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CA 2855178 C 2019/10/29

(11)(21) **2 855 178**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2012/10/30
(87) Date publication PCT/PCT Publication Date: 2013/05/16
(45) Date de délivrance/Issue Date: 2019/10/29
(85) Entrée phase nationale/National Entry: 2014/05/09
(86) N° demande PCT/PCT Application No.: CN 2012/001473
(87) N° publication PCT/PCT Publication No.: 2013/067764
(30) Priorité/Priority: 2011/11/10 (CN201110353591.7)

(51) Cl.Int./Int.Cl. *C01B 39/48* (2006.01), *B01J 29/70* (2006.01)

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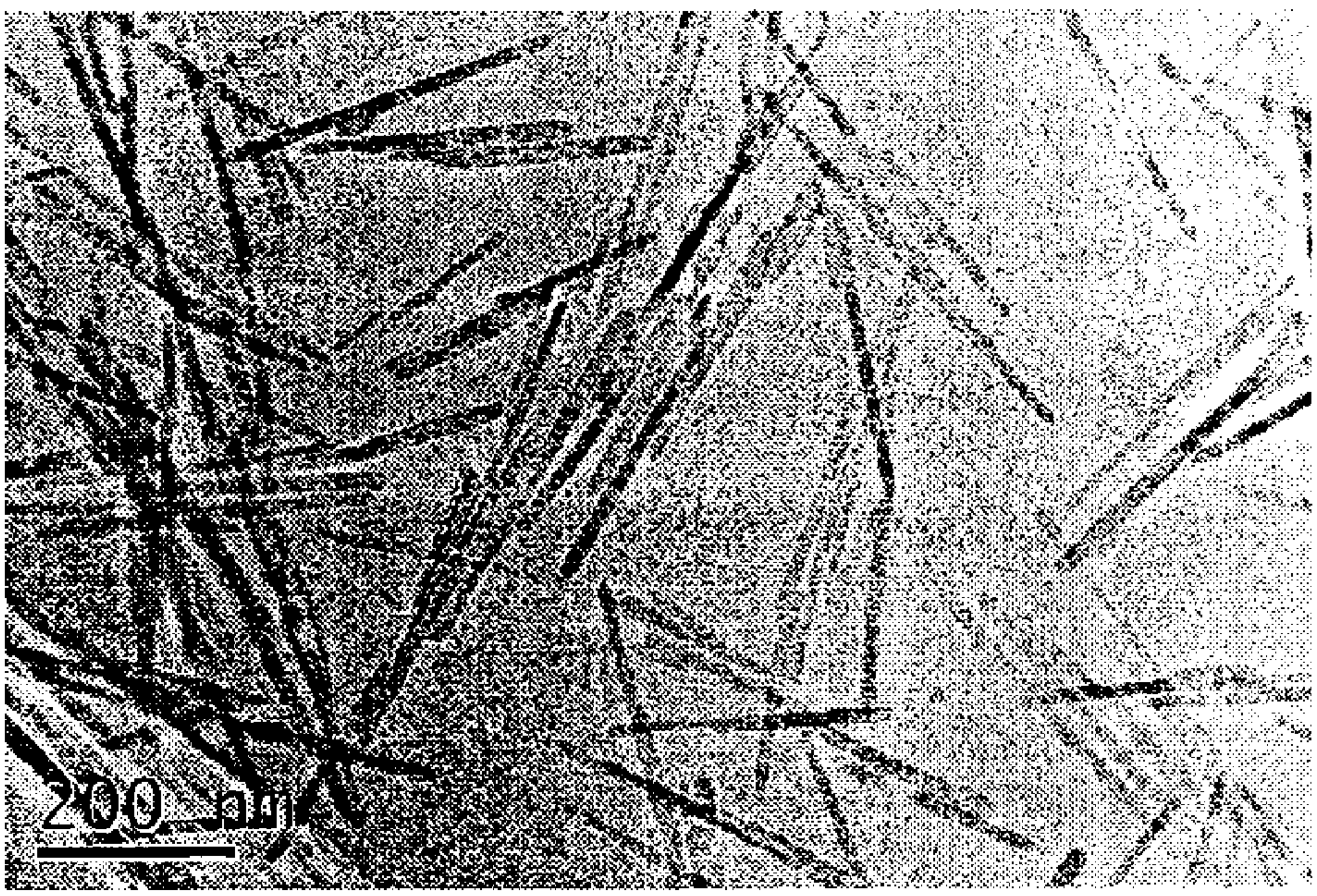
(54) Titre : UN TAMIS MOLECULAIRE IM-5 FIBREUX ET SON PROCEDE DE PREPARATION
(54) Title: A FIBROUS IM-5 MOLECULAR SIEVE AND THE PREPARATION PROCESS THEREOF



(57) Abrégé/Abstract:
The present invention provides a fibrous IM-5 molecular sieve and the preparation process thereof. According to the process according to the present invention, by adding an appropriate amount of a quaternary ammonium salt with a long carbon chain to the preparation system so as to occur a synergistic action with the organic templet agent, an IM-5 molecular sieve which would be otherwise a rodlike form is converted into the fibrous form. The IM-5 molecular sieve according to the present invention has an aspect ratio greater than that of the rodlike IM-5 molecular sieve obtained according to the prior art, such that the proportion of the exposed periphery crystal face is higher, which benefit to increasing the selectivity of the catalytic reaction for the corresponding crystal face.

