Beta Molecular Sieve Catalyst, Preparation therefor and Use Thereof

TECHNICAL FIELD

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

BACKGROUND TECHNOLOGY

The alkyl aromatic hydrocarbon is an important basic organic raw material with very extensive uses and play an important role in the development of the national economy. In particular, isopropyltoluene, also known as cymene, has extensive uses and is an important organic chemical raw material. Isopropyltoluene has three isomers, which are respectively p-isopropyltoluene, m-isopropyltoluene, and o-isopropyltoluene.

Among them, p-isopropyltoluene is mainly used for the production of p-cresol, and further for the manufacture of plasticizers, disinfectants, or as a raw material for dyes and pesticides. m-Isopropyltoluene is mainly used for the production of m-cresol with a very high added value. m-cresol is mainly used for the manufacture of insecticides or high-end pesticides, and can also be used as an intermediate for the manufacture of plasticizers or coatings.

The alkyl aromatic hydrocarbon can be prepared by the alkylation of the aromatic hydrocarbon and the olefin, and the alkylation of the aromatic hydrocarbon and the olefin is usually carried out in the presence of an aromatic hydrocarbon alkylation catalyst. Therefore, a lot of researches on the aromatic hydrocarbon alkylation catalyst have been conducted in the art.

In particular, isopropyltoluene can be produced by the alkylation reaction

of toluene and propylene under the action of a molecular sieve. In the actual industrial production process, if the raw material of toluene or propylene contains water or alkaline impurities, the performance of the catalyst will be seriously affected, as affects the normal production. Specifically: first, if the industrial raw material of toluene or propylene contains impurity water, and if the catalyst does not have an excellent water resistance, water molecules will easily undergo a competitive adsorption with toluene or propylene molecules at the acidic active centers of the catalyst during the reaction process, resulting in the decreased catalytic performance. Second, if the industrial raw material of toluene or propylene carries alkaline substances, the alkaline substances very easily undergo acid-base neutralization reactions with the acidic active centers of the catalyst during the reaction process, resulting in the rapid alkaline poisoning and deactivation of the catalyst.

The prior art focuses on the development of aromatic hydrocarbon alkylation molecular sieve catalysts having a high activity or a high selectivity, and does not well solve the water resistance and the alkaline impurity resistance of the catalysts. Therefore, in order to ensure the long-term stable operation of the aromatic hydrocarbon alkylation (for example, the alkylation of toluene and propylene to produce isopropyltoluene) industrial units, it is quite important to develop the molecular sieve catalysts having a good water resistance and an alkaline impurity resistance.

CONTENTS OF THE INVENTION

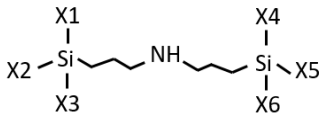
The present invention provides a Beta molecular sieve catalyst, a preparation therefor and a use thereof. When used in the reaction for preparing an alkyl aromatic hydrocarbon by the alkylation of an aromatic hydrocarbon and an olefin, the catalyst has not only good activity and alkyl aromatic hydrocarbon selectivity, but also good water resistance and alkaline impurity resistance.

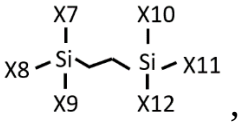
In a first aspect, the present invention provides a Beta molecular sieve catalyst, comprising a Beta molecular sieve connected with a bis-silyl group, wherein the catalyst has a static water initial contact angle of 140-165° and a static water adsorption amount of 130-170 mg/g.

In one embodiment of the above technical solutions, the static water initial contact angle is for example 145°, 152°, 157°, or 160°, and/or the static water adsorption amount is for example 135 mg/g, 140 mg/g, 145 mg/g, 150 mg/g, 154 mg/g, 160 mg/g, or 165 mg/g.

In one embodiment of the above technical solutions, the Beta molecular sieve catalyst is a binder-free molecular sieve catalyst.

