MWW-Type 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 an MWW-type molecular sieve catalyst, a preparation therefor and a use thereof for the alkylation of an aromatic hydrocarbon and an olefin.

BACKGROUND TECHNOLOGY

An 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, ethylbenzene is mainly used downstream for the production of styrene, and is further used as a raw material monomer for the synthesis of polystyrene, styrene-butadiene rubber, ABS and SBS polymers, the use of which is quite extensive.

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 where series and parallel side reactions coexist. In addition to 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 by-products, in the actual industrial production, an excess of raw material benzene needs to be added to the reaction system, and the molar ratio of benzene to ethylene is much higher than the stoichiometric ratio of 1:1. The excessive 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 selectivity and a low benzene-to-ethylene ratio is particularly important for reducing the benzene-to-ethylene ratio in the actual reaction process and for the energy saving and the consumption reduction of the unit.

The MCM-22 molecular sieve belonging to the MWW topological structure has a layered structure, and its layer surface is rich in the "cup-shaped" half-supercages. The diffusion resistance of reaction molecules at the half-supercages is small, which is beneficial for the rapid conversion of reactants and the rapid diffusion of products out of the reaction system, suppressing the occurrence of side reactions and improving selectivity. Therefore, MWW-type molecular sieves have achieved good application effects in various catalytic reactions, especially alkylation reactions. CN201911019842.0 discloses a liquid-phase alkylation catalyst and a preparation method therefor and an application thereof, as well as a method for the liquid-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 cm^3/g. The use of the catalyst is beneficial for improving ethylene conversion and ethyl selectivity. However, under the applicable process conditions of the catalyst, the ethylene conversion is still lower than 99.8%, and the ethyl selectivity is lower than 99.7%, which presents problems of the low conversion and the low selectivity.

Industrial catalysts have a certain shape, so it is necessary to carry out a molding treatment on the synthesized molecular sieve powder. In order to meet mechanical strength requirements, a large amount of binder needs to be added

during the molding process. The addition of the binder will bring a series of negative effects, such as diluting the active centers of the catalyst, blocking the micropore channels of the molecular sieve, slowing down the diffusion rate of reaction molecules, reducing the conversion while increasing the probability of side reactions, as well as reducing selectivity. 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, 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 mention solving the problem of catalyst selectivity.

CN201811248443.7 discloses a method for synthesizing MWW structural ultra-thin nanosheet molecular sieves. Alkanes, cycloalkanes or aromatic hydrocarbons are introduced into the conventional MWW structural molecular sieve synthesis system to obtain thin-layer SCM-1, SCM-2, SCM-6, MIT-1 or ITQ-2 molecular sieve powders. However, in the actual application, the molecular sieve powders still need to be mixed and molded with a large amount of binder, and the problems of the low conversion and the low selectivity of the catalyst still exist.

CONTENTS OF THE INVENTION

In view of the deficiencies in the prior art, the present invention provides an MWW-type molecular sieve catalyst, a preparation thereofor 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 can effectively suppress side reactions, has high activity and selectivity, and is simultaneously applicable to feed conditions with a lower molar ratio of the aromatic hydrocarbon to the olefin.

In a first aspect, the present invention provides an MWW-type molecular sieve catalyst, wherein 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 molecular sieve accounts for ≤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 aluminum at the T2 site accounts for ≥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.

In one embodiment of the above technical solutions, 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 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, T5, T6, T7 and T8.

In one embodiment of the above technical solutions, the MWW-type molecular sieve catalyst is a binder-free molecular sieve catalyst, and/or the static water initial contact angle of the MWW-type molecular sieve catalyst is 10-15°, for example 11° or 12°, the static water adsorption amount is 220-280 mg/g, for example 247 mg/g, 256 mg/g or 270 mg/g, and/or, based on the mass of the catalyst, the mass content of the molecular sieve is 98%-100%.

In one embodiment of the above technical solutions, the MWW-type molecular sieve catalyst is a silicoaluminate molecular sieve catalyst having a twelve-membered ring pore structure, preferably an MCM-22, MCM-49 or MCM-56 molecular sieve catalyst. Preferably, in the MCM-22 molecular sieve catalyst, the MCM-22 molecular sieve 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 SiO_2/Al_2O_3 molar ratio of the MWW-type molecular sieve catalyst is 15-60:1, for example 30:1.

In the above technical solutions, preferably, the specific surface area of the MWW-type molecular sieve catalyst is 480-550 m^2/g, for example 500 m^2/g, 520 m^2/g.

