

A BI-MICROPOROUS/MESOPOROUS COMPOSITE MOLECULAR SIEVE AND PREPARATION PROCESS THEREOF

FIELD OF THE INVENTION

The present invention relates to a catalyst carrier material prepared by combining zeolites with bi-microporous phases (Y type and Beta type zeolites) and a molecular sieve with mesoporous phase (MCM-41), and to the preparation process thereof.

BACKGROUND OF THE INVENTION

Microporous molecular sieve is an important inorganic material and is widely used as a catalyst, an adsorbent, an ion-exchanger as well as a novel functional material due to its high specific surface area, high hydrothermal stability, uniform pore diameter and variable surface property. In 1959, Union Carbide Corporation put a Y type zeolite-based catalyst into use for isomerisation, which is the first industrial application of the molecular sieve in the field of catalysis. Subsequently, X type zeolite is applied to catalytic cracking by US Mobile Company in 1962, and ultra-stable Y type zeolite (USY) catalyst is developed by Grace Company in 1969. Besides the application in cracking and hydrocracking, the catalytic processes using molecular sieves have been industrialized in the fields of isomerisation of normal paraffin, low temperature isomerisation of C₈ aromatic hydrocarbon, disproportionation of toluene and shape-selective catalysis at that time.

Microporous molecular sieves have uniform and developed effective micropores as well as strong acidity. However, the pore of microporous molecular sieves has a relatively small diameter (smaller than 2 nm) and can not let macromolecules in, which severely limits their industrial application. Since Mobile Company synthesized the M41S family of mesoporous molecular sieves in 1992, the synthesis technology, property characterization and crystallization mechanism of the mesoporous molecular sieves with pore diameters of 2 nm to 50 nm have been the hot topics in international research. However, the pore wall of mesoporous molecular sieves is amorphous, which results in their weak acidity and poor hydrothermal stability. From the 1990s, the desire for novel catalytic materials is growing with the developing of

petrochemical industry and fine chemical industry as well as the increasing requirement for environment protection. Therefore, the researchers intend to combine the advantages of both microporous and mesoporous molecular sieves in order to synthesize novel material of microporous/mesoporous composite molecular sieve. A microporous/mesoporous composite molecular sieve has double mode of both microporous and mesoporous structure and combines the advantage of the pore from mesoporous materials with the advantages of strong acidity and high hydrothermal stability from microporous materials. Thus the two materials can have complementary advantages due to synergistic effect in the composite molecular sieve. Moreover, composite molecular sieves with different pore structures and acid distributions can be prepared by adjusting the pore structure and acidity, i.e. by selecting two materials with different pore structure and acidity property so as to optimize the combination. Chemist Davis who is world-famous in the field of molecular sieves has pointed out that the successful preparation of the hierarchically porous molecular sieves characterized by the assembling process and their various modes will be widely applied in more fields.

Therefore, more researches focus on the composite molecular sieves in recent years. The researchers have synthesized composite molecular sieves using a variety of processes. Huang et al. have synthesized two micro-mesoporous composite molecular sieves of ZSM-5/MCM-41 (*J Phys Chem B*, 2000, 104(13): 2817~2823) and β /MCM-41 (*Chemical Journal of Chinese Universities*, 1999, 20(3): 356~358) by a two-step crystallization process utilizing two templates. However, such process requires little difference between the synthesis conditions of the two microporous and mesoporous molecular sieves, or the ranges of their synthesis conditions overlap. Kloetstra et al. have reported a technology for the overgrowth of a mesoporous MCM-41 molecular sieve on a Y type molecular sieve (*Microporous Mesoporous Mater*, 1996, 6(5~6):287~293) as well as a process for the recrystallization of MCM-41 using tetrapropylammonium ion-exchange (*Div Pet Chem*, 1996, 41(2): 412~414). However, the Y/MCM-41 composite molecular sieve synthesized by the former has disordered mesoporous arrangement, and the synthetic efficiency is low, while both acidity property and hydrothermal stability are not satisfying; the ZSM-5/MCM-41 composite

