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(54) Title: SYNTHESIS OF MTW FRAMEWORK TYPE MOLECULAR SIEVES

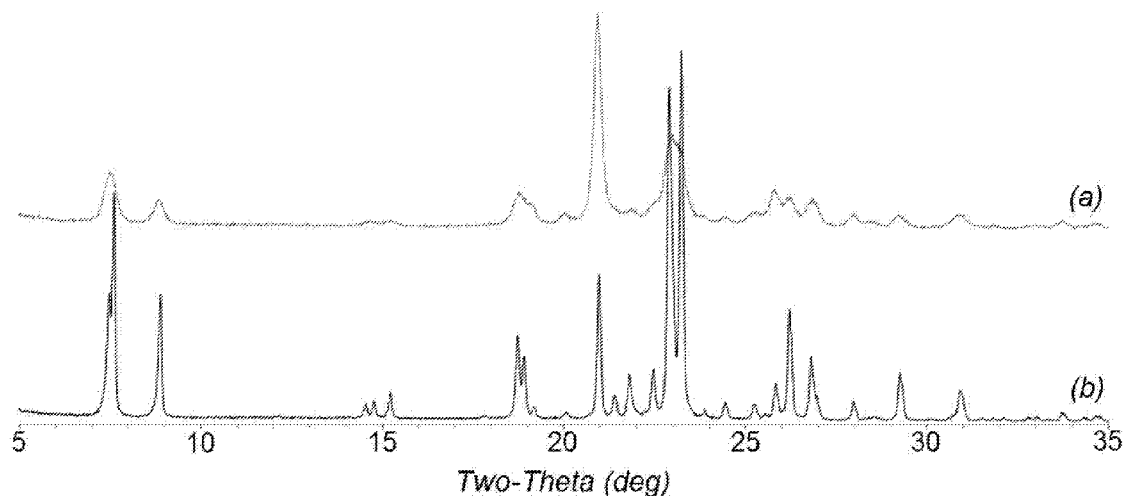


FIG. 1

(57) Abstract: A method is disclosed for synthesizing MTW framework type molecular sieves using 1,1-diethyl-4-methylpiperidinium cations as a structure directing agent.



## **SYNTHESIS OF MTW FRAMEWORK TYPE MOLECULAR SIEVES**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

[001] This application claims priority to U.S. Provisional Application Ser. No. 62/411,788, filed on October 24, 2016, the disclosure of which is incorporated herein by reference.

### **TECHNICAL FIELD**

[002] The present disclosure is directed to the synthesis of MTW framework type molecular sieves.

### **BACKGROUND**

[003] Because of their unique sieving characteristics as well as their catalytic properties, crystalline molecular sieves and zeolites are especially useful in applications such as hydrocarbon conversion, gas drying and separation.

[004] Molecular sieves identified by the International Zeolite Association as having the framework type MTW are known. Examples of MTW framework type materials include CZH-5, NU-13, Theta-3, TPZ-12, and ZSM-12. MTW framework type materials have a one-dimensional pore system with 12-membered rings.

[005] U.K. Patent Application No. 2,079,735 discloses CZH-5 and its synthesis using choline as a structure directing agent.

[006] U.S. Patent No. 4,743,437 discloses NU-13 and its synthesis in the presence of a piperazine compound as a structure directing agent.

[007] European Patent Application No. 162,719 discloses Theta-3 and its synthesis in the presence of a quaternary nitrogen compound of formula  $BzNR_3^+X^-$  where Bz is a benzyl radical, R is hydrocarbyl group and  $X^-$  is an anion.

[008] U.S. Patent No. 4,557,919 discloses TPZ-12 and its synthesis in the presence of a pyrrolidine- or piperidine-containing diammonium compound as a structure directing agent.

[009] ZSM-12 and its conventional preparation in the presence of a tetramethylammonium or tetraethylammonium structure directing agent are disclosed in U.S. Patent No. 3,832,449.