In the above technical solutions, preferably, the micropore volume of the MWW-type molecular sieve catalyst is 0.19-0.21 cm^3/g, for example 0.20 cm^3/g.

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

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

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

3) treating the mixture to obtain the MWW-type molecular sieve 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.

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

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

the SiO_2/Al_2O_3 molar ratio of the molecular sieve raw powder is 15-60:1, for example 30:1;

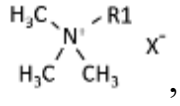
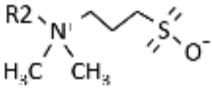
the aluminum source is selected from at least one of aluminum chloride, aluminum nitrate, aluminum sulfate, aluminum isopropoxide, pseudo-boehmite,

aluminum hydroxide, and sodium metaaluminate;

the silicon source is selected from silicon powder (i.e., silica powder), the particle size of which is preferably 10 nm-1000 nm, for example 100 nm;

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

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

one quaternary ammonium salt (also referred to as "first quaternary ammonium salt") has a structural formula of , wherein R1 is selected from C12-C20 alkyl, preferably C16-C18 alkyl, and X is selected from halogen atoms, preferably Cl or Br atoms; and/or, the other quaternary ammonium salt (also referred to as "second quaternary ammonium salt") has a structural formula of , wherein R2 is selected from C1-C18 alkyl, preferably C2-C14 alkyl; and

the molar ratio of the one quaternary ammonium salt to the other quaternary ammonium salt is preferably 1:(0.03-0.12), more preferably 1:(0.05-0.1), for example 1:0.075.

In the above technical solutions, preferably, in the step 1),

the first quaternary ammonium salt includes but is not limited to at least one of cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, octadecyltrimethylammonium bromide, and octadecyltrimethylammonium chloride; and/or

the second quaternary ammonium salt includes but is not limited to 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; and/or

the 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 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), 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 silicon source and the silica sol to the Al_2O_3 in the aluminum source is preferably 15-60:1, for example 30:1.

In the above technical solutions, there is no strict limitation on the specific manner of the molding in the 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 the step 1), 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, for example 1.6 mm, 2.0 mm, and the length is 2-10 mm, for example 3-8 mm;

In the above technical solutions, in the 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 solutions, preferably, the step 2) has at least one of the following characteristics:

the template agent 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;

the mass concentration of the template agent solution is 8%-12%, for

example 10%;

the mass ratio of the catalyst preform to the template agent solution is 1:(1.7-3), for example 1:2.

In the above technical solutions, preferably, the sealed heating treatment in the step 3) comprises subjecting the 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 the step 3), after the sealed heating treatment and before the calcination, conventional steps such as washing, drying, ammonium exchange may be included. The washing may be carried out by a conventional method, for example, 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 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, wherein the ammonium salt used 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 a third aspect, the present invention provides a method for the alkylation of an aromatic hydrocarbon and an olefin, comprising contacting reaction raw materials of the aromatic hydrocarbon and the olefin with the above MWW-type molecular sieve catalyst 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, more preferably selected from at least one of

benzene, toluene, ethylbenzene, propylbenzene, and butylbenzene; preferably, the olefin is selected from C2-C6 olefins, more 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%.

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 MWW-type molecular sieve catalyst of the present invention may be a binder-free molecular sieve catalyst, and the mass content of the molecular sieve can be as high as 98%-100%. In the molecular sieve, 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 accounts for as low as ≤45% 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 accounts for ≥23% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7 and T8. Since the MWW-type molecular sieve has a special layered structure and three types of pore channels, which are respectively the half-supercages located on the layer surface, the supercages between layers, and the ten-membered rings located within the layers, and since the diffusion rate of reaction molecules is very slow under low-temperature reaction conditions in the liquid-phase alkylation reaction process of benzene and ethylene, so that the intralayer ten-membered rings are difficult to utilize, a reasonable aluminum distribution is crucial for improving the performance of the catalyst. The smaller the proportion of aluminum in the intralayer ten-membered ring pore channel, the greater the proportion of the aluminum distribution in the other two pore

channels, as is more favorable for the progress of the reaction process. In addition, the catalyst can have a specific contact angle and a specific static water adsorption amount, i.e. a static water initial contact angle of 10-15° and a static water adsorption amount of 220-280 mg/g. Preferably, the catalyst is an MCM-22 molecular sieve catalyst, wherein the MCM-22 molecular sieve has an ultra-thin layered structure, 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;

The inventors of the present invention have found through research that the MWW-type molecular sieve catalyst having the above characteristics has the advantages of an excellent diffusion performance and a good accessibility of active centers. In particular, in the liquid-phase alkylation reaction of the aromatic hydrocarbon and the olefin, the catalyst can effectively suppress side reactions, reduce the generation amount of heavy components, improve selectivity, thereby effectively reducing the molar ratio of the aromatic hydrocarbon to the olefin in the feed during the reaction process, which is beneficial for the energy saving and the consumption reduction, and the catalyst has a good activity.

