

ZSM-23 zeolite and a preparation process and use thereof

5 Technical Field

The present invention relates to a ZSM-23 zeolite and a preparation process and use thereof, specifically to a mesopore-rich ZSM-23 zeolite and a preparation process and use thereof.

Background Technology

10 ZSM-23 zeolite is a zeolite material with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and MTT topology structure, and its one-dimensional tear-drop-shaped porous channels are constituted with 10-member rings. With its unique porous channel structure and adjustable acid properties, ZSM-23 zeolite is widely used in the fields of separation, adsorption, and catalysis, playing an irreplaceable role. Especially in the petrochemical industry, it has shown outstanding performance in the
15 hydrocracking of long-chain alkanes and olefins, the isomerization of alkanes and aromatic hydrocarbons, and the like. However, ZSM-23 is a microporous zeolite, which is limited in its ability to handle the conversion of larger molecules due to the porous channel size limitations. Therefore, in order to further expand its application range, it is of great significance to prepare high-performance mesopore-rich ZSM-23 zeolites.

20 There are currently few publicly available patents that introduce mesoporous structures into microporous ZSM-23 zeolites.

CN106513035 discloses a preparation method for composite zeolite with the ZSM-23 zeolite as the core and MCM-41 or SBA-15 as the shell. According to this method, the mesopores are provided by mesoporous zeolites MCM-41 or SBA-15. Due to its inherent stability and limited
25 range of silica-alumina ratio, the prepared composite zeolite also has disadvantages such as poor stability and narrow adjustable silica-alumina ratio range.

Cn105540607 discloses a preparation method for multi-stage pore channel composite zeolite ZSM-22/ZSM-23, but both ZSM-22 and ZSM-23 zeolites have microporous structures, so the mesoporous structures involved are mainly stacked pores, with poor regularity and stability.

According to CN107235497, starch is added to regulate the synthesis path of ZSM-23 zeolite, and calcined at a later stage to be removed, so as to obtain a ZSM-23 zeolite having a mesoporous-microporous hierarchical composite structure. This method has a simple process and low cost, but due to its mesoporous structure obtained by removing the pore expanding agent, it will affect thermal stability and hydrothermal stability.

Common methods for preparing micropore-mesopore composite zeolites include alkali or acid post-treatment, hard template method, surfactant method, etc, and the detailed processing processes have been reported multiple times in articles or patents. However, these methods may lead to the destruction of the microporous structure of the zeolite, resulting in poor stability of the products produced, or the process being too complex and costly, with worrying application prospects.

Therefore, developing a ZSM-23 zeolite rich in mesoporous structure with simple process, low cost, and excellent product performance is a technical problem that needs to be solved by those skilled in the art.

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Summary of the Invention

In order to overcome the shortcomings in the existing technology, the present invention provides a ZSM-23 zeolite and a preparation process thereof, and zeolite has a rich mesoporous structure and good hydrothermal stability.

20 The present invention provides a ZSM-23 zeolite, wherein the pore volume of mesopores having a pore size of 3-8 nm, preferably 3-6 nm of the zeolite is 45-90%, preferably 50-85%, further preferably 55-81% of the total pore volume of the zeolite; the zeolite has a relative crystallinity of 95-120%, and the zeolite has a relative crystallinity retention of 95-100% after a hydrothermal treatment with steam for 2 hours at 600°C.

25 According to the above-mentioned zeolite, the zeolite has a specific surface area of 300-430 m²/g, and a pore volume of 0.31-0.5 cm³/g, the specific surface area of micropores is 50-170 m²/g, and the specific surface area of mesopores is 150-310 m²/g; Preferably, the specific surface area is 320-405 m²/g, the pore volume is 0.34-0.45 cm³/g, the specific surface area of micropores is 80-140 m²/g, and the specific surface area of mesopores is 261-295 m²/g.

30 The present invention also provides a process for preparing the ZSM-23 zeolite, wherein the process comprises the following steps:

(1) preparing or selecting a silicon source for preparing the ZSM-23 zeolite, such as amorphous silica;

(2) performing an alkali treatment on the silicon source for preparing the ZSM-23 zeolite mentioned in step (1);

- 5 (3) preparing the ZSM-23 zeolite by using the alkali-treated amorphous silica as the silicon source.

In step (1) of the above-mentioned process, the silicon source used for preparing the ZSM-23 zeolite can be amorphous silica, as well as other silicon sources that are known in the art, such as one or more of fumed silica, silica sol, and water glass.

- 10 In step (1) of the above-mentioned process, said amorphous silica has a specific surface area of 600-1300 m²/g, preferably 700-1200 m²/g; a pore volume of 0.6-1.3 cm³/g, preferably 0.7-1.2 cm³/g; and a pore diameter of 1-15 nm, preferably 2-10 nm.

- In step (1) of the above-mentioned process, the preparation process of the amorphous silica is as follows: adding a silicon source to deionized water to be uniformly dispersed, and then
15 adding a surfactant and stirring; adjusting the pH of the resulting solution to 1-5, preferably 1.5-4, and then heating it in a water bath for a period of time; filtering, washing, drying, and calcining to produce the amorphous silica.