Abstract

The present invention provides a fibrous IM-5 molecular sieve and the preparation process thereof. According to the process according to the present invention, by adding an appropriate amount of a quaternary ammonium salt with a long carbon chain to the preparation system so as to occur a synergistic action with the organic templet agent, an IM-5 molecular sieve which would be otherwise a rodlike form is converted into the fibrous form. The IM-5 molecular sieve according to the present invention has an aspect ratio greater than that of the rodlike IM-5 molecular sieve obtained according to the prior art, such that the proportion of the exposed periphery crystal face is higher, which benefit to increasing the selectivity of the catalytic reaction for the corresponding crystal face.

A fibrous IM-5 molecular sieve and the preparation process thereof

Technical field

The present invention relates to a fibrous IM-5 molecular sieve and the preparation process thereof, and thus belongs to the field of preparing an inorganic material.

Background

The microporous molecular sieve material has regular pore structures and a large surface area, thus is widely used in the fields of adsorption, separation, chemical engineering, catalysis and the like. In recent years, some new structures of molecular sieve materials have been prepared continuously.

IM-5 molecular sieve is a new zeolite prepared using a bi-quaternary ammonium salt as the templet agent. The IM-5 molecular sieve has a pore-passage structure similar to that of ZSM-5, has a two dimensional 10MR crossing pore structure, and has relatively high thermal stability and hydrothermal stability. Thus the ZSM-5 has a broad prospect of application for catalysis in the petrochemical fields of paraffin cracking, isomerization of n-butylene, preparation of gasoline from Synthesis Gas and the like.

Journal of Molecular Catalysis A: Chemical, 2000, 162: 175-189 Discloses to obtain an IM-5 molecular sieve from crystallization for 10 days using 1,1-(pentamethylene) bis-(1-methylpyrrolidinium) bromide as the templet agent, under the condition of adding a promoter of sodium bromide and static hydrothermal conditions at a temperature of 175 degrees C.

Journal of Catalysis 215 (2003) 151-170 discloses to obtain an IM-5 molecular sieve from crystallization for 14 days using 1,1-(pentamethylene) bis-(1-methylpyrrolidinium) bromide as the templet agent, under the dynamic hydrothermal condition at a temperature of 160 degrees C.

CN1234012A discloses an IM-5 molecular sieve and the preparation process thereof. The IM-5 molecular sieve is obtained with high crystallinity from hydrothermal crystallization for 8 days at a temperature of 170 degrees C by adding additional NU-88 powder as a seed crystal.

By studying the IM-5 products prepared according to the documents above, it can be seen that the IM-5 molecular sieves prepared from prior arts have an morphology of two dimensional rodlike form with a diameter of generally 50nm or more and an aspect ratio of generally about 5. Regarding a two dimensional rodlike molecular sieve, the aspect ratio determines the proportional relation between the crystal face in the radial direction and the crystal face in the axial direction. The more the aspect ratio is, the more the area of the periphery crystal face, and correspondingly the less the area of the sectional plane crystal face. It is currently known that a certain crystal face of a crystalline material has specific reactivity, such that the more the crystal face exposes, the higher the corresponding reaction selectivity. Therefore, by controlling the proportional relation between the periphery crystal face and the sectional crystal face through the aspect ratio of the two dimensional rodlike molecular sieve, the reaction selectivity of the corresponding crystal face can be increased.

Summary of the invention

The present invention provides a fibrous IM-5 molecular sieve and the preparation process thereof. According to the process of the present invention, a fibrous IM-5 molecular sieve can be prepared by adding a cationic surfactant to the reaction system so as to occur a synergistic action with the organic templet agent.

The IM-5 molecular sieve according to the present invention is in the fibrous form. The fibrous IM-5 molecular sieve has an average diameter of about 5-about 30nm, preferably not less than about 6nm, not less than about 7nm, not less than about 8nm, not less than about 9nm, or not less than about 10nm; and preferably not more than about 29nm, not more than about 28nm, not more than about 27nm, not more than about 26nm, or not more than about 25nm. The average aspect ratio is about 15-about 100, preferably not less than about 16, not less than about 17, not less than about 18, not less than about 19, or not less than about 20; and preferably not more than about 90, not more than about 80, not more than about 70, not more than about 60, or not more than about 50.

For example, the average diameter is preferably about 10-about 25 nm, and/or the average aspect ratio is preferably about 20-about 50.

The fibrous IM-5 molecular sieve according to the present invention has an average length of about 100-about 3000nm, preferably not less than about 120nm, not less than about 140nm, not less than about 160nm, not less than about 180nm, or not less than about 200nm; and preferably not more than about 2500nm, not more than about 2000nm, not more than about 1750nm, not more than about 1500nm, or not more than about 1250nm. For example, the average length is preferably about 200-about 1250nm.