molecular sieve synthesized by the later still has highly disordered mesopore wall, wherein the crystallized portion only appears on the surface of the mesopore wall and thus lacks hydrothermal stability. USA researcher Pinnavaia et al. have prepared built-in composite molecular sieves by nano assembling, wherein crystal seeds of Y zeolite are preliminary prepared and then subjected to self-assembling with cetyl trimethyl ammonium bromide (CTAB) (*J Am Chem Soc*, 2000, 122: 8791~8792). The composite molecular sieves prepared by such process have quite high acidity and pronounced hydrothermal stability, but the preparation of crystal seeds of the microporous molecular sieve must be firstly carried out, which is difficult to control, that is, the assembling result would be affected if the seeds are too large, whereas the acidity property of the material would be affected if the seeds are too small. After that, Y/MCM-41, β /MCM-41 and β /MCM-48 are reported in succession. The micro-mesoporous composite molecular sieves have excellent catalytic performance, for example, the ZSM-5/MCM-41 composite molecular sieve has higher catalytic activity for the cracking of n-dodecane than the mechanical mixture thereof. Currently, the domestic and foreign researches focus on the binary microporous/mesoporous composite molecular sieve, while the ternary bi-microporous/mesoporous composite molecular sieve has not been reported yet. With respect to Y type and Beta type zeolites that have been widely used in hydrocracking industry at present, the present inventors have combined the characterizations of the two in the hydrocracking process, that is, the heavy naphtha having a high potential aromatic content and the tail oil having a low BMCI value are obtained using Y type zeolite, whereas the Beta type zeolite has high selectivity to middle distillates and high activity but the heavy naphtha has a low potential aromatic content and the tail oil has a high BMCI value and have set forth the present invention wherein a novel bi-microporous/mesoporous composite molecular sieve (Y-Beta/MCM-41) is synthesized by the hydrothermal overgrowth process in basic system utilizing the supramolecular assembling effect of mixed cationic and nonionic surfactants. The present invention is further development of molecular sieve catalytic material, and the synthesized bi-microporous/mesoporous composite molecular sieve (Y-Beta/MCM-41) can be used as a novel carrier of a hydrocracking catalyst, which has potential application in fields such as petrochemical industry.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a catalyst carrier material prepared by combining zeolites with bi-microporous phases (Y and Beta zeolites) and a molecular sieve with mesoporous phase (MCM-41), and to provide the preparation process thereof which is easy to operate and reproducible.

The bi-microporous/mesoporous composite molecular sieve according to the present invention is prepared by combining Y and Beta type bi-microporous zeolites with MCM-41 molecular sieve, wherein the pore wall of the hexagonal mesoporous phase is compactly surrounded by the bi-microporous phases so as to exhibit a number of spherical or hemispherical hollow shell structures, which form a network by cross-linking, and both the silica-alumina ratio and the content of the microporous phases can be adjusted.

The bi-microporous/mesoporous composite molecular sieve (Y-Beta/MCM-41) according to the present invention is prepared by the supramolecular self-assembling of inorganic precursors (I^-) of pretreated microporous phases, silicon source and aluminum source through $S^+S^0I^-$ route under the function of cationic (S^+) /nonionic (S^0) mixed surfactants, so that the overgrowth of mesoporous phase on the microporous phases is achieved.

The preparation procedure is as follows:

- (1) pretreatment of the microporous phases: mixing homogenously Y type and Beta type zeolites in proper proportion, and then adding the mixture into deionized water, stirring the resulted solution until homogenous at specific temperature and denoting it as Mixture A for further usage;
- (2) mixing certain amounts of surfactants, i.e., cetyl trimethyl ammonium bromide (CTAB), and polyoxyethylene alkylphenol ether (OP-10) in proper proportion, and then adding the mixture into deionized water, stirring uniformly the resulted solution at room temperature and denoting it as Solution B after clarification for further usage;
- (3) adding the obtained Mixture A into Solution B and stirring until

homogenous at room temperature, and then adding dropwise slowly both silicon source and aluminum source, or adding dropwise slowly only silicon source into the mixture, followed by further stirring at room temperature until each component in the mixture is uniform and steady, then introducing inorganic acids and/or bases so as to adjust the pH value of the system, followed by further uniform stirring until the system is steady, then loading the obtained colloidal liquid into a stainless steel reactor with inner liner, and crystallizing at specific temperature;

(4) subjecting the crystallized product obtained by step (3) to filtration, washing and drying so as to provide a white solid powder, calcining this solid product in nitrogen stream and then transferring it to a muffle furnace for calcining in air, ion-exchanging the calcined product in solution of ammonium salt in proportion, followed by filtration and drying, after final calcining in air, obtaining a hydrogen-typed Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve.