In one embodiment of the above technical solutions, 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 bis-silyl group refers to an organic group containing two silicon atoms in one group. The structural formula of the bis-silyl group is preferably 

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 at one or more of the positions X1-X12.

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, for example 5-12 nm, 15-18 nm, or 16-20 nm.

In the above technical solutions, preferably, the SiO_2/Al_2O_3 molar ratio of the molecular sieve in the 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

catalyst is 550-650 m^2/g, for example 600-630 m^2/g.

In the above technical solutions, preferably, the micropore volume of the catalyst is 0.18-0.21 cm^3/g, for example 0.20 cm^3/g.

In a second aspect, the present invention provides a preparation method of the above Beta molecular sieve catalyst, comprising the following steps:

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

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

c) contacting the catalyst preform with a template agent solution to obtain a mixture;

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

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

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

wherein the first modifier and the second modifier are different.

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

the molecular sieve in the molecular sieve raw powder is a Beta molecular sieve;

the SiO_2/Al_2O_3 molar ratio of the molecular sieve raw powder is 16-50, for example 20-40, more specifically for example 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 tetramethyldivinyldisilazane;

the mass ratio of the 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);

the contacting comprises mixing and stirring the first aromatic hydrocarbon and the first modifier at 10-40°C for 5-30 minutes, then adding a 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 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 solutions, preferably, the step b) includes one or more of the following characteristics:

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

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

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

the modified molecular sieve raw powder, the silicon source, and the silica sol are all calculated as SiO_2, the aluminum source is calculated as Al_2O_3, and

the molar ratio of the modified molecular sieve raw powder, the silicon source, the silica sol, and the 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 silicon source and the silica sol to the Al_2O_3 in the 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 in the art may be used. For example, the extrusion molding may be employed;

In the above technical solutions, in step b), the 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 catalyst preform is 1.0-3.0 mm and the length is 2-10 mm.

In the above technical solutions, in the 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 technical solutions, preferably, the step c) includes one or more of the following characteristics:

the template agent solution is selected from at least one of tetraethylammonium hydroxide aqueous solution, tetraethylammonium bromide aqueous solution, trimethylcyclohexylammonium hydroxide aqueous solution, and dimethylethylcyclohexylammonium hydroxide aqueous solution;

the mass concentration of the template agent solution is 6%-15%, for example 10% or 12%;

the mass ratio of the catalyst preform to the template agent solution is 1:(1-1.5), for example 1:1.2.

In the above technical solutions, preferably, in the step d), the sealed

heating treatment comprises subjecting the mixture to standing or stirring in a sealed space at 140-170°C for 36-96 hours. In the step d), after the sealed heating treatment and before the calcination, conventional steps such as washing and drying may be included. The washing and the 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: a calcination temperature 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 and time of 1-5 hours. The ammonium salt may be at least one of ammonium chloride, ammonium sulfate, ammonium oxalate, and ammonium nitrate, and the mass concentration of the ammonium salt solution may be 1%-10%.

In the above technical solutions, preferably, the step e) includes 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 liquid is preferably 5%-15%;

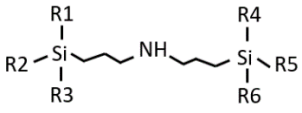
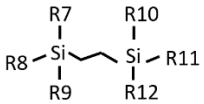
the mass ratio of the catalyst precursor to the pore-forming liquid is 1:(1.5-2), for example 1:1.7.

In the above technical solutions, preferably, the sealed heating treatment in the step e) comprises subjecting the catalyst precursor and the pore-forming liquid to standing or stirring at 160-180°C for 24-96 hours. In the 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: a calcination temperature of 520-580°C and calcination time of 4-8 hours.

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

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

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 selected from at least one of bis[(3-triethoxysilyl)propyl]amine, bis[(3-trimethoxysilyl)propyl]amine, and 1,2-bis(triethoxysilyl)ethane;

the mass ratio of the modified 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).