2. The inventors of the present invention have found through further research that it is difficult to obtain a binder-free MCM-22 molecular sieve catalyst with a layer thickness of only 2.5-5.5 nm by conventional techniques. During the preparation of the catalyst in the present invention, an additive is added and cooperates with other steps, which effectively inhibits the interlayer adhesion and thickening growth of the MCM-22 molecular sieve during the crystallization process, thereby obtaining an ultra-thin, binder-free MCM-22 molecular sieve catalyst.

3. The catalyst 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 a pure ethylene, or may be off-gas with a low

ethylene concentration from FCC or DCC units, or a 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 MWW-type molecular sieve catalyst prepared in Example 1 of the present invention;

Figure 2 is an ^{27}Al MAS NMR spectrum of the MWW-type molecular sieve catalyst prepared in Example 1 of the present invention;

Figure 3 is a static water contact angle test photograph of the MWW-type molecular sieve catalyst prepared in Example 1 of the present invention;

Figure 4 is an SEM photograph of the MWW-type molecular sieve catalyst prepared in Example 1 of the present invention;

Figure 5 is a TEM photograph of the MWW-type 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 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 by 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 $Al(NO_3)_3$ solution (δ = 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.

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 (ambient temperature 25°C). An automatic titration system of the equipment is used to drop a water droplet (5 μL volume of deionized water), 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 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 using the *t-plot* method.

In the present invention, the SiO_2/Al_2O_3 molar ratio is obtained by 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 an MWW-type molecular sieve catalyst. The specific preparation process is as follows:

30 g of MCM-22 molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder, the silicon powder, the silica sol, the 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 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 catalyst preform A1 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a mixture B1. The 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 catalyst C1.

The characterization test results of the 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 ^{27}Al MAS NMR spectrum is shown in Figure 2, 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; 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 static water contact angle test photograph is shown in Figure 3, with a value of 12°; in the catalyst, the MCM-22 molecular sieve content is 100%; the static water adsorption amount is 247 mg/g; the SiO_2/Al_2O_3 molar ratio is 30; the specific surface area is 516 m^2/g, and the micropore volume is 0.20 cm^3/g. 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 La is 5.3-5.4 nm, the dimension Lb perpendicular to the c-axis crystal plane is 260-280 nm, and Lb/La = 48-53.

[Example 2]

The example is used for preparing an MWW-type molecular sieve catalyst. The specific preparation process is as follows:

60 g of MCM-22 molecular sieve (SiO_2/Al_2O_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, wherein the molar ratio of the molecular sieve raw powder, the silicon powder, the silica sol, the 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 catalyst preform A2 with a diameter of 1.6 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 catalyst preform A2 was immersed in 300 g of piperidine aqueous solution (mass concentration of 8%) to obtain a mixture B2. The 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, 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 C2.

The characterization test results of the catalyst C2 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 10°; 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 32% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8; 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. In the catalyst, the MCM-22 molecular sieve content is 100%; the static water adsorption amount is 280 mg/g; the SiO_2/Al_2O_3 molar ratio is 15; the specific surface area is 550 m^2/g, and the micropore volume is 0.21 cm^3/g. The c-axis sheet thickness La of the MCM-22 molecular sieve is 2.5-2.7 nm, the dimension Lb perpendicular to the c-axis crystal plane is 180-220 nm, and Lb/La = 67-88.

[Example 3]

The example is used for preparing an MWW-type molecular sieve catalyst. The specific preparation process is as follows:

12 g of MCM-22 molecular sieve (SiO_2/Al_2O_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 0.93 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, wherein the molar ratio of the molecular sieve raw powder, the silicon powder, the silica sol, the 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 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 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 mixture B3. The 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 catalyst C3.