[010] U.S. Patent No. 4,391,785 discloses a method for the synthesis of ZSM-12 from a reaction mixture comprising, as a structure directing agent, a compound selected from the group consisting of a dimethylpyridinium halide and a dimethylpyrrolidinium halide.

[011] U.S. Patent Nos. 4,452,769 and 4,537,758 disclose methods for synthesizing ZSM-12 from a reaction mixture containing methyltriethylammonium cations as the structure directing agent.

[012] Other structure directing agents that have been used to synthesize ZSM-12 include DABCO- $C_n$ -diquat cations where  $n=4, 5, 6$  or  $10$  (see U.S. Patent No. 4,482,531), bis(dimethylpiperidinium)trimethylene cations (see U.S. Patent No. 4,539,193), benzyltriethylammonium cations (see U.S. Patent No. 4,552,738), dibenzyl dimethylammonium cations (see U.S. Patent No. 4,636,373), dimethyldiethylammonium cations (see U.S. Patent No. 4,552,739), benzyltrimethylammonium cations (see U.S. Patent No. 4,585,637), bis(*N*-methylpyridyl)ethylinium cations (see U.S. Patent No. 4,585,746), hexamethyleneimine (U.S. Patent No. 5,021,141), decamethonium cations (see U.S. Patent No. 5,192,521), bis(methylpyrrolidinium) diquat- $n$  ions where  $n=4, 5,$  or  $6$  (see U.S. Patent No. 5,137,705), and 1,6-bis(2,3-dimethylimidazolium)hexane dications (see U.S. Patent No. 8,679,451).

[013] According to the present disclosure, MTW framework type molecular sieves have now been synthesized using 1,1-diethyl-4-methylpiperidinium cations as a structure directing agent, and, in some cases, it has been found that small crystal forms of the molecular sieve can be produced.

## SUMMARY

[014] In one aspect, there is provided a method of synthesizing a molecular sieve of MTW framework type, the method comprising: (a) preparing a reaction mixture comprising: (1) a source of silicon oxide; (2) a source of an oxide of a trivalent element; (3) a source of Group 1 or 2 metal; (4) a structure directing agent comprising 1,1-diethyl-4-methylpiperidinium cations; and (5) hydroxide ions; and (6) water; and (b) subjecting the reaction mixture to crystallization condition sufficient to form crystals of the molecular sieve.

[015] In one aspect, there is provided a molecular sieve of MTW framework type comprising 1,1-diethyl-4-methylpiperidinium cations within its pore structure.

[016] In its as-synthesized and anhydrous form, the MTW framework type molecular sieve has a chemical composition comprising, in terms of molar ratios, the following:

$\text{SiO}_2/\text{X}_2\text{O}_3$	10 to 250	15 to 150
$\text{Q}/\text{SiO}_2$	>0 to 0.1	>0 to 0.1
$\text{M}/\text{SiO}_2$	>0 to 0.1	>0 to 0.1

wherein X is a trivalent element, Q comprises 1,1-diethyl-4-methylpiperidinium cations and M is Group 1 or Group 2 metal.

## BRIEF DESCRIPTION OF THE DRAWINGS

[017] FIG. 1 compares the powder X-ray diffraction (XRD) patterns of (a) the as-synthesized borosilicate product of Example 1 and (b) a conventional MTW framework type molecular sieve.

[018] FIG. 2 is a Scanning Electron Micrograph (SEM) image of the as-synthesized product of Example 1.

## DETAILED DESCRIPTION

### Reaction Mixture

[019] In general, the MTW framework type molecular sieve is synthesized by: (a) preparing a reaction mixture comprising (1) a source of silicon oxide; (2) a source of an

oxide of a trivalent element (X); (3) a source of a Group 1 or 2 metal (M); (4) a structure directing agent (Q) comprising 1,1-diethyl-4-methylpiperidinium cations; (5) hydroxide ions; and (6) water; and (b) subjecting the reaction mixture to crystallization conditions sufficient to form crystals of the molecular sieve.