In the above technical solutions, preferably, the sealed heating treatment in the 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 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 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 reaction raw materials of the aromatic hydrocarbon and the olefin are contacted with the above Beta molecular sieve catalyst 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; preferably, 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 the catalyst may be a binder-free Beta molecular sieve catalyst, comprising a Beta molecular sieve connected with a bis-silyl group, and the static water initial contact angle and the static water adsorption amount of the catalyst are within specific ranges, wherein the static water initial contact angle is 140-165° and the static water adsorption amount is 130-170 mg/g. The catalyst having the above characteristics has not only good activity and selectivity in the alkylation reaction of toluene and propylene to produce isopropyltoluene, but also good water resistance and alkaline impurity resistance. If alkaline substances are

carried in the industrial raw material of toluene or propylene, the use of the above catalyst can ensure the long-term stable operation of the unit. In addition, the molecular sieve in the catalyst of the present invention may be small crystals of 5-20 nm and has a suitable pore structure, and further has good activity and selectivity.

2. During the preparation of the catalyst of the present invention, a stepwise modification treatment is carried out by using the first modifier and the second modifier, wherein the modification treatment with the first modifier is beneficial for inhibiting the growth of the grain size of the Beta molecular sieve, and a binder-free Beta molecular sieve catalyst having an ultra-small grain size can be obtained, with the grain size being only 5-20 nm, which can further improve the activity and the selectivity of the catalyst; the modification treatment with the second modifier enables the outer surface of the second catalyst to retain specific bis-silane modification components, which is beneficial for the water resistance during the reaction process, and simultaneously beneficial for rapidly adsorbing alkaline impurities, improving the overall poison resistance of the catalyst.

DESCRIPTION OF THE DRAWINGS

Figure 1 is an XRD pattern of the Beta molecular sieve catalyst prepared in Example 1 of the present invention;

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

Figure 3 is a TEM photograph of the Beta molecular sieve catalyst 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 the present invention is not limited by the specific embodiments.

In the present invention, an XRD pattern of the catalyst is obtained by 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 $0.3°\cdot min^{-1}$.

In the present invention, the static water initial contact angle of the molecular sieve is measured by using a JY-82C video contact angle measuring instrument from Chengde Dingsheng. An appropriate amount of ground powder sample is placed in a tableting machine and pressed into a sheet, which is then placed on a contact angle test platform. An automatic titration system of the equipment is used to drop a water droplet, a test photograph is taken, and then the contact angle is measured by using an angle measuring method.

In the present invention, the static water adsorption amount is measured by using a BSD-VVS multi-station gravimetric gas vapor adsorption instrument from BSD Instrument Technology 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 by 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 by using a Tecnai G220 S-TWIN transmission electron microscope.

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

volume is calculated by using the *t-plot* method.

In the present invention, the SiO_2/Al_2O_3 molar ratio is obtained by the ICP testing that is performed by using a Model S-35 ICP-AES analyzer from Kontron to obtain the data of the silica-alumina ratio.

[Example 1]

The example is used for preparing a Beta molecular sieve catalyst. The specific preparation process is as follows:

500 g of toluene and 10 g of N,O-bistrimethoxyalkylacetamide were mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder A1, wherein the mass ratio of the molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:5:0.1. Then, 18 g of the modified molecular sieve raw powder A1, 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 molecular sieve raw powder, the silicon powder, the silica sol, and the aluminum source was 0.3:1:1.5:0.1; and then, a strip-shaped catalyst preform B1 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 catalyst preform B1 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a mixture C1. The mixture C1 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 catalyst precursor D1. 100 g of the catalyst precursor D1 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 catalyst precursor E1. 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 catalyst precursor E1 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified 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 catalyst F1.