The molar proportion of the raw materials according to the present invention is as follows: 0.10~0.25 of CTAB/SiO₂, 5~7 of CTAB/OP-10, 58~78 of SiO₂/H₂O, and Si / Al $\geq$ 25; the mass ratio of (Y+Beta)/SiO₂ is 0.26~0.80; and the amount of the microporous phases Y type and Beta type zeolites can be adjusted in any scale provided.

The temperature for the pretreatment of the microporous phases is 30°C~50°C, and the pretreatment time is 25min~30min;

the pH value of the synthesis system is in the range of 10.1~12.1;

the crystallization temperature $\leq$ 100°C, and the crystallization time is 48h~72h;

the crystallized product is calcined in nitrogen stream at a calcining temperature of 500°C~550°C and a calcining time of 1 hour; the temperature for the calcining in air is 500°C~600°C and the calcining time is 4.0h~6.0h;

the concentration of the ammonium salt in the solution is 0.05mol/L~0.20mol/L, the ratio between the calcined product and the solution of ammonium salt is 1g : 150mol/L~300mol/L, and the time for ion-exchange is 2.0h~4.0h.

The inorganic acid used in the present invention may be any one of hydrochloric acid, sulfuric acid or nitric acid, or a mixture of any two thereof; the inorganic base is mainly sodium hydroxide or potassium hydroxide.

Industrial sodium silicate may be used as the silicon source of the basic system according to the present invention, and the aluminum source may be any one of aluminum chloride, aluminum sulfate or aluminum nitrate, or a mixture of any two thereof.

According to the present invention, when the silicon and aluminum sources are added into the mixture, the stirring time before adjusting the pH value of the system is typically 1.0h~1.5h, and the time of stirring after adjusting the pH value is about 0.5 h.

According to the present invention, when the calcined product is ion-exchanged in the solution of ammonium salt, the ammonium salt used may be any one of ammonium nitrate or ammonium chloride, or the mixture thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1a is a XRD pattern of MY β -1.

Figure 1b is a XRD pattern of MY β -1.

Figure 2 shows the low temperature N₂ adsorption/desorption isotherm of MY β -1 and the relationship between the pore volume and the pore diameter obtained by BJH desorption (inserted figure).

Figure 3a is a SEM image of MY β -1.

Figure 3b is a SEM image of MY β -1.

Figure 4 compares the catalytic performance of MY β -1 on the probe molecule α -methylnaphthalene with that of the mechanical mixture of three materials of Y, Beta and MCM-41.

Figure 5a compares the XRD pattern of MCM-41 before and after hydrothermal treatment (the hydrothermal treatment is carried out in water vapour at 550°C for 4 hours), wherein a and b represent before and after the

hydrothermal treatment, respectively.

Figure 5b compares the XRD pattern of MY β -1 before and after hydrothermal treatment (the hydrothermal treatment is carried out in water vapour at 550°C for 4 hours), wherein a and b represent before and after the hydrothermal treatment, respectively.

DETAILED DESCRIPTION OF THE INVENTION

The implementing of the present invention will be further described with reference to the following examples, but the present invention is not limited to these examples.

Example 1

0.47 g of Y type and 0.47 g of Beta type zeolite powders are mixed and pretreated and then added to a blended solution containing CTAB and OP-10. After stirring at room temperature for 30 minutes, the mixture is added dropwise slowly 5 ml of sodium silicate (SiO₂ 25.4%, Na₂O 7.4%), and 0.389 g of Al₂(SO₄)₃·18H₂O is added slowly 5 minutes later. The molar proportion of the raw materials is 1 SiO₂ : 0.15 CTAB : 0.025 OP-10 : x (Y+Beta) : 0.02 Al₂O₃ : 0.28 Na₂O : 60 H₂O, wherein the mass ratio of (Y+Beta)/SiO₂ is 0.53. After the system is stirred for 1.0 hour, its pH value is adjusted to about 11.1. After further stirring for 30 minutes, the colloidal liquid is loaded into a reactor with inner liner and crystallized at 100°C for 48 hours. The obtained product is subjected to filtration, washing, drying and calcining, and the calcined product is ion-exchanged in 0.10 mol/L solution of ammonium nitrate in the proportion of 1 : 200 for 2.5 hours, followed by filtration and drying. After final calcining in air, a Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve is obtained, which is synthesized in the basic system in the microporous phase proportion of 1 : 1 in the feedstock, and the relative content of which is 53%. This sample is named as MY β -1.