- According to the above-mentioned process, in the preparation of said amorphous silica, the silicon source is an inorganic silicon source, preferably one or more of water glass, silica sol,
20 or white carbon black.

According to the above-mentioned process, in the preparation of said amorphous silica, the surfactant is one or more of hexadecyltrimethylammonium chloride, hexadecyltrimethylammonium bromide, octodecyltrimethylammonium chloride, octodecyltrimethylammonium bromide.

- 25 According to the above-mentioned process, in the preparation of said amorphous silica, the molar ratio of said silicon source as SiO₂ to the surfactant is 1:(0.02-0.3), preferably 1:(0.05-0.2).

- According to the above-mentioned process, in the preparation of said amorphous silica, the molar ratio of said silicon source as SiO₂ to the deionized water is 1:(30-300), preferably
30 1:(50-220).

According to the above-mentioned process, in the preparation of said amorphous silica, the temperature for heating is 30-80°C, preferably 40-70°C, and the time for heating is 0.5-8 hours, preferably 3-6 hours.

In step (2) of the above-mentioned process, the alkali treatment involves adding the amorphous silica prepared in step (1) to an alkaline solution, heating and stirring.

According to the above-mentioned process, the alkali treatment is performed by using an inorganic alkali, and the inorganic alkali is one or more of sodium hydroxide, potassium hydroxide, or ammonia water.

According to the above-mentioned process, in said alkali treatment, the time for heating and stirring is 0.5-12 hours, preferably 2-8 hours; and the temperature for heating is 25-60°C, preferably 30-50°C.

According to the above-mentioned process, the molar ratio of the inorganic alkali as OH⁻ to the amorphous silica as SiO₂ is 0.05-0.24, preferably 0.06-0.22. The mole number of the inorganic alkali as OH⁻ can be obtained by conventional analytical chemistry means, the details of which will not be repeated herein.

In step (3) of the above-mentioned process, in the preparation of the ZSM-23 zeolite by using an alkali-treated amorphous silica as the silicon source, any known method for preparing the ZSM-23 zeolite in the existing technology can be used, or a method for preparing the ZSM-23 zeolite that is not yet known in the existing technology but will be known in the future can be used. For example, known methods had been disclosed, for example Rohrman Jr, A. C., et al. "The framework topology of ZSM-23: A high silica zeolite." Zeolites 5.6 (1985): 352-354, US4076842, US5405596, US5707601 and US7157075.

In step (3) of the above-mentioned process, preferably, an alkali-treated amorphous silica is used as the silicon source, the silicon source is mixed with an aluminum source, an alkali source (MOH), a template agent (R) and water to form a gel, which is crystallized, filtered, washed, dried and calcined to produce the ZSM-23 zeolite;

More preferably, in the gel, the molar ratio of the silicon source (as SiO₂):the aluminum source(as Al₂O₃):the alkali source (as hydroxide):the template agent:H₂O is 1:(0.003-0.03):(0.03-0.3):(0.05-2):(10-90); further preferably, in the gel, the molar ratio of the silicon source (as SiO₂):the aluminum source(as Al₂O₃):the alkali source (as hydroxide):the template agent:H₂O is 1:(0.005-0.02):(0.03-0.16):(0.08-1.6):(20-70); and/or

More preferably, the gel is crystallized at 150-200°C, preferably 170-180°C for 24-96 hours, preferably 36-72 hours, filtered, washed, dried, and calcined to produce the ZSM-23 zeolite; and/or

More preferably, the temperature for drying is 80-120°C, the time for drying is 4-12 hours, the
5 temperature for calcining is 500-600°C, the time for calcining is 2-6 hours.

Specifically, the present invention discloses the following technical solutions:

1. A ZSM-23 zeolite, which is characterized in that the pore volume of mesopores having a pore size of 3-8 nm, preferably 3-6 nm of the zeolite is 45-90%, preferably 50-85%, further preferably 55-81% of the total pore volume of the zeolite.
- 10 2. The ZSM-23 zeolite according to solution 1, which is characterized in that the zeolite has a relative crystallinity of 95-120%, and the zeolite has a relative crystallinity retention of 95-100% after a hydrothermal treatment with steam for 2 hours at 600°C.
3. The ZSM-23 zeolite according to any of the previous solutions, which is characterized in that the zeolite has a specific surface area of 300-430 m²/g, and a pore volume of 0.31-0.5
15 cm³/g, the specific surface area of micropores is 50-170 m²/g, and the specific surface area of mesopores is 150-310 m²/g, for example, the zeolite has a specific surface area of 320-405 m²/g, and a pore volume of 0.34-0.45 cm³/g, the specific surface area of micropores is 80-140 m²/g, and the specific surface area of mesopores is 261-295 m²/g.
4. The ZSM-23 zeolite according to any of the previous solutions, which is characterized in
20 that said ZSM-23 zeolite has an XRD pattern comprising the following characteristic peaks expressed by 2θ degree: about 11.3°±0.3° (for example ±0.2° or ±0.1°).
5. The ZSM-23 zeolite according to any of the previous solutions, which is characterized in that said ZSM-23 zeolite has an XRD pattern comprising the following characteristic peaks expressed by 2θ degree: 11.2-11.5°, 19.5-19.9°, 20.7-21.0°, 22.8-23.1°.
- 25 6. A process for preparing the ZSM-23 zeolite according to any of solutions 1-3, wherein the process comprises the following steps:
 - (1) preparing or selecting a silicon source for preparing the ZSM-23 zeolite, such as amorphous silica;
 - (2) performing an alkali treatment on the silicon source for preparing the ZSM-23 zeolite
30 mentioned in step (1);