The characterization test results of the catalyst F1 are as follows: the XRD pattern is shown in Figure 1, having characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test photograph is shown in Figure 2, with a value of 152°; the mass content of the Beta molecular sieve in the catalyst is 97.0%; the static water adsorption amount is 154 mg/g; the SiO_2/Al_2O_3 molar ratio is 25; the specific surface area of the catalyst is 602 m^2/g, and the micropore volume is 0.19 cm^3/g. The TEM photograph of the catalyst F1 is shown in Figure 3, wherein the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

[Example 2]

The example is used for preparing a Beta molecular sieve catalyst. The specific preparation process is as follows:

1000 g of toluene and 20 g of tetramethyldivinyldisilazane were mixed and stirred at 40°C for 5 minutes, added with 100 g of Beta molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder A2, wherein the mass ratio of the molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:10:0.2. Then, 30 g of the modified molecular sieve raw powder A2, 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 molecular sieve raw powder, the silicon powder, the silica sol, and the aluminum source was 0.5:1:2.5:0.22, and then, a strip-shaped catalyst preform B2 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 catalyst preform B2 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 mixture C2. The mixture C2 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 catalyst precursor D2. 100 g of the catalyst precursor D2 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 catalyst precursor E2. 500 g of benzene and 50 g of 1,2-bis(triethoxysilyl)ethane were mixed and stirred at 80°C for 10 minutes,

then added with 100 g of the modified catalyst precursor E2 and allowed to stand at 140°C for 30 minutes, wherein the mass ratio of the modified 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 catalyst F2.

The characterization test results of the catalyst F2 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 mass content of the Beta molecular sieve in the catalyst is 95.0%; the static water adsorption amount is 130 mg/g; the SiO_2/Al_2O_3 molar ratio is 16; the specific surface area of the catalyst is 648 m^2/g, and the micropore volume is 0.21 cm^3/g. The TEM photograph of the catalyst F2 shows that the Beta molecular sieve has a granular morphology with a grain size of 5-12 nm.

[Example 3]

The example is used for preparing a Beta molecular sieve catalyst. The specific preparation process is as follows:

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 (SiO_2/Al_2O_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 molecular sieve raw powder A3, wherein the mass ratio of the molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:1.5:0.05. Then, 6 g of the modified molecular sieve raw powder A3, 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 molecular sieve raw powder, the silicon powder, the silica sol, and the aluminum source was

0.1:1:1:0.04. Then, a strip-shaped catalyst preform B3 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 catalyst preform B3 was immersed in 100 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 6%) to obtain a mixture C3. The mixture C3 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 catalyst precursor D3. 100 g of the catalyst precursor D3 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 catalyst precursor E3. 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 catalyst precursor E3 and allowed to stand at 100°C for 60 minutes, wherein the mass ratio of the modified 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 catalyst F3.

The characterization test results of the catalyst F3 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 mass content of the Beta molecular sieve in the catalyst is 98.0%; the static water adsorption amount is 170 mg/g; the SiO_2/Al_2O_3 molar ratio is 50; the specific surface area of the catalyst is 551 m^2/g, and the micropore volume is 0.18 cm^3/g. The TEM photograph of the catalyst F3 shows that the Beta molecular sieve has a granular morphology with a grain size of 16-20 nm.

[Comparative Example 1]

The example merely differs from Example 1 in that: in the process of preparing the catalyst, the first modifier of N,O-bistrimethoxyalkylacetamide was not added. The specific preparation process of the catalyst is as follows:

500 g of toluene was mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder A4. Then, 18 g of the modified molecular sieve raw powder A4, 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 molecular sieve raw powder, the silicon powder, the silica sol, and the aluminum source was 0.3:1:1.5:0.1; and then, a strip-shaped catalyst preform B4 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 catalyst preform B4 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a mixture C4. The mixture C4 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 catalyst precursor D4. 100 g of the catalyst precursor D4 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 catalyst precursor

E4. 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 catalyst precursor E4 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified 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 catalyst F4.

The characterization test results of the catalyst F4 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 131°; the mass content of the Beta molecular sieve in the catalyst is 97.5%; the static water adsorption amount is 184 mg/g; the SiO_2/Al_2O_3 molar ratio is 25; the specific surface area of the catalyst is 508 m^2/g, and the micropore volume is 0.20 cm^3/g. The TEM photograph of the catalyst F4 shows that the Beta molecular sieve has a granular morphology with a grain size of 36-55 nm.