Referring to Figure 1a and 1b, which are X-ray diffraction (XRD) patterns of MY β -1, it can be seen that a diffraction peak with strong intensity of the hexagonal mesoporous phase appears at the position of [100] in the small angle diffraction zone. [110] and [200] diffraction peaks with lower intensity

are also distinct, which represents the fine structure within the hexagonal mesoporous phase. This result shows that the synthesized bi-microporous/mesoporous composite molecular sieve (Y-Beta/MCM-41) has a relatively good regularity. In the high angle diffraction zone, the characteristic peaks of Y zeolite [111] and Beta zeolite [302] are both distinct, which shows that the microporous phases are not completely destroyed in the system.

Figure 2 provides the low temperature N₂ adsorption/desorption isotherm of MYβ-1 and the relationship between the pore volume and the pore diameter obtained by BJH desorption (inserted figure). It has a specific surface area of 829.68 m²/g, a pore volume of 1.104 cm³/g (wherein the pore volume of micropores is 0.046 cm³/g), an average pore diameter of 5.32 nm (wherein the most probable mesopore diameter is 2.84 nm), and a pore wall thickness of mesopores of about 1.52 nm.

Referring to the SEM images of MYβ-1 in Figure 3a and 3b, it can be seen that the molecular sieve prepared by combining two microporous phases with a mesoporous phase has a number of spherical or hemi-spherical hollow shell structures, which form a network by cross-linking.

Figure 4 compares the catalytic performance of MYβ-1 on the probe molecule α-methylnaphthalene with that of the mechanical mixture of three materials of Y, Beta and MCM-41. It can be seen that the Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve has stronger acidity and better catalytic activity since its ring-opening, dealkylating and isomerizing abilities are all substantially better than those of the mechanical mixture.

Referring to the XRD patterns of MYβ-1 after hydrothermal treatment in Figure 5b, it can be seen that, after the hydrothermal treatment, the [100] diffraction peak of MYβ-1 has a relatively high intensity, and the [110] and [200] diffraction peaks can be recognized, indicating this sample remains hexagonal ordered mesoporous structure and good order degree of structure. Meanwhile, referring to the XRD patterns of MCM-41 after hydrothermal

treatment in Figure 5a, after the hydrothermal treatment, the diffraction intensity of [100] diffraction peak is significantly decreased, and the [110] and [200] diffraction peaks disappear, indicating significant reduction of its order degree of structure.

Example 2

0.47 g of Y type and 0.47 g of Beta type zeolite powders are mixed and pretreated and then added to a blended solution containing CTAB and OP-10. After stirring at room temperature for 30 minutes, the mixture is added dropwise slowly 5 ml of sodium silicate (SiO_2 25.4%, Na_2O 7.4%), and 0.156g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is added slowly 5 minutes later. The molar proportion of the raw materials is 1 SiO_2 : 0.15 CTAB : 0.025 OP-10 : x (Y+Beta) : 0.008 Al_2O_3 : 0.28 Na_2O : 60 H_2O , wherein the mass ratio of (Y+Beta)/ SiO_2 is 0.53. After the system is stirred for 1.0 hour, its pH value is adjusted to about 11.1. After further stirring for 30 minutes, the colloidal liquid is loaded into a reactor with inner liner and crystallized at 100°C for 48 hours. The obtained product is subjected to filtration, washing, drying and calcining, and the calcined product is ion-exchanged in 0.15 mol/L solution of ammonium chloride in the proportion of 1 : 300 for 2.0 hours, followed by filtration and drying. After final calcining in air, a Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve is obtained, which is synthesized in the basic system with a Si/Al of 62.5 in the feedstock. This sample is named as MY β -2.

