylammonio)propane-1-sulfonate inner salt, and 3-(N,N-dimethyloctylammonio)propane-1-sulfonate inner salt;

(3) the molar ratio of the first quaternary ammonium salt to the second quaternary ammonium salt is 1:(0.03-0.12), more preferably 1:(0.05-0.1);

(4) in step 1), the molecular sieve raw powder, the silicon source, and the silica sol are all calculated as SiO₂, the aluminum source is calculated as Al₂O₃, and the molar ratio of the molecular sieve raw powder, the silicon source, the silica sol, the aluminum source, and the additive is (0.2-1.0):1:(1.5-3.0):(0.04-0.27):(0.1-0.2), and the molar ratio of the total SiO₂ in the silicon source and the silica sol to the Al₂O₃ in the aluminum source is preferably 15-60:1;

(5) in step 2), the organic base solution is selected from at least one of hexamethyleneimine aqueous solution, piperidine aqueous solution, piperazine aqueous solution, trimethylcyclohexylammonium hydroxide aqueous solution, and dimethylethylcyclohexylammonium hydroxide aqueous solution; and/or
5 the mass concentration of the template solution is 8%-12%;

(6) in step 2), the mass ratio of the catalyst preform to the template solution is 1:(1.7-3);

(7) in step 3), the sealed heating treatment comprises subjecting the mixture to standing or stirring in a sealed space at 130-180°C for 24-72 hours.

10 11. The method according to any one of claims 8-10, characterized in that the preparation method of the second catalyst comprises:

a) contacting a second molecular sieve raw powder with a first aromatic hydrocarbon and a first modifier, and drying to obtain a modified second molecular sieve raw powder;

15 b) mixing the modified second molecular sieve raw powder with a second silicon source, a second aluminum source, and a second silica sol, molding, and drying to obtain a second catalyst preform;

c) contacting the second catalyst preform with a structure-directing agent solution to obtain a second mixture;

20 d) treating the second mixture to obtain a second catalyst precursor, wherein the treating may comprise sealed heating, calcination, and ammonium exchange;

e) contacting the second catalyst precursor with a pore-forming liquid, and treating to obtain a modified second catalyst precursor, wherein the treating may
25 comprise sealed heating and calcination;

f) contacting the modified second catalyst precursor with a second aromatic hydrocarbon and a second modifier, and treating to obtain the second catalyst, wherein the treating may comprise sealed heating, washing, and drying,

wherein the first modifier and the second modifier are different.

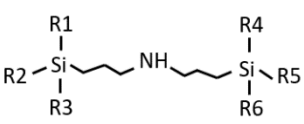
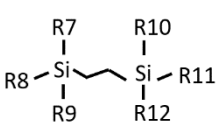
12. The method according to claim 11, characterized in that the preparation method of the second catalyst comprises at least one of the following features:

(1) the first aromatic hydrocarbon is selected from at least one of benzene, ethylbenzene, and toluene;

(2) the first modifier is a silazane, the silazane being preferably selected from at least one of hexamethyldisilazane, hexamethyldisilurea, N,O-bis(trimethoxyalkyl)acetamide, and tetramethyldivinylsilazane;

(3) the second aromatic hydrocarbon is selected from at least one of benzene, ethylbenzene, and toluene;

(4) the second modifier is a bis-silane, the structural formula of which is

preferably  and/or , wherein R1-R12 are each independently selected from C1-C6 alkoxy and C1-C6 alkoxy-C1-C6 alkyl, preferably each independently methoxy, ethoxy, or 3-methoxypropyl; preferably, the bis-silane is at least one of bis[(3-triethoxysilyl)propyl]amine, bis[(3-trimethoxysilyl)propyl]amine, and 1,2-bis(triethoxysilyl)ethane.

13. A method for the alkylation of an aromatic hydrocarbon and an olefin, comprising contacting the aromatic hydrocarbon with the olefin in the presence of the catalyst composition according to any one of claims 1-7 or the catalyst composition prepared by the method according to any one of claims 8-12 to carry out an alkylation reaction to obtain an alkyl aromatic hydrocarbon;

preferably, the aromatic hydrocarbon is selected from at least one of benzene and alkylbenzene, preferably selected from at least one of benzene, toluene, ethylbenzene, propylbenzene, and butylbenzene; preferably, the olefin is selected from C2-C6 olefins, preferably selected from at least one of ethylene, propylene, and butylene;

preferably, the conditions of the alkylation reaction comprise: a reaction temperature of 120-250°C, a reaction pressure of 2.0-5.0 MPa, an olefin mass hourly space velocity of 0.5-3.0 h⁻¹, and an aromatic hydrocarbon-to-olefin molar ratio of 1.0-3.0.

- 5 14. Use of the catalyst composition according to any one of claims 1-7 or the catalyst composition prepared by the method according to any one of claims 8-12 in the alkylation reaction of an aromatic hydrocarbon and an olefin.