[Comparative Example 2]

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

500 g of toluene and 10 g of N,O-bistrimethoxyalkylacetamide were mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder A5, wherein the mass ratio of the molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:5:0.1. Then, 18 g of the modified molecular sieve raw powder A5, 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 molecular sieve raw powder, the silicon powder, the silica sol, and the aluminum source was 0.3:1:1.5:0.1; and then, a strip-shaped catalyst preform B5 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 catalyst preform B5 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a mixture C5. The mixture C5 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 catalyst precursor D5. 100 g of the catalyst precursor D5 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 catalyst precursor E5. 300 g of ethylbenzene was stirred at 60°C for 15 minutes, then added with 100 g of the modified catalyst precursor E5 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 catalyst F5.

The characterization test results of the catalyst F5 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 mass content of the Beta molecular sieve in the catalyst is 99.0%; the static water adsorption amount is 201 mg/g; the SiO_2/Al_2O_3 molar ratio is 25; the specific surface area of the catalyst is 626 m^2/g, and the micropore volume is 0.20 cm^3/g. The TEM photograph of the catalyst F5 shows that the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

[Comparative Example 3]

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

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 (SiO_2/Al_2O_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 molecular sieve raw powder A6. Then, 18 g of the modified molecular sieve raw powder A6, 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 molecular sieve raw powder, the silicon powder, the silica sol, and the aluminum source was 0.3:1:1.5:0.1; and then, a strip-shaped catalyst preform B6 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 catalyst preform B6 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a mixture C6. The mixture C6 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 catalyst precursor D6. 100 g of the catalyst precursor D6 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 catalyst precursor E6. 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 catalyst precursor E6 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the modified 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 catalyst F6.

The characterization test results of the catalyst F6 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 mass content of the Beta molecular sieve in the catalyst is 97.3%; the static water adsorption amount is 181 mg/g; the SiO_2/Al_2O_3 molar ratio is 25; the specific surface area of the catalyst is 526 m^2/g, and the micropore volume is 0.19 cm^3/g. The TEM photograph of the catalyst F6 shows that the Beta molecular sieve has a granular morphology with a grain size of 28-45 nm.

[Comparative Example 4]

The example merely differs from Example 1 in that: the pore-forming liquid treatment in step e) of the preparation process was not carried out. The specific preparation process of the catalyst is as follows:

500 g of toluene and 10 g of N,O-bistrimethoxyalkylacetamide were mixed and stirred at 20°C for 20 minutes, added with 100 g of Beta molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder A7, wherein the mass ratio of the molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier was 1:5:0.1. Then, 18 g of the modified

molecular sieve raw powder A7, 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 molecular sieve raw powder, the silicon powder, the silica sol, and the aluminum source was 0.3:1:1.5:0.1; and then, a strip-shaped catalyst preform B7 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 catalyst preform B7 was immersed in 120 g of tetraethylammonium hydroxide aqueous solution (mass concentration of 10%) to obtain a mixture C7. The mixture C7 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 catalyst precursor D7. 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 catalyst precursor D7 and allowed to stand at 120°C for 50 minutes, wherein the mass ratio of the 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 catalyst F7.

The characterization test results of the catalyst F7 are as follows: the XRD pattern has characteristic diffraction peaks of a typical Beta molecular sieve; the static water contact angle test value is 102°; the mass content of the Beta molecular sieve in the catalyst is 98.5%; the static water adsorption amount is 189 mg/g; the SiO_2/Al_2O_3 molar ratio is 25; the specific surface area of the catalyst is 483 m^2/g, and the micropore volume is 0.17 cm^3/g. The TEM photograph of the catalyst F7 shows that the Beta molecular sieve has a granular morphology with a grain size of 15-18 nm.