Example 3

0.235g of Y type and 0.235g of Beta type zeolite powders are mixed and pretreated and then added to a blended solution containing CTAB and OP-10. After stirring at room temperature for 30 minutes, the mixture is added dropwise slowly 5 ml of sodium silicate (SiO_2 25.4%, Na_2O 7.4%), and 0.389g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is added slowly 5 minutes later. The molar proportion of the raw materials is 1 SiO_2 : 0.15 CTAB : 0.025 OP-10 : x (Y+Beta) : 0.02 Al_2O_3 : 0.28 Na_2O : 60 H_2O , wherein the mass ratio of (Y+Beta)/ SiO_2 is 0.27. After stirring for 1.0 hour, the pH value of the system is adjusted to about 11.1. After further stirring for 30 minutes, the colloidal liquid is loaded into a reactor with inner liner and crystallized at 100°C for 48

hours. The obtained product is subjected to filtration, washing, drying and calcining, and the calcined product is ion-exchanged in 0.10 mol/L solution of ammonium nitrate in the proportion of 1 : 200 for 2.5 hours, followed by filtration and drying. After final calcining in air, a Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve is obtained, which is synthesized in the basic system in the microporous phase proportion of 1 : 1 in the feedstock, and the relative content of which is 27%. This sample is named as MY β -3.

Example 4

0.31g of Y type and 0.62g of Beta type zeolite powders are mixed and pretreated and then added to a blended solution containing CTAB and OP-10. After stirring at room temperature for 30 minutes, the mixture is added dropwise slowly 5 ml of sodium silicate (SiO₂ 25.4%, Na₂O 7.4%), and 0.078g of Al₂(SO₄)₃·18H₂O is added slowly 5 minutes later. The molar proportion of the raw materials is 1 SiO₂ : 0.15 CTAB : 0.025 OP-10 : x (Y+Beta) : 0.004 Al₂O₃ : 0.28 Na₂O : 60 H₂O, wherein the mass ratio of (Y+Beta)/SiO₂ is 0.53. After stirring for 1.0 hour, the pH value of the system is adjusted to about 11.1. After further stirring for 30 minutes, the colloidal liquid is loaded into a reactor with inner liner and crystallized at 100°C for 48 hours. The obtained product is subjected to filtration, washing, drying and calcining, and the calcined product is ion-exchanged in 0.05 mol/L solution of ammonium chloride in the proportion of 1 : 300 for 3.0 hours, followed by filtration and drying. After final calcining in air, a Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve is obtained, which is synthesized in the basic system in the microporous phase proportion of 1 : 2 in the feedstock, and the relative content of which is 53%, Si/Al=125. This sample is named as MY β -4.

Industrial applicability

The novel bi-microporous/mesoporous composite molecular sieve (Y-Beta/MCM-41) set forth by the present invention has the following characterizations:

(1) With regards to the micro morphology, significantly differing from the mechanical mixture, the bi-microporous/mesoporous composite molecular

sieve exhibits a number of spherical or hemi-spherical hollow shell structures, which form a network by cross-linking, and the pore wall of the mesoporous phase is compactly surrounded by the microporous phases.

(2) The bi-microporous/mesoporous composite molecular sieve has a specific surface area up to 829.68 m²/g, a pore volume of 1.104 cm³/g (wherein the pore volume of micropores is 0.046 cm³/g), an average pore diameter of 5.32 nm (wherein the most probable mesopore diameter is 2.84 nm for mesopores), and a pore wall thickness of mesopores of about 1.52 nm.

(3) The bi-microporous/mesoporous composite molecular sieve is obtained by utilizing the supramolecular assembling effect of mixed surfactants (CTAB and OP-10) and by hydrothermal overgrowth synthesis process.

(4) The Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve can be synthesized in a basic system and both the silica-alumina ratio and the content of the micropores of the microporous phases can be adjusted.

(5) The bi-microporous/mesoporous composite molecular sieve has good hydrothermal stability, and it remains good order degree of structure even after treating in water vapour at 550°C for 4 hours.

(6) The bi-microporous/mesoporous composite molecular sieve has stronger acidity and combines the advantages of both Y type and Beta type zeolites in the hydrocracking process, and thus has good catalysis performance.