- (3) preparing the ZSM-23 zeolite by using the alkali-treated amorphous silica as the silicon source.
7. Use of the alkali-treated amorphous silica obtained in step (2) of the process of solution 4 as the silicon source in the preparation of the ZSM-23 zeolite.
- 5 8. The process or use according to any of the previous solutions, which is characterized in that in step (1), said amorphous silica has a specific surface area of 600-1300 m²/g, preferably 700-1200 m²/g; a pore volume of 0.6-1.3 cm³/g, preferably 0.7-1.2 cm³/g; and a pore diameter of 1-13 nm, preferably 2-10 nm.
9. The process or use according to any of the previous solutions, which is characterized in that
- 10 in step (1), the preparation process of the amorphous silica is as follows: adding a silicon source to deionized water to be uniformly dispersed, and then adding a surfactant and stirring; adjusting the pH of the resulting solution to 1-5, preferably 1.5-4, and then heating it in a water bath for a period of time; filtering, washing, drying, and calcining to produce the amorphous silica.
- 15 10. The process or use according to any of the previous solutions, which is characterized in that in step (1), the silicon source is an inorganic silicon source, preferably one or more of water glass, silica sol, or white carbon black.
11. The process or use according to any of the previous solutions, which is characterized in that in step (1), the surfactant is one or more of hexadecyltrimethylammonium chloride,
- 20 hexadecyltrimethylammonium bromide, octadecyltrimethylammonium chloride, octadecyltrimethylammonium bromide.
12. The process or use according to any of the previous solutions, which is characterized in that in step (1), the molar ratio of said silicon source as SiO₂ to the surfactant is 1:(0.02-0.3), preferably 1:(0.05-0.2).
- 25 13. The process or use according to any of the previous solutions, which is characterized in that in step (1), the molar ratio of said silicon source as SiO₂ to the deionized water is 1:(30-300), preferably 1:(50-220).
14. The process or use according to any of the previous solutions, which is characterized in that in step (1), the temperature for heating is 30-80°C, preferably, 40-70°C, the time for heating is
- 30 0.5-8 hours, preferably, 3-6 hours.

15. The process or use according to any of the previous solutions, which is characterized in that in step (1), the temperature for drying is 80-120°C, the time for drying is 4-12 hours, the temperature for calcining is 500-600°C, the time for calcining is 2-6 hours.
16. The process or use according to any of the previous solutions, which is characterized in that in step (2), the alkali treatment involves adding the amorphous silica prepared in step (1) to an alkaline solution, heating and stirring.
17. The process or use according to any of the previous solutions, which is characterized in that in step (2), the alkali treatment is performed by using an inorganic alkali, and the inorganic alkali is one or more of sodium hydroxide, potassium hydroxide, or ammonia water.
18. The process or use according to any of the previous solutions, which is characterized in that in step (2), in the alkali treatment, the time for heating and stirring is 0.5-12 hours, preferably 2-8 hours; and the temperature for heating is 25-60°C, preferably 30-50°C.
19. The process or use according to any of the previous solutions, which is characterized in that in step (2), the molar ratio of the inorganic base as OH^- to the amorphous silica as SiO_2 is 0.05-0.24, preferably 0.06-0.22.
20. The process or use according to any of the previous solutions, which is characterized in that in step (3), an alkali-treated amorphous silica is used as the silicon source, the silicon source is mixed with an aluminum source, an alkali source (MOH), a template agent (R) and water to form a gel, which is crystallized, filtered, washed, dried and calcined to produce the ZSM-23 zeolite.
21. The process or use according to any of the previous solutions, which is characterized in that: in the gel, the molar ratio of the silicon source (as SiO_2):the aluminum source (as Al_2O_3):the alkali source (as hydroxide):the template agent: H_2O is 1:(0.003-0.03):(0.03-0.3):(0.05-2):(10-90); further preferably, in the gel, the molar ratio of the silicon source (as SiO_2):the aluminum source(as Al_2O_3):the alkali source (as hydroxide):the template agent: H_2O is 1:(0.005-0.02):(0.03-0.16):(0.08-1.6):(20-70).
22. The process or use according to any of the previous solutions, which is characterized in that the gel is crystallized at 150-200°C, preferably 170-180°C for 24-96 hours, preferably 36-72 hours, filtered, washed, dried, and calcined to produce the ZSM-23 zeolite.

23. The process or use according to any of the previous solutions, which is characterized in that in step (3), the temperature for drying is 80-120°C, the time for drying is 4-12 hours, the temperature for calcining is 500-600°C, the time for calcining is 2-6 hours.

24. an alkali-treated amorphous silica, which is characterized in that: the specific surface area is 600-1300 m²/g, preferably 700-1200 m²/g; the pore volume is 0.6-1.3 cm³/g, preferably 0.7-1.2 cm³/g; the pore diameter is 1-13 nm, preferably 2-10 nm.