[Test Example 1]

The catalysts F1-F7 prepared in Examples 1-3 and Comparative Examples 1-4 were respectively tested for their single-pass lifetime in the alkylation reaction of toluene and propylene to produce isopropyltoluene under reaction conditions with overproof water and alkaline impurities. Tests were conducted under the conditions of a reaction temperature of 230°C, a pressure of 3.5 MPa, a propylene mass hourly space velocity of 2.0 h^{-1}, a toluene-to-propylene molar ratio of 3.0, a mass content of water impurities in the material of 1000 ppm, and a mass content of alkaline impurities of 3.5 ppm. The single-pass lifetime refers to the time taken from the start of the reaction until the propylene conversion decreases to 45% of the initial conversion. The test results are shown in Table 1 below, wherein the single-pass lifetime of catalysts F1-F3 is significantly longer than that of catalysts F4-F7.

Table 1 Test Results of Single-Pass Lifetime of Catalysts under Reaction Conditions with Overproof Water and Alkaline Impurities

Catalyst No.	Single-Pass Lifetime, h
F1	644
F2	723
F3	670
F4	291
F5	214
F6	338
F7	239

[Test Example 2]

The catalysts F1-F7 prepared in Examples 1-3 and Comparative Examples 1-4 were respectively applied to the alkylation reaction of toluene and propylene

to produce isopropyltoluene. Under the conditions of a reaction temperature of 220°C, a pressure of 3.5 MPa, a propylene mass hourly space velocity of 1.5 h^{-1}, and a toluene-to-propylene molar ratio of 3.0, the propylene conversion and the isopropyltoluene selectivity in the alkylation product were tested. The propylene conversion (calculated on a molar basis) and the isopropyltoluene selectivity (calculated on a mass basis) were calculated according to the following formulas, and the test results are shown in Table 2.

Propylene conversion % = (inlet propylene content - outlet propylene content) / inlet propylene content × 100%.

Isopropyltoluene selectivity % = mass of isopropyltoluene / total mass of alkylation product × 100%.

Table 2 Test Results of Alkylation Reaction of Toluene and Propylene to Produce Isopropyltoluene

Catalyst No.	Propylene Conversion, %	Isopropyltoluene Selectivity, %
F1	99.8	98.4
F2	99.9	98.6
F3	99.6	98.9
F4	92.2	93.3
F5	91.6	92.4
F6	94.7	96.1
F7	92.3	92.7

It can be seen from Table 2 that the catalysts F1-F3 are significantly superior to the catalysts F4-F7 in terms of the propylene conversion and the isopropyltoluene selectivity.

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

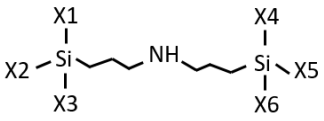
1. A Beta molecular sieve catalyst, characterized in that the catalyst comprises a Beta molecular sieve connected with a bis-silyl group, wherein the catalyst has a static water initial contact angle of 140-165° and a static water adsorption amount of 130-170 mg/g.

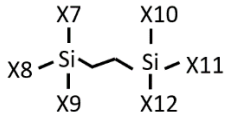
2. The Beta molecular sieve catalyst according to claim 1, characterized in that,

the catalyst is a binder-free molecular sieve catalyst, and/or

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%.

3. The Beta molecular sieve catalyst according to claim 1 or 2, characterized in that, the bis-silyl group has a structural formula of 

and/or 

, wherein X1-X12 represent positions where the bis-silyl group is connected to the Beta molecular sieve

4. The Beta molecular sieve catalyst according to any one of claims 1 to 3, characterized in that, the Beta molecular sieve in the catalyst has a granular morphology with a grain size of 5-20 nm, and/or

the Beta molecular sieve has a SiO_2/Al_2O_3 molar ratio of 16-50, and/or

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

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

5. A method for preparing the Beta molecular sieve catalyst according to any one of claims 1 to 4, comprising the following steps:

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

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

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

c) contacting the catalyst preform with a template agent solution to obtain a mixture;

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

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

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

wherein the first modifier and the second modifier are different.