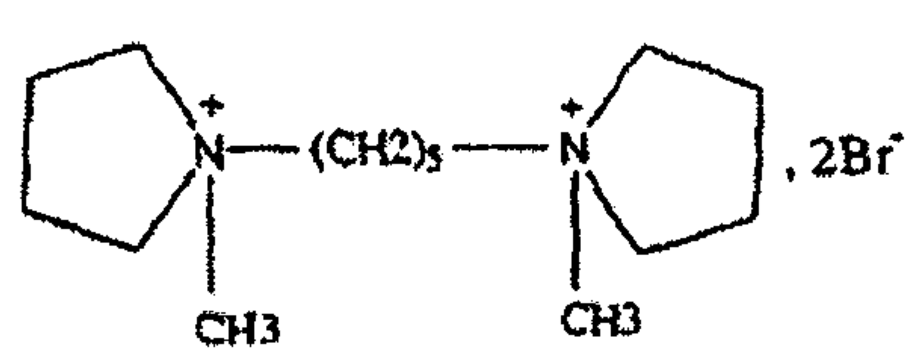
The process of preparing the fibrous IM-5 molecular sieve according to the present invention comprises:

(1) mixing an alkali source, a templet agent, an aluminum source, water, a silicon source and a cationic surfactant homogeneously, and stirring the mixture at a suitable temperature to generate a sol; and

(2) elevating the temperature of the mixture of step (1) in a hydrothermal reactor to about 140-about 200 degrees C, after hydrothermal crystallization of about 2-about 15 days, taking out and separating the solid product, drying and calcinating to obtain an IM-5 molecular sieve in the fibrous form.

In step (1), the temperature for stirring is about 20-about 70 degrees C, preferably about 55-about 65 degrees C. The duration of stirring is about 1-about 24 hours, preferably about 3-about 12 hours.

In step (1), the templet agent is 1,1'-(pentamethylene) bis(1-methylpyrrolidinium), having a structural formula of:



The aluminum source is aluminum nitrate, aluminum chloride, aluminum sulfate, or a combination the thereof, preferably aluminum nitrate. The alkali source is sodium hydroxide, potassium hydroxide, lithium hydroxide or the combination thereof, preferably sodium hydroxide. The silicon source is white carbon, silicic acid, silanolate, silica sol, silica gel, or a combination thereof, preferably white carbon. The surfactant is one or more cationic quaternary ammonium salt having a carbon chain of 12-16 carbon atoms, and the corresponding negative ion is a bromide ion or chloride ion, preferably bromide ion. The cationic quaternary ammonium salt having a carbon chain of 12-16 carbon atoms includes, but not limited to, cetyl trimethylammonium bromide, myristyl trimethylammonium bromide, and dodecyl trimethylammonium bromide.

In step (1), the molar ratios calculated based on the following species for the various components of the reaction mixture are:

SiO_2/Al_2O_3 of about 40-about 70, preferably of about 50-about 70;

R/ SiO_2 of about 0.15-about 0.4, preferably about 0.15-about 0.3, R representing the templet agent;

H_2O/SiO_2 of about 30-about 70, preferably of about 40-about 60;

OH^-/SiO_2 of about 0.6-about 0.8, preferably about 0.70-about 0.75; and

R/SUR^+ of about 5-about 20, preferably not less than about 6, not less than about 7, or not less than about 8; and preferably not more than about 19, not more than about 18, not more than about 17, or not more than about 16; for example, the ratio is preferably about 8-about 16, wherein the SUR^+ represents the cationic surfactant.

In step (2), the temperature for the hydrothermal crystallization is about 160-about 185 degrees C, more preferably about 165-about 175 degrees C; and the duration of the hydrothermal crystallization is about 7-about 12 days.

The IM-5 molecular sieve according to the present invention has an aspect ratio greater than that of the rodlike IM-5 molecular sieve obtained according to the prior art, such that the proportion of the exposed periphery crystal face is higher, which benefits to increasing the selectivity of the catalytic reaction for the corresponding crystal face. Meanwhile, the diameter of the molecular sieve having a large aspect ratio prepared according to the invention is less than the diameter of the IM-5 obtained according the prior art, and reaches to the nano-scale, which is then more beneficial for the mass transfer in the radial direction, such that the reactivity and selectivity of the periphery crystal face can be further increased.

Description of drawings

Figure 1 is a XRD curve of the fibrous IM-5 molecular sieve prepared according to Example 1 of the present invention.

Figure 2 is a transmission electron micrograph of the fibrous IM-5 molecular sieve prepared according to Example 1 of the present invention.

Figure 3 is a transmission electron micrograph of the fibrous IM-5 molecular sieve prepared according to Example 2 of the present invention.

Figure 4 is a transmission electron micrograph of a conventional IM-5 molecular sieve prepared according to Comparative Example 1 provided by the present invention.

Embodiments

In the present invention, the length and diameter of the fibrous molecular sieve are measured according the method as follows. The diameter and length of the fibrous molecular sieve are measured with a transmission electron microscope. 20 transmission electron micrographs are taken randomly, from which the diameter and length of the fibrous molecular sieve are measured using an image processing software, Image J. The lengths and diameters of at least 5 fibers that can be displayed integrally on each image are measured, so as to obtain the aspect ratio with the length and diameter data.

Average length= the sum of the lengths of all the fibers measured /the total number of the fibers

Average diameter= the sum of the diameters of all the fibers measured /the total number of the fibers

Average aspect ratio= the sum of the aspects of all the fibers measured /the total number of the fibers

The embodiments and effects of the present invention will be further illustrated below with Examples.

In the examples, the transmission electron microscope (TEM) is manufactured by JEOL Ltd., with a model of JEM 2100 (HR), an accelerating voltage of 200KV, and a resolution of 0.23nm.

Example 1

Sodium hydroxide, 1,1'-(pentamethylene) di-(1-methylpyrrolidinium) bromide, aluminum nitrate, water, white carbon and cetyl trimethylammonium bromide (CTAB) were mixed at a room temperature, according to molar ratios calculated based on the following species as follows: SiO_2/Al_2O_3=55, OH^-/SiO_2=0.73, R/SiO_2=0.2, H_2O/SiO_2=50, and R/CTAB=8.