25. an alkali-treated amorphous silica, which is characterized in that: the specific surface area is 600-1300 m²/g, preferably 700-1200 m²/g; the pore volume is 0.6-1.3 cm³/g, preferably 0.7-1.2 cm³/g; the pore diameter is 1-13 nm, preferably 2-10 nm;

wherein the alkali treatment is carried out according to step (2) of the process as described in any of solutions 6 and 8-19.

Compared with the prior art, the present invention relates to a ZSM-23 zeolite and a preparation process and use thereof, and has the following advantages:

According to the process of the present invention, a mesoporous amorphous silica is initially prepared with the assistance of the surfactant and used as the silicon source for the later synthesis of the ZSM-23 zeolite. The amorphous silica generated during this process has a mesoporous structure and has not been highly crystallized into a stable crystal form. After a further treatment in a low concentration of the alkaline solution for a period of time, some of the -Si-O- bonds are opened, which facilitates the formation of -Si-O-Al bonds in the zeolite structure; but a majority of the mesoporous structures are retained and generate a microporous structure in a suitable ZSM-23 zeolite synthesis system under the action of the microporous template agent in the later stage. At the same time, the mesoporous structures are further crystallized and stabilized, resulting in the production of a microporous-mesoporous composite ZSM-23 zeolite. The process is a feasible industrial production route due to its easy operational process, the relatively used amounts of the surfactant and the micropore template agent, the relatively low cost, and the excellent product performance of the obtained zeolite.

The ZSM-23 zeolite synthesized by the process of the present invention not only has adjustable acid properties contributive to microporous structure, but also has large pore characteristics contributive to mesoporous structure, high specific surface area and pore volume, as well as high crystallinity, high thermal stability, and high hydrothermal stability. It can be used as an excellent adsorbent or catalyst material and has broader application prospects in the field of shape selective catalysis, further improving its application performance in the petrochemical

reactions such as the cracking and isomerization of long-chain alkanes and olefins and the isomerization of aromatics.

Brief description of the drawings

- 5 Figure 1 shows the XRD spectrum of the synthesized product of Example 1 of the present invention.

Figure 2 shows the nitrogen gas physical adsorption diagram of the synthesized product of Example 1 of the present invention.

10 Detailed description

Analysis methods according to the present invention:

- The specific surface area and the pore volume of the zeolite are measured with the ASAP 2405 physical adsorption instrument from Micromeritics Corporation (USA), where the specific surface area refers to the sum of the specific surface area of micropores and the specific surface
15 area of mesopores.

- The XRD spectra of the samples are obtained by using the Dmax2500 X-ray diffractometer produced by Rigaku Corporation (Japan), and the relative crystallinity of the sample is obtained by calculation. The relative crystallinity of the zeolite is determined as follows: taking the sum of the heights of diffraction peaks by 2θ degree of approximately 11.3° and $19.5\text{--}23^\circ$ in
20 the XRD spectrum of a conventional ZSM-23 zeolite as 100% crystallinity and comparing with that of other samples to obtain the relative crystallinity.

According to the present invention, the ZSM-23 zeolite has an XRD pattern comprising the following characteristic peaks expressed by 2θ degree: about $11.3^\circ \pm 0.3^\circ$ (for example $\pm 0.2^\circ$ or $\pm 0.1^\circ$).

- 25 According to the present invention, the ZSM-23 zeolite has an XRD pattern comprising the following characteristic peaks expressed by 2θ degree: $11.2\text{--}11.5^\circ$, $19.5\text{--}19.9^\circ$, $20.7\text{--}21.0^\circ$, and $22.8\text{--}23.1^\circ$.

In order to better illustrate the present invention, the present invention is further described below in conjunction with Examples and Comparative Examples. But the scope of the present invention is not limited to the scope of these examples.

Example 1

5 (1) Preparation of mesoporous silicon source

To 250g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octodecyltrimethylammonium chloride (C18TMACl) was added and the resulting mixture was stirred for 0.5 hours, wherein the molar ratio of SiO₂ to C18TMACl was 1:0.08. The solution was adjusted with hydrochloric
10 acid to the pH of 2, and heated in a 50°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried at 80°C for 8 hours, and calcined at 550°C for 3 hours to produce an amorphous silica.

(2) Preparation of microporous-mesoporous ZSM-23 zeolite

a) 0.35g of NaOH was dissolved in 35mL of deionized water, 3.7g of the mesoporous silicon
15 source (OH⁻/SiO₂ molar ratio=0.14) prepared in step (1) was added, and the mixture was stirred in a 45°C water bath for 3 hours;

b) aluminum sulfate and isopropylamine (IPA) were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the aluminum
20 source:OH⁻:IPA:H₂O=1:0.01:0.08:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume, and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. Its XRD spectrum was shown in Figure 1 (confirming that the obtained product is a
25 ZSM-23 zeolite), and the nitrogen gas physical adsorption curve was shown in Figure 2. The specific properties were shown in Table 1.

Example 2

(1) Preparation of mesoporous silicon source

To 250g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of
30 27%). The mixture was stirred and dispersed evenly. Then octodecyltrimethylammonium

chloride (C18TMACl) was added and the resulting mixture was stirred for 0.5 hours, wherein the molar ratio of SiO₂ to C18TMACl was 1:0.08. The solution was adjusted with hydrochloric acid to the pH of 2, and heated in a 50°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried at 100°C for 4 hours, and calcined at 550°C for 3 hours to produce an
5 amorphous silica.