6. The method according to claim 5, characterized in that, the step a) includes one or more of the following characteristics:

(1) the molecular sieve raw powder is a Beta molecular sieve;

(2) the SiO_2/Al_2O_3 molar ratio of the molecular sieve raw powder is 16-50;

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

(4) the first modifier is a silazane, the silazane being preferably selected from at least one of hexamethyldisilazane, hexamethyldisilurea, N,O-bistrimethoxyalkylacetamide, and tetramethyldivinyldisilazane;

(5) the mass ratio of the molecular sieve raw powder, the first aromatic hydrocarbon, and the first modifier is 1:(1.5-10):(0.05-0.2);

(6) the contacting comprises mixing and stirring the first aromatic

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

7. The method according to claim 5 or 6, characterized in that, the step b) includes one or more of the following characteristics:

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

(2) the silicon source is selected from silicon powder, preferably having a particle size of 10 nm-2000 nm;

(3) the silica sol is an alkaline silica sol;

(4) in the silica sol, the mass content of silica is 35%-60%;

(5) the modified molecular sieve raw powder, the silicon source, and the silica sol are all calculated as SiO_2, the aluminum source is calculated as Al_2O_3, and the molar ratio of the modified molecular sieve raw powder, the silicon source, the silica sol, and the aluminum source is (0.1-0.5):1:(1.0-2.5):(0.04-0.22), and preferably, the molar ratio of the total SiO_2 in the silicon source and the silica sol to the Al_2O_3 in the aluminum source is 16-50:1;

and/or, the step c) includes one or more of the following characteristics:

(1) the template agent solution is selected from at least one of tetraethylammonium hydroxide aqueous solution, tetraethylammonium bromide aqueous solution, trimethylcyclohexylammonium hydroxide aqueous solution, and dimethylethylcyclohexylammonium hydroxide aqueous solution;

(2) the mass concentration of the template agent solution is 6%-15%;

(3) the mass ratio of the catalyst preform to the template agent solution is 1:(1-1.5);

and/or, in the step d), the sealed heating treatment comprises subjecting the mixture to standing or stirring in a sealed space at 140-170°C for 36-96 hours.

8. The method according to any one of claims 5 to 7, characterized in that, the step e) includes one or more of the following characteristics:

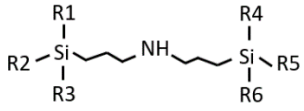
(1) the pore-forming liquid is a tetraethylammonium hydroxide aqueous solution or a mixed aqueous solution of tetraethylammonium hydroxide and tetraethylammonium bromide, and the mass concentration of the pore-forming liquid is preferably 5%-15%;

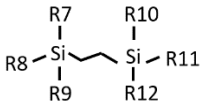
(2) the mass ratio of the catalyst precursor to the pore-forming liquid is 1:(1.5-2).

(3) the sealed heating treatment comprises subjecting the catalyst precursor and the pore-forming liquid to standing or stirring at 160-180°C for 24-96 hours.

9. The method according to any one of claims 5 to 8, characterized in that, the step f) includes one or more of the following characteristics:

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

(2) 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 selected from at least one of bis[(3-triethoxysilyl)propyl]amine, bis[(3-trimethoxysilyl)propyl]amine, and 1,2-bis(triethoxysilyl)ethane;

(3) the mass ratio of the modified catalyst precursor, the second aromatic hydrocarbon, and the second modifier is 1:(1.5-5.0):(0.1-0.5);

(4) the sealed heating treatment 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.

10. 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 Beta molecular sieve catalyst according to any one of claims 1 to 4 or the Beta molecular sieve catalyst prepared by the method according to any one of claims 5 to 9 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; and

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.

11. Use of the Beta molecular sieve catalyst according to any one of claims 1 to 4 or the Beta molecular sieve catalyst prepared by the method according to any one of claims 5 to 9 in the alkylation reaction of an aromatic hydrocarbon and an olefin.