The novel bi-microporous/mesoporous composite molecular sieve (Y-Beta/MCM-41) set forth by the present invention is an excellent catalyst carrier material, which structure substantially differs from the mechanical mixture of the three. Both synergistic effect of microporous phases and that between the microporous phases and the mesoporous phase in the composite molecular sieve are generated by controlling the synthesis condition and introducing two zeolite structure units, and consequently such composite molecular sieve exhibits better catalytic activity. For the catalytic reaction of the probe molecule α -methylnaphthalene using the synthesized bi-microporous/mesoporous composite molecular sieve (Y-Beta/MCM-41), its conversion is more than double of that using the mechanical mixture of Y, Beta and MCM-41. Therefore, this novel bi-microporous/mesoporous composite molecular sieve has wide potential application in industry.

What is claimed is:

1. A bi-microporous/mesoporous composite molecular sieve, characterized in that said molecular sieve is prepared by combining Y type and Beta type bi-microporous zeolites with MCM-41 molecular sieve, wherein the pore wall of the hexagonal mesoporous phase is compactly surrounded by the bi-microporous phases so as to exhibit a number of spherical or hemi-spherical hollow shell structures, which form a network by cross-linking, and both the silica-alumina ratio and the content of the micropores of the microporous phases can be adjusted.

2. A process for preparing the bi-microporous/mesoporous composite molecular sieve according to claim 1, characterized in that:

(1) mixing Y type and Beta type zeolites with deionized water and stirring until homogenous, denoting this mixture as Mixture A for further usage;

(2) mixing cetyl trimethyl ammonium bromide and polyoxyethylene alkylphenol ether as surfactants with deionized water and stirring until homogenous, denoting this solution as Solution B for further usage;

(3) mixing Mixture A with Solution B and stirring until homogenous, and then adding dropwise both silicon source and aluminum source, or adding dropwise only silicon source; after stirring, introducing inorganic acids and/or bases so as to adjust the pH value of the system, followed by further stirring; crystallization, filtration and drying so as to provide a white solid powder; calcining said solid powder in nitrogen stream and ion-exchanging the calcined product in a solution of ammonium salt, followed by filtration and drying; after final calcining in air, obtaining a hydrogen-typed Y-Beta/MCM-41 bi-microporous/mesoporous composite molecular sieve;

wherein the molar proportion of the raw materials is as follows: 0.10~0.25 of CTAB/SiO₂, 5~7 of CTAB/OP-10, 58~78 of SiO₂/H₂O, and Si / Al $\geq$ 25; the mass ratio of (Y+Beta)/SiO₂ is 0.26~0.80; and the amount of the microporous phases Y type and Beta type zeolites can be adjusted in any scale provided; the temperature for the pretreatment is 30°C~50°C, and the pretreatment time is 25min~30min;

the pH value of the synthesis system is in the range of 10.1~12.1.

the crystallization temperature $\leq 100^{\circ}\text{C}$, and the crystallization time is 48h~72h;

the crystallized product is calcined in nitrogen stream at a calcining temperature of $500^{\circ}\text{C}\sim 550^{\circ}\text{C}$ and a calcining time of 1.0h; the temperature for the calcining in air is $500^{\circ}\text{C}\sim 600^{\circ}\text{C}$ and the calcining time is 4.0h~6.0h;

the concentration of the ammonium salt in the solution is $0.05\text{mol/L}\sim 0.20\text{mol/L}$, the ratio between the calcined product and the solution of ammonium salt is 1 g : $150\text{ mol/L}\sim 300\text{ mol/L}$, and the time for ion-exchange is 2.0h~4.0h.

3. A process for preparing the bi-microporous/mesoporous composite molecular sieve according to claim 2, characterized in that said inorganic acid is any one of hydrochloric acid, sulfuric acid or nitric acid, or a mixture of any two thereof; said inorganic base is sodium hydroxide or potassium hydroxide.

4. A process for preparing the bi-microporous/mesoporous composite molecular sieve according to claim 2, characterized in that said silicon source is industrial sodium silicate; said aluminum is any one of aluminum chloride, aluminum sulfate or aluminum nitrate, or a mixture of any two thereof.

5. A process for preparing the bi-microporous/mesoporous composite molecular sieve according to claim 2, characterized in that the time of stirring before adjusting the pH value of the system is typically 1.0h~1.5h, and the time of stirring after adjusting the pH value is 0.5h.

6. A process for preparing the bi-microporous/mesoporous composite molecular sieve according to claim 2 characterized in that when ion-exchanging the calcined product in the solution of ammonium salt, the ammonium salt used is any one of ammonium nitrate or ammonium chloride, or the mixture thereof.