(2) Preparation of microporous-mesoporous ZSM-23 zeolite

- a) 0.42g of NaOH was dissolved in 40mL of deionized water, 3.7g of the mesoporous silicon source (OH⁻/SiO₂ molar ratio=0.17) prepared in step (1) was added, and the mixture was stirred in a 35°C water bath for 6 hours;
- 10 b) aluminum sulfate and isopropylamine (IPA) were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the aluminum source:OH⁻:IPA:H₂O=1:0.005:0.10:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative
15 crystallinity, its specific surface area, its pore volume, and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. Its XRD spectrum was similar to Figure 1, and the nitrogen gas physical adsorption curve was similar to Figure 2. The specific properties were shown in Table 1.

Example 3

20 (1) Preparation of mesoporous silicon source

- To 1200g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octodecyltrimethylammonium chloride (C18TMACl) was added and the resulting mixture was stirred for 2 hours, wherein the molar ratio of SiO₂ to C18TMACl was 1:0.2. The solution was adjusted with hydrochloric acid
25 to the pH of 3, and heated in a 50°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried at 80°C for 4 hours, and calcined at 500°C for 3 hours to produce an amorphous silica.

(2) Preparation of microporous-mesoporous ZSM-23 zeolite

- a) 0.15g of NaOH was dissolved in 35mL of deionized water, 3.7g of the mesoporous silicon
30 source (OH⁻/SiO₂ molar ratio=0.06) prepared in step (1) was added, and the mixture was stirred in a 45°C water bath for 3 hours;

b) aluminum sulfate, isopropylamine (IPA) and NaOH were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO_2 in the silicon source: Al_2O_3 in the aluminum source: OH^- :IPA: H_2O =1:0.01:0.08:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume, and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. Its XRD spectrum was similar to Figure 1, and the nitrogen gas physical adsorption curve was similar to Figure 2. The specific properties were shown in Table 1.

Example 4

(1) Preparation of mesoporous silicon source

To 800g of deionized water was added 50g of water glass (having a SiO_2 mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octodecyltrimethylammonium chloride (C18TMACl) was added and the resulting mixture was stirred for 2 hours, wherein the molar ratio of SiO_2 to C18TMACl was 1:0.15. The solution was adjusted with hydrochloric acid to the pH of 4, and heated in a 50°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried at 90°C for 4 hours, and calcined at 550°C for 3 hours to produce an amorphous silica.

(2) Preparation of microporous-mesoporous ZSM-23 zeolite

a) 0.42g of NaOH was dissolved in 40mL of deionized water, 3.7g of the mesoporous silicon source (OH^-/SiO_2 molar ratio=0.17) prepared in step (1) was added, and the mixture was stirred in a 40°C water bath for 3 hours;

b) aluminum sulfate and isopropylamine (IPA) were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO_2 in the silicon source: Al_2O_3 in the aluminum source: OH^- :IPA: H_2O =1:0.005:0.10:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume, and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. Its XRD spectrum was similar to Figure 1, and the nitrogen gas physical adsorption curve was similar to Figure 2. The specific properties were shown in Table 1.

Example 5

(1) Preparation of mesoporous silicon source

To 210g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octodecyltrimethylammonium chloride (C18TMACl) was added and the resulting mixture was stirred for 1 hour, wherein the molar ratio of SiO₂ to C18TMACl was 1:0.05. The solution was adjusted with hydrochloric acid to the pH of 2, and heated in a 60°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried at 80°C for 8 hours, and calcined at 550°C for 3 hours to produce an amorphous silica.

10 (2) Preparation of microporous-mesoporous ZSM-23 zeolite

a) 0.35g of NaOH was dissolved in 35mL of deionized water, 3.7g of the mesoporous silicon source (OH⁻/SiO₂ molar ratio=0.14) prepared in step (1) was added, and the mixture was stirred in a 50°C water bath for 2 hours;

b) aluminum sulfate and isopropylamine (IPA) were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the aluminum source:OH⁻:IPA:H₂O=1:0.01:0.08:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume, and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. Its XRD spectrum was similar to Figure 1, and the nitrogen gas physical adsorption curve was similar to Figure 2. The specific properties were shown in Table 1.

Example 6

(1) Preparation of mesoporous silicon source

25 To 210g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octodecyltrimethylammonium chloride (C18TMACl) was added and the resulting mixture was stirred for 1 hour, wherein the molar ratio of SiO₂ to C18TMACl was 1:0.06. The solution was adjusted with hydrochloric acid to the pH of 2, and heated in a 60°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried at 80°C for 8 hours, and calcined at 550°C for 3 hours to produce an amorphous silica.