[020] The composition of the reaction mixture from which the molecular sieve is formed, in terms of molar ratios, is identified in Table 1 below:

TABLE 1

Reactants	Useful	Exemplary
$\text{SiO}_2/\text{X}_2\text{O}_3$	10 to 250	15 to 150
$\text{M}/\text{SiO}_2$	0.05 to 0.30	0.05 to 0.20
$\text{Q}/\text{SiO}_2$	0.05 to 0.40	0.10 to 0.30
$\text{OH}/\text{SiO}_2$	0.10 to 0.50	0.20 to 0.45
$\text{H}_2\text{O}/\text{SiO}_2$	10 to 60	15 to 40

wherein X is a trivalent element (e.g., one or more of boron and aluminum), Q comprises 1,1-diethyl-4-methylpiperidinium cations and M is Group 1 or Group 2 metal.

[021] Suitable sources of silicon oxide include colloidal silica, fumed silica, precipitated silica, alkali metal silicates, and tetraalkyl orthosilicates.

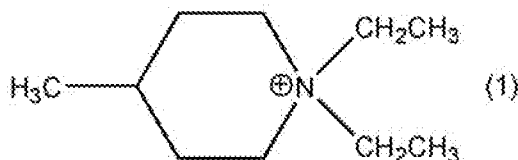
[022] Suitable sources of the trivalent element (X) can depend on the element X selected. Where X comprises or is boron, suitable sources of boron include boric acid and water-soluble borate salts (e.g., sodium borate). Where X comprises or is aluminum, suitable sources of aluminum include hydrated alumina and water-soluble aluminum salts (e.g., aluminum nitrate).

[023] Combined sources of silicon and boron can additionally or alternatively be used and can include borosilicate zeolites (e.g., borosilicate beta zeolite).

[024] Combined sources of silicon and aluminum can additionally or alternatively be used and can include aluminosilicate zeolites (e.g., zeolite Y) and clays or treated clays (e.g., metakaolin).

[025] Examples of suitable Group 1 or Group 2 metals (M) include sodium, potassium and calcium, with sodium being preferred. The metal (M) is generally present in the reaction mixture as the hydroxide.

[026] The structure directing agent (Q) comprises 1,1-diethyl-4-methylpiperidinium cations, represented by the following structure (1):



[027] Suitable sources of Q are the hydroxides, chlorides, bromides, and/or other salts of the quaternary ammonium compound.

[028] The reaction mixture may also contain seeds of a molecular sieve material, such as a MTW framework type molecular sieve, from a previous synthesis, desirably in an amount of from 0.01 to 10,000 ppm by weight (e.g., 100 to 5000 ppm by weight) of the reaction mixture.

[029] For each embodiment described herein, the reaction mixture can be supplied by more than one source. Also, two or more reaction components can be provided by one source.

[030] The reaction mixture can be prepared either batch wise or continuously. Crystal size, morphology and crystallization time of the crystalline molecular sieve described herein can vary with the nature of the reaction mixture and the crystallization conditions.

#### Crystallization and Post-Synthesis Treatment

[031] Crystallization of the molecular sieve from the above reaction mixture can be carried out under either static, tumbled or stirred conditions in a suitable reactor vessel, such as for example polypropylene jars or Teflon-lined or stainless steel autoclaves, at a temperature of from 125°C to 200°C for a time sufficient for

crystallization to occur at the temperature used, e.g., from 5 to 15 days. Crystallization is usually carried out in a closed system under autogenous pressure.

[032] Once the molecular sieve crystals have formed, the solid product is recovered from the reaction mixture by standard mechanical separation techniques such as centrifugation or filtration. The crystals are water-washed and then dried to obtain the as-synthesized molecular sieve crystals. The drying step is typically performed at a temperature of less than 200°C.

[033] As a result of the crystallization process, the recovered crystalline molecular sieve product contains within its pore structure at least a portion of the structure directing agent used in the synthesis.