The mixture obtained was then stirred in a water bath at a temperature of 60 degrees C to be a homogeneous sol, which sol was kept at the constant temperature for 5 hours with stirring for pre-gelation. Subsequently, the gel was transferred into a hydrothermal reactor, heated to 165 degrees C, hydrothermal crystallized for 11 days, then cooled naturally, filtered and dried to provide a molecular sieve coarse powder. By the XRD measurement, the products obtained were all well crystallized fibrous IM-5 molecular sieve, which were observed for the morphology with the TEM at low range, having an average diameter of 13nm, an average length of 357nm, and an average aspect ratio of 27.5.

Example 2

Sodium hydroxide, 1,1'-(pentamethylene) di-(1-methylpyrrolidinium) bromide, aluminum nitrate, water, white carbon and cetyl trimethylammonium bromide(CTAB) were mixed at a room temperature, according to molar ratios calculated based on the following species as follows: SiO_2/Al_2O_3=55, OH^-/SiO_2=0.73, R/SiO_2=0.2, H_2O/SiO_2=50, and R/CTAB=11.

The mixture obtained was then stirred in a water bath at a temperature of 60 degrees C to be a homogeneous sol, which sol was kept at the constant temperature for 5 hours with stirring for pre-gelation. Subsequently, the gel was transferred into a hydrothermal reactor, heated to 165 degrees C, hydrothermal crystallized for 11 days, then cooled naturally, filtered and dried to provide a molecular sieve coarse powder. By the XRD measurement, the products obtained were all well crystallized fibrous IM-5 molecular sieve, which were observed for the morphology with the TEM at low range, having an average diameter of 12nm, an average length of 550nm, and an average aspect ratio of 24.

Example 3

Sodium hydroxide, 1,1'-(pentamethylene) di-(1-methylpyrrolidinium) bromide, aluminum nitrate, water, white carbon and cetyl trimethylammonium bromide(CTAB) were mixed at a room temperature, according to molar ratios calculated based on the following species as follows: SiO_2/Al_2O_3=55, OH^-/SiO_2=0.71, R/SiO_2=0.27, H_2O/SiO_2=60, and R/CTAB=10.

The mixture obtained was then stirred in a water bath at a temperature of 65 degrees C to be a homogeneous sol, which sol was kept at the constant temperature for 10 hours with stirring for pre-gelation. Subsequently, the gel was transferred into a hydrothermal reactor, heated to 165 degrees C, hydrothermal crystallized for 11 days, then cooled naturally, filtered and dried to provide a molecular sieve coarse powder. By the XRD measurement, the products obtained were all well crystallized fibrous IM-5 molecular sieve, which were observed for the morphology with the TEM at low range, having an average diameter of 17nm, an average length of 700nm, and an average aspect ratio of 38.

Example 4

Sodium hydroxide, 1,1'-(pentamethylene) di-(1-methylpyrrolidinium) bromide, aluminum nitrate, water, white carbon and dodecyl trimethylammonium bromide(DTAB) were mixed at a room temperature, according to molar ratios calculated based on the following species as follows: SiO_2/Al_2O_3=68, OH^-/SiO_2=0.75, R/SiO_2=0.15, H_2O/SiO_2=45, and R/DTAB=16.

The mixture obtained was then stirred in a water bath at a temperature of 60 degrees C to be a homogeneous sol, which sol was kept at the constant temperature for 10 hours with stirring for pre-gelation. Subsequently, the gel was transferred into a hydrothermal reactor, heated to 175 degrees C, hydrothermal crystallized for 7 days, then cooled naturally, filtered and dried to provide a molecular sieve coarse powder. By the XRD measurement, the products obtained were all well crystallized fibrous IM-5 molecular sieve, which were observed for the morphology with the TEM at low range, having an average diameter of 24nm, an average length of 1050nm, and an average aspect ratio of 43.

Comparative example 1

An IM-5 molecular sieve was prepared referring to the process disclosed by Journal of Catalysis 215 (2003) 151-170. The raw materials, ratios and reaction temperature were same as example 1, except that the raw material mixture was not added with the cetyl trimethylammonium bromide, but, instead, transferred directly and respectively to the hydrothermal reactor after the homogeneous stirring, so as to carry out a hydrothermal crystallization for 11 days at a temperature of 165 degrees C. By the XRD measurement, the products obtained were conventional rodlike IM-5, which were conventional rodlike crystal grains of IM-5 measured by TEM, having typically a particle diameter of about 111nm, a length of about 428nm, and an aspect ratio of about 3.9.

Claims

1. An IM-5 molecular sieve, characterized in that the IM-5 molecular sieve is in a fibrous form, having an average diameter of from 5nm to 30nm and an average aspect ratio of 15-100.

2. The IM-5 molecular sieve according to claim 1, having an average diameter of from 10 nm to 25nm.

3. The IM-5 molecular sieve according to claim 1 or 2, having an average aspect ratio of from 20 to 50.

4. The IM-5 molecular sieve according to any one of claims 1 to 3, wherein the average length of the fibrous IM-5 molecular sieve is from 100nm to 3000nm.

5. The IM-5 molecular sieve according to claim 4, wherein the average length of the fibrous IM-5 molecular sieve is from 200 nm to 1250nm.