(2) Preparation of microporous-mesoporous ZSM-23 zeolite

a) 0.10g of NaOH and 1.36g of concentrated ammonia water (having a mass fraction of about 27%) was dissolved in 35mL of deionized water, 3.7g of the mesoporous silicon source (OH⁻/SiO₂ molar ratio=0.22) prepared in step (1) was added, and the mixture was stirred in a 40°C water bath for 6 hours;

b) aluminum sulfate and isopropylamine (IPA) were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the aluminum source:OH⁻:IPA:H₂O=1:0.01:0.15:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume, and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. Its XRD spectrum was similar to Figure 1, and the nitrogen gas physical adsorption curve was similar to Figure 2. The specific properties were shown in Table 1.

15 Comparative Example 1 (according to CN105540607A)

0.51 g of pseudo-boehmite and 0.3 g of sodium hydroxide were added to 26 mL of deionized water under stirring at 35°C. The resulting solution was homogenized, then 0.3g of isopropylamine was added, then 21g of white carbon black was added, and the resulting mixture was homogenized and mixed for 1 hour. 24.5g of cereal starch was added, and the resulting mixture was heated to 90°C, stirred and aged for 6 hours. Finally, the resulting mixture was transferred to a hydrothermal reaction vessel lined with PTFE, statically crystallized at 160°C for 144 hours, taken out, cooled, filtered, and dried at 80°C to obtain the raw powder of zeolite. The raw powder was calcined at 500°C for 12 hours under an air atmosphere to produce a micropore-mesopore composite ZSM-23 zeolite, which was measured for its relative crystallinity, its specific surface area, its pore volume and its pore size distribution, and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. The specific properties were shown in Table 1.

Comparative Example 2

(1) Preparation of mesoporous silicon source

To 250g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octadecyltrimethylammonium

chloride (C18TMACl) was added and the resulting mixture was stirred for 0.5 hours, wherein the molar ratio of SiO₂ to C18TMACl was 1:0.08. The solution was adjusted with hydrochloric acid to the pH of 2, and heated in a 50°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried, and calcined at 550°C to produce an amorphous silica.

5 (2) a) 3.7g of the mesoporous silicon source prepared in step (1) was dispersed in 35 mL of deionized water, and the mixture was stirred in a 50°C water bath for 2 hours;

b) aluminum sulfate, isopropylamine (IPA) and NaOH were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the
10 aluminum source:NaOH:IPA:H₂O=1:0.01:0.08:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume, and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. The specific properties were shown in Table 1.

15 **Comparative Example 3**

(1) Preparation of mesoporous silicon source

To 1200g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octadecyltrimethylammonium chloride (C18TMACl) was added and the resulting mixture was stirred for 2 hours, wherein the
20 molar ratio of SiO₂ to C18TMACl was 1:0.2. The solution was adjusted with hydrochloric acid to the pH of 3, and heated in a 50°C water bath for 4 hours. Then, the reaction system was filtered, washed, dried, and calcined at 550°C to produce an amorphous silica.

(2) a) 0.70g of NaOH was dissolved in 40mL of deionized water, 3.7g of the mesoporous silicon source (OH/SiO₂ molar ratio=0.28) prepared in step (1) was added, and the mixture
25 was stirred in a 45°C water bath for 3 hours;

b) aluminum sulfate and isopropylamine (IPA) were successively dissolved in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the aluminum source:NaOH:IPA:H₂O=1:0.01:0.16:1.0:50. The resulting gel was crystallized at 180°C for 48
30 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume, and its pore size distribution; and

measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C.

Comparative Example 4

(1) Preparation of mesoporous silicon source

5 To 1200g of deionized water was added 50g of water glass (having a SiO₂ mass fraction of 27%). The mixture was stirred and dispersed evenly. Then octodecyltrimethylammonium chloride (C18TMACl) was added and the resulting mixture was stirred for 2 hours, wherein the molar ratio of SiO₂ to C18TMACl was 1:0.2. The solution was adjusted with hydrochloric acid to the pH of 3, and heated in a 50°C water bath for 4 hours. Then, the reaction system was
10 filtered, washed, dried, and calcined at 550°C to produce an amorphous silica.

(2) a) 0.10g of NaOH was dissolved in 40mL of deionized water, 3.7g of the mesoporous silicon source (OH⁻/SiO₂ molar ratio=0.04) prepared in step (1) was added, and the mixture was stirred in a 45°C water bath for 3 hours;

b) aluminum sulfate, isopropylamine (IPA) and sodium hydroxide were successively dissolved
15 in the remaining water, and to the resulting mixture was added the silicon source dispersion obtained from step a) to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the aluminum source:NaOH:IPA:H₂O=1:0.01:0.08:1.0:50. The resulting gel was crystallized at 180°C for 48 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity, its specific surface area, its pore volume,
20 and its pore size distribution; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C.

Comparative Example 5 (Preparation of the conventional ZSM-23 zeolite)

Water glass, aluminum sulfate, isopropylamine (IPA), sodium hydroxide and water were mixed to produce a gel with a total molar ratio of SiO₂ in the silicon source:Al₂O₃ in the aluminum
25 source:NaOH:IPA:H₂O=1:0.01:0.08:1.0:50. The resulting gel was heated at 180°C for 72 hours, filtered, washed, dried, and calcined. The resulting product was measured for its relative crystallinity; and measured for its hydrothermal stability after a hydrothermal treatment with steam for 2 hours at 600°C. The specific properties were shown in Table 1.