The characterization test results of the 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 ^{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 40% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8; 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. In the catalyst, the MCM-22 molecular sieve content is 100%; the static water adsorption amount is 220 mg/g; the SiO_2/Al_2O_3 molar ratio is 60; the specific surface area is 480 m^2/g, and the micropore volume is 0.19 cm^3/g. The c-axis sheet thickness of the MCM-22 molecular sieve is 5.4-5.5 nm, the dimension Lb perpendicular to the c-axis crystal plane is 120-150 nm, and Lb/La = 22-27.

[Example 4]

This example is used for preparing an MWW-type molecular sieve catalyst. The specific preparation process is as follows:

30 g of MCM-22 molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder, the silicon powder, the silica sol, the aluminum source, and the 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 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 catalyst preform A4 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a mixture B4. The 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 catalyst C4.

The characterization test results of the catalyst C4 are as follows: the XRD pattern has characteristic diffraction peaks of a typical MCM-22 molecular sieve; 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 36% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8; 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 static water contact angle test value is 11°; in the catalyst, the MCM-22 molecular sieve content is 100%; the static water adsorption amount is 256 mg/g; the SiO_2/Al_2O_3 molar ratio is 30; the specific surface area is 501 m^2/g, and the micropore volume is 0.21 cm^3/g. 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 La is 5.2-5.4 nm, the dimension Lb perpendicular to the c-axis crystal plane is 250-270 nm, and Lb/La = 46-52.

[Comparative Example 1]

The example merely differs from Example 1 in that: in the process of

preparing the 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 is as follows:

30 g of MCM-22 molecular sieve (SiO_2/Al_2O_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 molecular sieve raw powder, the silicon powder, the silica sol, the aluminum source, and cetyltrimethylammonium bromide was 0.5:1:2:0.1:0.15; and then, a strip-shaped 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 catalyst preform A5 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a mixture B5. The 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 catalyst C5.

The characterization test results of the 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 ^{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 52% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8; 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. In the catalyst, the MCM-22 molecular sieve content is 100%; the static water adsorption amount is 205 mg/g; the SiO_2/Al_2O_3 molar ratio is 30; the specific surface area is 465 m^2/g, and the micropore volume is 0.20 cm^3/g. The c-axis sheet thickness La of the MCM-22 molecular sieve is 10.6-16.2 nm, the dimension Lb perpendicular to the c-axis crystal plane is 260-280 nm, and Lb/La = 16-26.

[Comparative Example 2]

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

30 g of MCM-22 molecular sieve (SiO_2/Al_2O_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 29.3 g of dimethylethyl(3-sulfopropyl)ammonium salt were uniformly mixed, wherein the molar ratio of the molecular raw sieve raw powder, the silicon powder, the silica sol, the aluminum source, and dimethylethyl(3-sulfopropyl)ammonium salt was 0.5:1:2:0.1:0.15; and then, a strip-shaped 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 catalyst preform A6 was immersed in 200 g of hexamethyleneimine aqueous solution (mass concentration of 10%) to obtain a mixture B6. The 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 mass concentration

of 5% at 50°C for 3 hours to obtain a catalyst C6.

The characterization test results of the 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 28°; 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 59% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7, and T8; 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. In the catalyst, the MCM-22 molecular sieve content is 100%; the static water adsorption amount is 186 mg/g; the SiO_2/Al_2O_3 molar ratio is 30; the specific surface area is 403 m^2/g, and the micropore volume is 0.19 cm^3/g. The c-axis sheet thickness of the MCM-22 molecular sieve is 16.0-26.5 nm, the dimension Lb perpendicular to the c-axis crystal plane is 260-280 nm, and Lb/La = 10-18.

[Test Example 1]

The catalysts C1-C6 prepared in Examples 1-4 and Comparative Examples 1-2 were respectively applied to the alkylation reaction of benzene and ethylene to produce ethylbenzene. Under the conditions of a reaction temperature of 180°C, a pressure of 3.5 MPa, an ethylene mass hourly space velocity of 2.5 h^{-1}, and a benzene-to-ethylene molar ratio of 1.5, the ethylene conversion, the ethyl selectivity in the alkylation product, and the weight ratio of heavy components having a boiling point higher than triethylbenzene to ethylbenzene in the product were tested. The ethylene 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 × 100%.

Ethyl selectivity % = (moles of ethylbenzene + moles of diethylbenzene × 2 + moles of triethylbenzene × 3) / moles of ethylene consumed in the reaction × 100%.