6. A process of preparing the IM-5 molecular sieve according to any one of claims 1 to 5, characterized in comprising the steps of:

(1) mixing an alkali source, a templet agent, an aluminum source, water, a silicon source and a cationic surfactant homogeneously, wherein the template agent is 1,1'-(pentamethylene) bis(1-methylpyrrolidinium) bromide and the cationic surfactant is a cationic quaternary ammonium salt having a carbon chain of 12-18 carbon atoms, and stirring the mixture at a temperature of 20 – 70°C for a duration of from 1 – 24 hours to generate a sol; and

(2) elevating the temperature of the mixture of step (1) in a hydrothermal reactor to 140 – 200°C, after a hydrothermal crystallization of 2 – 15 days, taking out and separating the solid product, drying and calcinating to obtain an IM-5 molecular sieve in the fibrous form,

wherein in step (1), the molar ratio of R/SUR^{+} is 5 – 20, wherein R represents the template agent and SUR^{+} represents the cationic surfactant.

7. The process according to claim 6, wherein in step (1), the temperature for 55 – 65°C.

8. The process according to claim 6 or 7, wherein in step (1), the duration of mixing is 3 – 12 hours.

9. The process according to any one of claims 6 to 8, wherein, in step (1), the aluminum source is aluminum nitrate, aluminum chloride, aluminum sulfate, or a combination thereof; the alkali source is sodium hydroxide, potassium hydroxide, lithium hydroxide, or a combination thereof; and the silicon source is white carbon, silicic acid, silanolate, silica sol, silica gel, or a combination thereof.

10. The process according to any one of claims 6 to 9, wherein, in step (1), the corresponding negative ion of the surfactant is a bromide ion or chloride ion.

11. The process according to any one of claims 6 to 10, wherein, in step (1), the surfactant is cetyl trimethylammonium bromide, myristyl trimethylammonium bromide or dodecyl trimethylammonium bromide.

12. The process according to any one of claims 6 to 11, wherein, in step (1), the molar ratios calculated based on the following species for the various components of the reaction mixture are:

SiO_2/Al_2O_3 of 40 – 70;

R/SiO_2 of 0.15 – 0.4, R representing the templet agent;

H_2O/SiO_2 of 30 – 70;

OH^-/SiO_2 of 0.6 – 0.8.

13. The process according to claim 12, wherein the ratio of SiO_2/Al_2O_3 is 50 – 70.

14. The process according to claim 12 or 13, wherein the ratio of R/SiO_2 is 0.15 – 0.3.

15. The process according to any one of claims 12 to 14, wherein the ratio of H_2O/SiO_2 is 40 – 60.

16. The process according to any one of claims 12 to 15, wherein the ration of OH^-/SiO_2 is 0.70 – 0.75.

17. The process of any one of claims 6 to 16, wherein the molar ratio of R/SUR^+ is 8 – 16.

18. The process according to any one of claims 6 to 17, wherein, in step (2), the temperature for the hydrothermal crystallization is 160 – 185°C.

19. The process according to claim 18, wherein, in step (2), the temperature for the hydrothermal crystallization is 165 – 175°C.

20. The process according to any one of claims 6 to 19, wherein, in step (2), the duration of the hydrothermal crystallization is 7 – 12 days.