Table 1

	Specific surface area, m ² /g	Microporous surface area, m ² /g	Microporous surface area, m ² /g	Pore volume, cm ³ /g	Content of mesopores with pore size of 3-8 nm, %	Relative crystallinity, %	Relative crystallinity after hydrothermal treatment, %	Relative crystallinity retention, % ^d
Example 1	395	105	290	0.42	77	102	103	100
Example 2	387	99	288	0.41	56	104	102	98
Example 3	398	107	291	0.45	80	114	110	96
Example 4	378	101	277	0.38	60	100	99	99
Example 5	384	91	293	0.40	69	113	108	96
Example 6	401	114	287	0.45	84	105	106	100
Comparative Example 1	289	126	163	0.28	31	103	74	72
Comparative Example 2	69	61	8	0.03	^a	^a	^a	^a
Comparative Example 3	232	167	65	0.24	^b	^b	^b	^b
Comparative Example 4	108	84	24	0.09	^c	^c	^c	^c
Comparative Example 5	228	188	40	0.24	18	100	101	100

- a Under this condition, the zeolite product was not produced through crystallization, so this property could not be analyzed.
- b Under this condition, the obtained products are mainly other zeolites, so this property could not be analyzed.
- c Under this condition, the crystallization was incompleted, so this property could not be analyzed.
- d Relative crystallinity retention= crystallinity after hydrothermal treatment/ relative crystallinity. Due to measurement errors, results greater than 5 100% were recorded as 100%.

It can be seen from the data in Table 1 that the preparation processes in the examples of the present invention could prepare ZSM-23 zeolites with micropore-mesopore composite structures through a simple synthesis process with a relatively small amount of surfactant at a relatively low cost. The obtained product, a micropore-mesopore composite ZSM-23 zeolite,
5 has high crystallinity, large specific surface area and pore volume, high mesopore content, relatively concentrated size distribution, good thermal stability and hydrothermal stability, and broad application prospects.

The performance of ZSM-23 zeolite samples was evaluated on a fixed bed micro reactor. The reaction conditions and catalytic results of Comparative Example 1, Comparative Example 5,
10 Example 4 and Example 6 in the linear C₂₀-C₃₀ hydroisomerization reaction were as follows:

Reaction raw materials: 90wt% decahydronaphthalene, 10wt% C₂₀-C₃₀ straight chain alkanes;

Reaction conditions: reaction temperature 280°C; Liquid hourly space velocity 1.0 h⁻¹;

Hydrogen to oil ratio 600; Reaction hydrogen pressure 4.0 MPa;

Comparative Example 1:

15 Liquid yield (C₅⁺): 93%; C₂₀-C₃₀Isomerization degree: 100%; C₂₀-C₃₀isomerization product yield: 46%; Ratio of multiple-branched chain components to single-branched chain components in C₂₀-C₃₀ isomerization product: 0.6.

Comparative Example 5:

Liquid yield (C₅⁺): 94%; C₂₀-C₃₀Isomerization degree: 100%; C₂₀-C₃₀isomerization product
20 yield: 44%; Ratio of multiple-branched chain components to single-branched chain components in C₂₀-C₃₀ isomerization product: 0.5.

Example 4:

Liquid yield (C₅⁺): 95%; C₂₀-C₃₀Isomerization degree: 100%; C₂₀-C₃₀isomerization product
25 yield: 53%; Ratio of multiple-branched chain components to single-branched chain components in C₂₀-C₃₀ isomerization product: 2.1.

Example 6:

Liquid yield (C₅⁺): 96%; C₂₀-C₃₀Isomerization degree: 100%; C₂₀-C₃₀isomerization product
yield: 54%; Ratio of multiple-branched chain components to single-branched chain
components in C₂₀-C₃₀ isomerization product: 2.3.

Claims

1. A ZSM-23 zeolite, which is characterized in that the pore volume of mesopores having a
5 pore size of 3-8 nm, preferably 3-6 nm of the zeolite is 45-90%, preferably 50-85%, further preferably 55-81% of the total pore volume of the zeolite.
2. The ZSM-23 zeolite according to claim 1, which is characterized in that the zeolite has a relative crystallinity of 95-120%, and the zeolite has a relative crystallinity retention of
10 95-100% after a hydrothermal treatment with steam for 2 hours at 600°C.
3. The ZSM-23 zeolite according to any of the previous claims, which is characterized in that the zeolite has a specific surface area of 300-430 m²/g, and a pore volume of 0.31-0.5 cm³/g, the specific surface area of micropores is 50-170 m²/g, and the specific surface area of
15 mesopores is 150-310 m²/g, for example, the zeolite has a specific surface area of 320-405 m²/g, and a pore volume of 0.34-0.45 cm³/g, the specific surface area of micropores is 80-140 m²/g, and the specific surface area of mesopores is 261-295 m²/g.
4. A process for preparing the ZSM-23 zeolite according to any of claims 1-3, wherein the
20 process comprises the following steps:
 - (1) preparing or selecting a silicon source for preparing the ZSM-23 zeolite, such as amorphous silica;
 - (2) performing an alkali treatment on the silicon source for preparing the ZSM-23 zeolite mentioned in step (1);
 - 25 (3) preparing the ZSM-23 zeolite by using the alkali-treated amorphous silica as the silicon source.