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

Catalyst No.	Ethylene Conversion, %	Ethyl Selectivity, %	Weight Ratio of Heavy Components Having a Boiling Point Higher than Triethylbenzene to Ethylbenzene, mg/kg
C1	99.9	99.8	1068
C2	100.0	99.9	820
C3	99.9	99.7	1321
C4	99.9	99.9	1089
C5	98.5	98.3	6043
C6	97.2	96.5	10258

It can be seen from the data in Table 1 that the technical solutions of Examples 1-4 of the present invention are significantly superior to the technical solutions of Comparative Examples 1-2 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.

The preferred 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. An MWW-type molecular sieve catalyst, characterized in that aluminum at a total of 5 T sites of T1, T3, T4, T5 and T8 located in an intralayer ten-membered ring pore channel in the molecular sieve accounts for ≤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 aluminum at T2 site accounts for ≥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.

2. The MWW-type molecular sieve catalyst according to claim 1, characterized in 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 in the molecular sieve accounts for 30%-42% 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% of the aluminum at a total of 8 T sites of T1, T2, T3, T4, T5, T6, T7 and T8, and/or

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

the catalyst has a static water initial contact angle of 10-15°, and a static water adsorption amount of 220-280 mg/g; and/or

based on the mass of the catalyst, the mass content of the molecular sieve is 98%-100%.

3. The MWW-type molecular sieve catalyst according to claim 1 or 2, characterized in that the catalyst is a silicoaluminate molecular sieve catalyst having a twelve-membered ring pore structure, preferably an MCM-22, MCM-49 or MCM-56 molecular sieve catalyst; preferably, in the MCM-22 molecular sieve catalyst, the MCM-22 molecular sieve has a sheet-like morphology, c-axis sheet thickness La is 2.5-5.5 nm, dimension Lb perpendicular to the c-axis crystal plane is 50-500 nm, and Lb/La = 20-100.

4. The MWW-type molecular sieve catalyst according to any one of claims 1 to 3, characterized in that,

the catalyst has a SiO_2/Al_2O_3 molar ratio of 15-60, and/or

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

the catalyst has a micropore volume of 0.19-0.21 cm^3/g.

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

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

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

3) treating the mixture to obtain the MWW-type molecular sieve 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.

6. The method according to claim 5, characterized in that, the step 1) has at least one of the following characteristics:

(1) the molecular sieve in the molecular sieve raw powder is a silicoaluminate molecular sieve having a twelve-membered ring pore structure, more preferably an MCM-22, MCM-49 or MCM-56 molecular sieve;

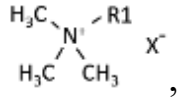
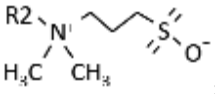
(2) the SiO_2/Al_2O_3 molar ratio of the molecular sieve raw powder is 15-60;

(3) 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;

(4) the silicon source is selected from silicon powder, the particle size of which is preferably 10 nm-1000 nm;

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

(6) in the silica sol, the mass content of silica is 30%-60%;

(7) one quaternary ammonium salt (also referred to as "first quaternary ammonium salt") has a structural formula of , wherein R1 is selected from C12-C20 alkyl, preferably C16-C18 alkyl, and X is selected from halogen atoms, preferably Cl or Br atoms; and/or, the other quaternary ammonium salt (also referred to as "second quaternary ammonium salt") has a structural formula of , wherein R2 is selected from C1-C18 alkyl, preferably C2-C14 alkyl; and

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

7. The method according to claim 5 or 6, characterized in that, in the step 1),

the first quaternary ammonium salt is at least one of cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, octadecyltrimethylammonium bromide, and octadecyltrimethylammonium chloride; and/or

the second quaternary ammonium salt is 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; and/or

the 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 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 SiO_2 in the silicon source and the silica sol to the

Al_2O_3 in the aluminum source is preferably 15-60:1.

8. The method according to any one of claims 5 to 7, characterized in that, in the step 2), the template agent 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

the mass concentration of the template agent solution is 8%-12%; and/or

the mass ratio of the catalyst preform to the template agent solution is 1:(1.7-3).

9. The method according to any one of claims 5 to 8, characterized in that, in the 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. A method for the alkylation of an aromatic hydrocarbon and an olefin, comprising contacting the aromatic hydrocarbon and the olefin in the presence of the MWW-type molecular sieve catalyst according to any one of claims 1 to 4 or the MWW-type 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 MWW-type molecular sieve catalyst according to any one

of claims 1 to 4 or the MWW-type 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.