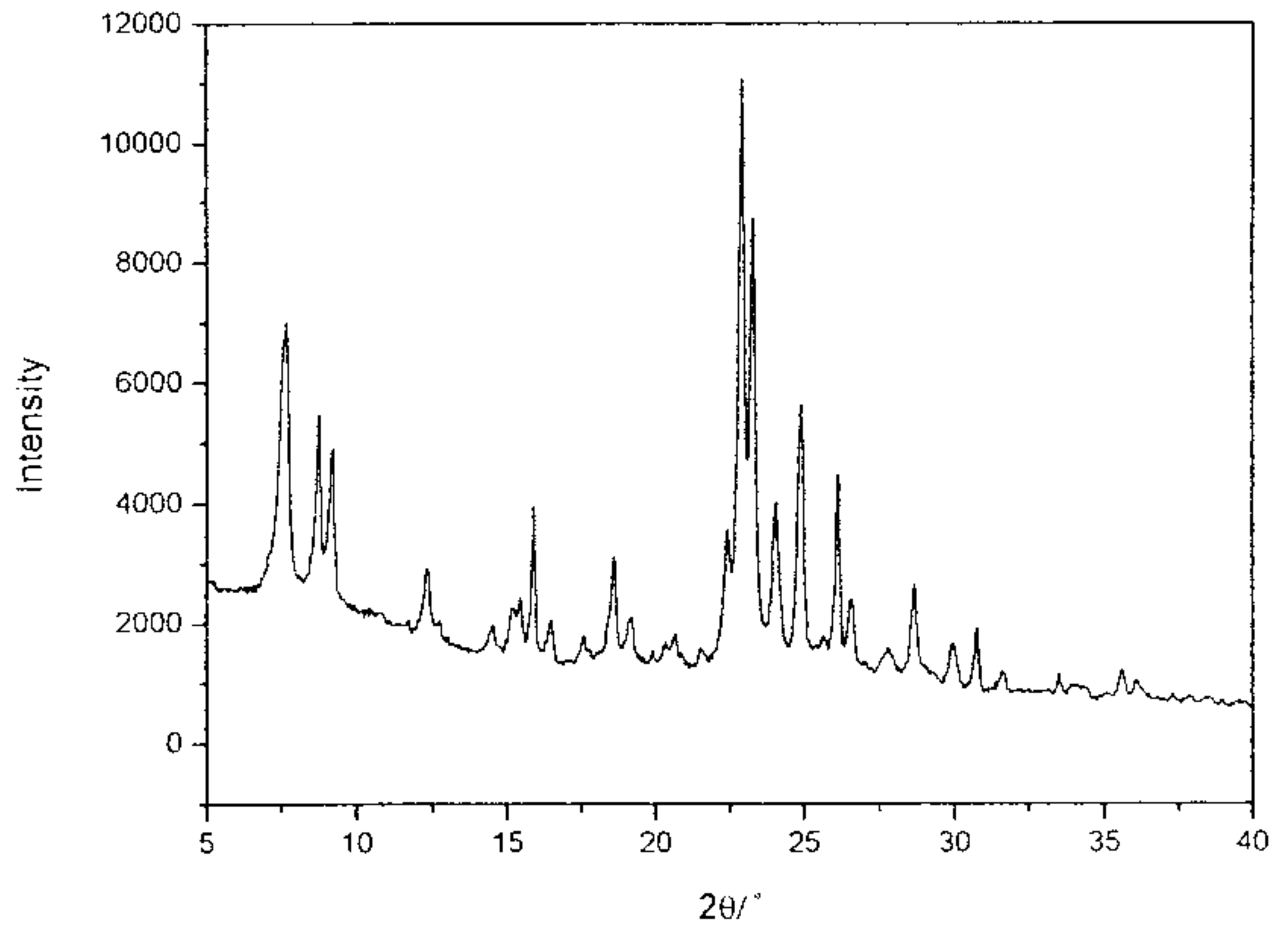


Fig. 1

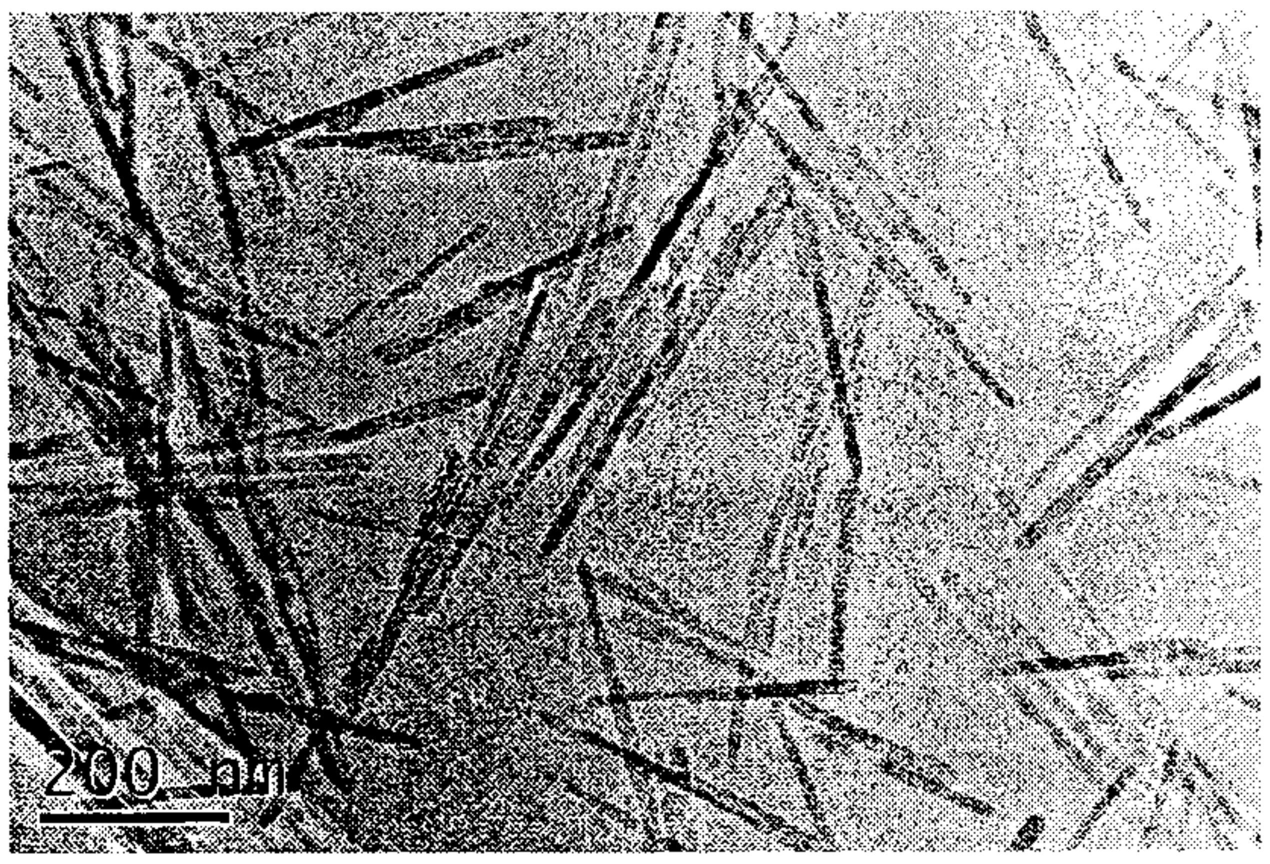