5. Use of the alkali-treated amorphous silica obtained in step (2) of the process of claim 4 as the silicon source in the preparation of the ZSM-23 zeolite.
6. The process or use according to any of claims 4-5, which is characterized in that in step (1),
5 said amorphous silica has a specific surface area of 600-1300 m²/g, preferably 700-1200 m²/g; a pore volume of 0.6-1.3 cm³/g, preferably 0.7-1.2 cm³/g; and a pore diameter of 1-13 nm, preferably 2-10 nm.
7. The process or use according to any of claims 4-6, which is characterized in that in step (1),
10 the preparation process of the amorphous silica is as follows: adding a silicon source to deionized water to be uniformly dispersed, and then adding a surfactant and stirring; adjusting the pH of the resulting solution to 1-5, preferably 1.5-4, and then heating it in a water bath for a period of time; filtering, washing, drying, and calcining to produce the amorphous silica.
- 15 8. The process or use according to claim 7, which is characterized in that in step (1), the silicon source is an inorganic silicon source, preferably one or more of water glass, silica sol, or white carbon black.
9. The process or use according to any of claims 7-8, which is characterized in that in step (1),
20 the surfactant is one or more of hexadecyltrimethylammonium chloride, hexadecyltrimethylammonium bromide, octadecyltrimethylammonium chloride, octadecyltrimethylammonium bromide.
10. The process or use according to any of claims 7-9, which is characterized in that in step (1),
25 the molar ratio of said silicon source as SiO₂ to the surfactant is 1:(0.02-0.3), preferably 1:(0.05-0.2).

11. The process or use according to any of claims 7-10, which is characterized in that in step (1), the molar ratio of said silicon source as SiO_2 to the deionized water is 1:(30-300), preferably 1:(50-220).
- 5 12. The process or use according to any of claims 7-11, which is characterized in that in step (1), the temperature for heating is 30-80°C, preferably, 40-70°C, the time for heating is 0.5-8 hours, preferably, 3-6 hours.
- 10 13. The process or use according to any of claims 7-12, which is characterized in that in step (1), the temperature for drying is 80-120°C, the time for drying is 4-12 hours, the temperature for calcining is 500-600°C, the time for calcining is 2-6 hours.
- 15 14. The process or use according to any of claims 4-13, which is characterized in that in step (2), the alkali treatment involves adding the amorphous silica prepared in step (1) to an alkaline solution, heating and stirring.
15. The process or use according to claim 14, which is characterized in that in step (2), the alkali treatment is performed by using an inorganic alkali, and the inorganic alkali is one or more of sodium hydroxide, potassium hydroxide, or ammonia water.
- 20 16. The process or use according to any of claims 14-15, which is characterized in that in step (2), in the alkali treatment, the time for heating and stirring is 0.5-12 hours, preferably 2-8 hours; and the temperature for heating is 25-60°C, preferably 30-50°C.
- 25 17. The process or use according to any of claims 4-16, which is characterized in that in step (2), the molar ratio of the inorganic alkali as OH^- to the amorphous silica as SiO_2 is 0.05-0.24, preferably 0.06-0.22.

18. The process according to any of claims 4-17, which is characterized in that in step (3), an alkali-treated amorphous silica is used as the silicon source, the silicon source is mixed with an aluminum source, an alkali source (MOH), a template agent (R) and water to form a gel, which is crystallized, filtered, washed, dried and calcined to produce the ZSM-23 zeolite.

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19. The process according to claim 18, which is characterized in that in the gel, the molar ratio of the silicon source (as SiO_2):the aluminum source(as Al_2O_3):the alkali source (as hydroxide):the template agent: H_2O is 1:(0.003-0.03):(0.03-0.3):(0.05-2):(10-90); further preferably, in the gel, the molar ratio of the silicon source (as SiO_2):the aluminum source(as Al_2O_3):the alkali source (as hydroxide):the template agent: H_2O is 1:(0.005-0.02):(0.03-0.16):(0.08-1.6):(20-70).

20. The process according to any of claims 18-19, which is characterized in that the gel is crystallized at 150-200°C, preferably 170-180°C for 24-96 hours, preferably 36-72 hours, filtered, washed, dried, and calcined to produce the ZSM-23 zeolite.

15

21. The process according to any of claims 18-20, which is characterized in that in step (3), the temperature for drying is 80-120°C, the time for drying is 4-12 hours, the temperature for calcining is 500-600°C, the time for calcining is 2-6 hours.

20

22. An alkali-treated amorphous silica, which is characterized in that: the specific surface area is 600-1300 m^2/g , preferably 700-1200 m^2/g ; the pore volume is 0.6-1.3 cm^3/g , preferably 0.7-1.2 cm^3/g ; the pore diameter is 1-13 nm, preferably 2-10 nm.

23. An alkali-treated amorphous silica, which is characterized in that: the specific surface area is 600-1300 m^2/g , preferably 700-1200 m^2/g ; the pore volume is 0.6-1.3 cm^3/g , preferably 0.7-1.2 cm^3/g ; the pore diameter is 1-13 nm, preferably 2-10 nm;

25

wherein the alkali treatment is carried out according to step (2) of the process as described in any of claims 4 and 6-17.