Fig. 2

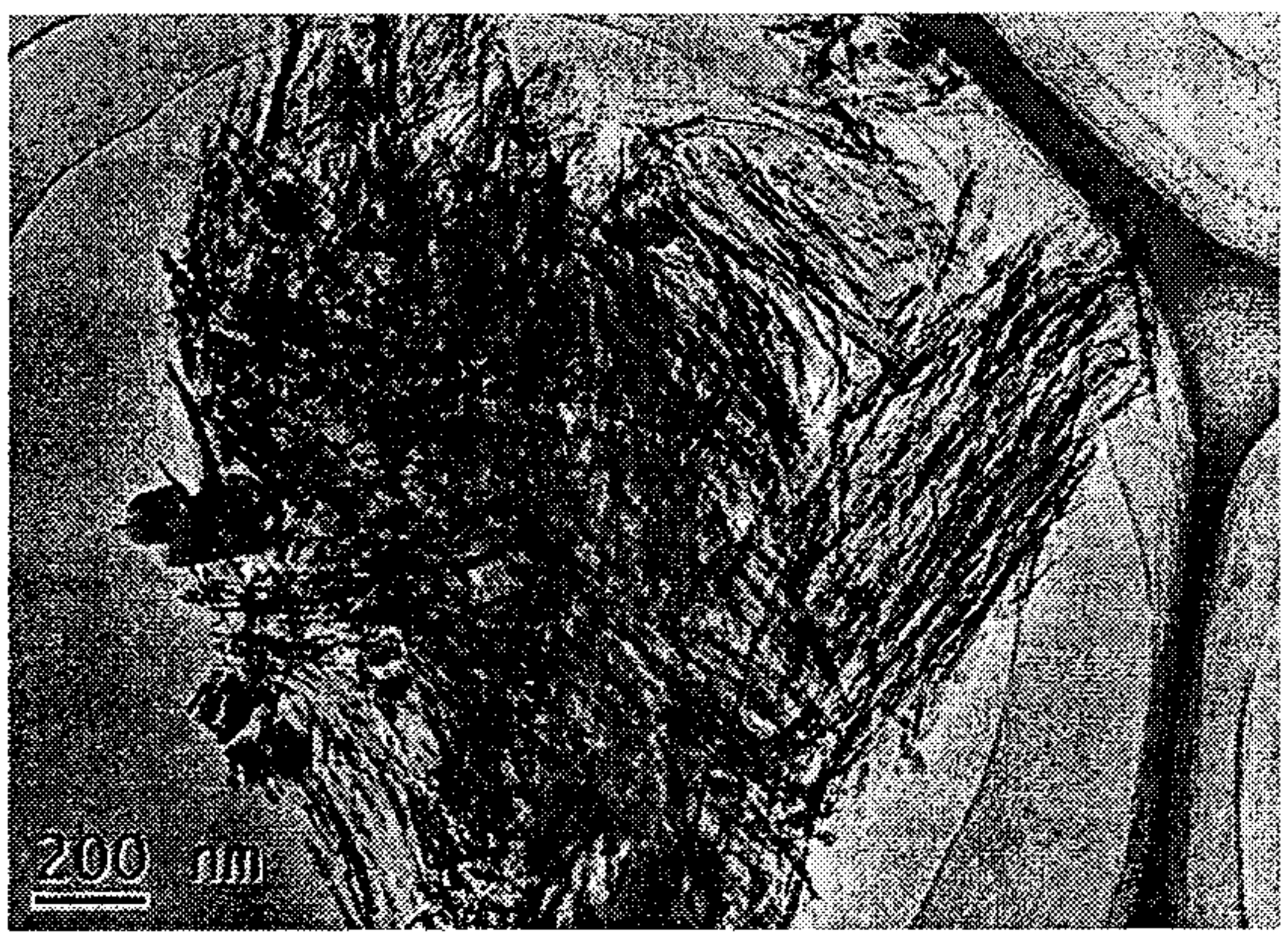


Fig. 3

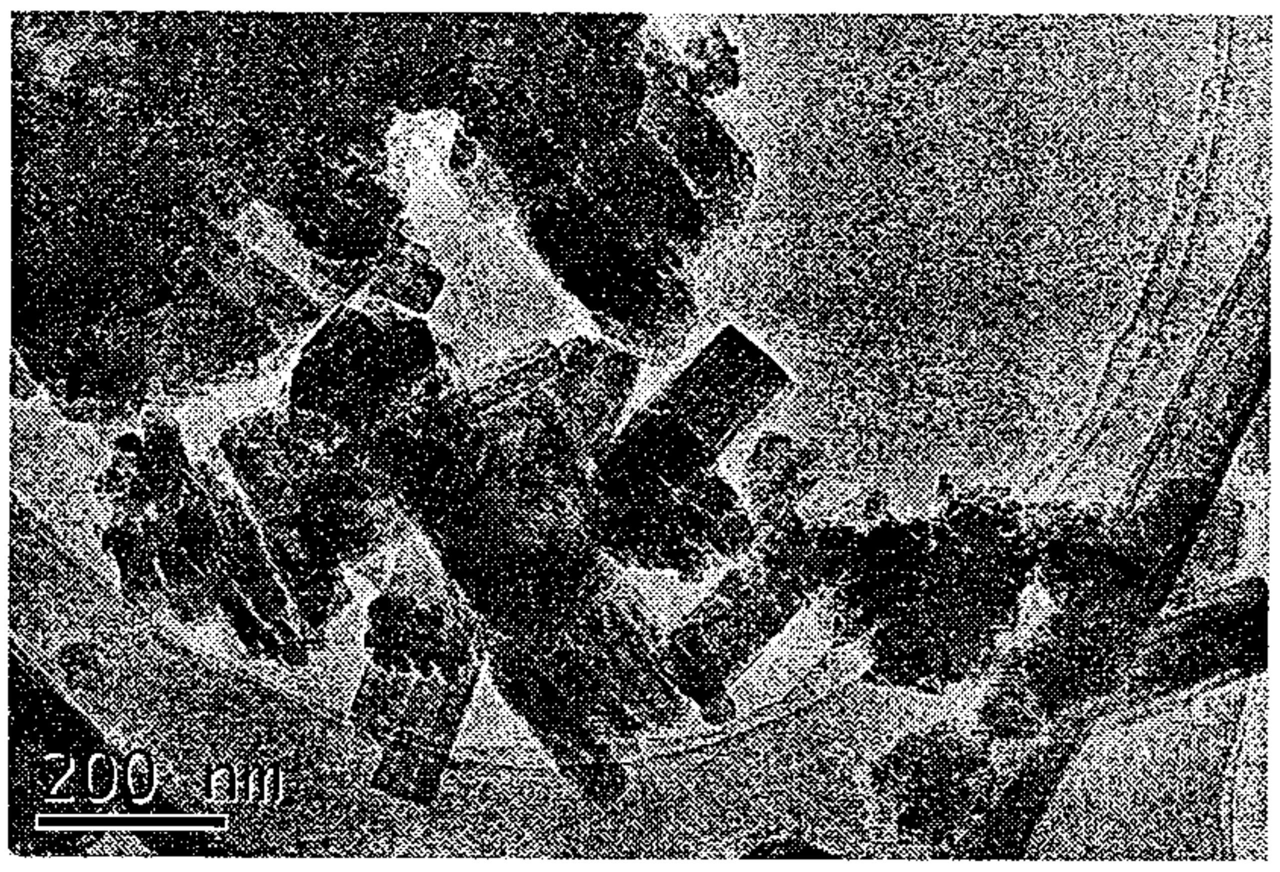
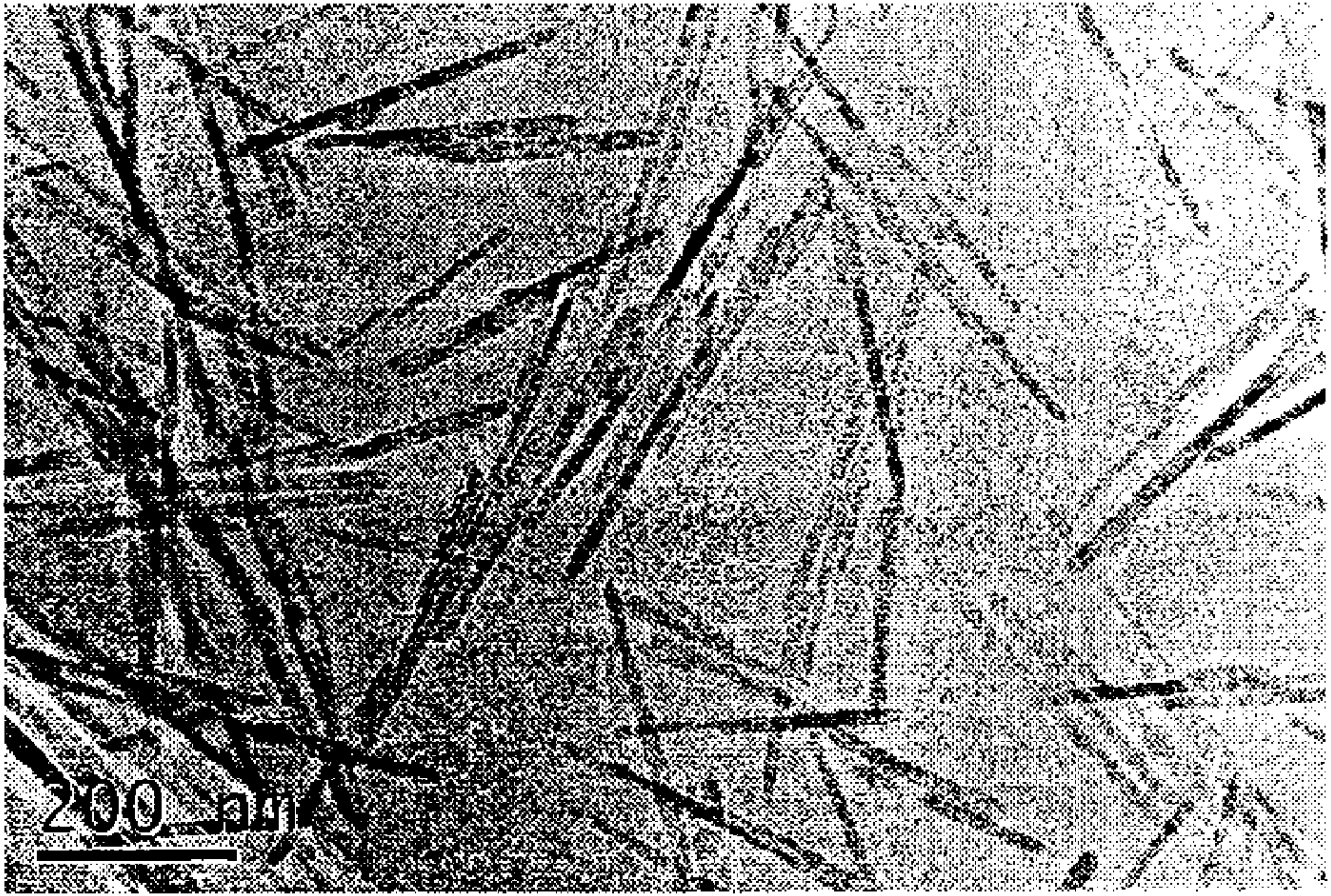


Fig. 4


200 nm