[034] The as-synthesized MTW framework type molecular sieve prepared as described herein may be subjected to subsequent treatment to remove part or all of the organic structure directing agent used in its synthesis. This can be conveniently effected by thermal treatment in which the as-synthesized material can be heated at a temperature of at least 370°C for at least 1 minute and not longer than 24 hours. While sub-atmospheric and/or super-atmospheric pressures can be employed for the thermal treatment, atmospheric pressure may typically be desired for reasons of convenience. The thermal treatment can be performed at a temperature up to 925°C. Additionally or alternatively, the organic structure directing agent can be removed by treatment with ozone (see, e.g., A.N. Parikh *et al.*, *Micropor. Mesopor. Mater.* 2004, 76, 17-22).

[035] To the extent desired, the original Group 1 or Group 2 metal cations (e.g., K<sup>+</sup>) of the as-synthesized molecular sieve can be replaced in accordance with techniques well known in the art by ion exchange with other cations. Preferred replacing cations include metal ions, hydrogen ions, hydrogen precursor (e.g., ammonium ions), and mixtures thereof. Particularly preferred replacing cations are those which tailor the catalytic activity for certain organic conversion reactions. These include hydrogen, rare earth metals and metals of Groups 2 to 15 of the Periodic Table of the Elements.

[036] Where the molecular sieve formed is an intermediate molecular sieve, the target molecular sieve can be achieved using post-synthesis techniques such as heteroatom lattice substitution techniques and acid leaching techniques. For example, a small crystal form of an aluminosilicate MTW framework type molecular sieve (Al-MTW) can be prepared from a small crystal form of the borosilicate MTW framework type molecular sieve (B-MTW) by post-synthetic replacement of the boron in the borosilicate framework with aluminum. Replacement of boron in the borosilicate MTW framework type molecular sieve can be readily achieved by suitable treatment with an aluminum salt (e.g., aluminum nitrate) such as described in U.S. Patent Nos. 6,468,501 and 6,790,433. At least 10% (e.g., at least 25%, or at least 50%) of the boron in borosilicate framework may be replaced with aluminum.

[037] While not wishing to be bound by any theory, it is believed that Al re-insertion from B-MTW (i.e., indirect synthesis of Al-MTW) may allow for more localized replacement of B atoms (e.g., those in the 12-membered ring openings) by Al atoms in the structure. In contrast, it is believed that direct synthesis of Al-MTW results in Al being distributed more randomly distributed throughout the structure. S.I. Zones *et al.* (*J. Am. Chem. Soc.* 2014, 136, 1462-1471) reported that catalytic behavior can be changed dramatically due to the change of Al atomic positions (acid sites).

[038] The present MTW framework type molecular sieve can be used as a sorbent. Alternatively or additionally, and particularly in its aluminosilicate form, the present MTW framework type molecular sieve can be used as a catalyst to facilitate one or more organic compound (e.g., hydrocarbon) conversion processes including many of present commercial/industrial importance. In particular, when combined with a hydrogenation component (e.g., Pt, Pd or Re), the present MTW framework type molecular sieve may be useful in the catalytic conversion of C<sub>9+</sub> alkylaromatic hydrocarbons, either alone or in the presence of toluene and/or benzene, to produce xylenes.



[039] The present MTW framework type molecular sieve can be formulated into a catalyst composition by combination with other materials, such as binders and/or matrix materials, which provide additional hardness or catalytic activity to the finished catalyst.

[040] Materials which can be blended with the present MTW framework type molecular sieve can be various inert or catalytically active materials. These materials include compositions such as kaolin and other clays, various forms of rare earth metals, other non-zeolite catalyst components, zeolite catalyst components, alumina or alumina sol, titania, zirconia, quartz, silica or silica sol, and mixtures thereof. These components are also effective in reducing overall catalyst cost, acting as a thermal sink to assist in heat shielding the catalyst during regeneration, densifying the catalyst and increasing catalyst strength. When blended with such components, the amount of the present MTW framework type molecular sieve contained in the final catalyst product can range from 1 to 90 wt. % (e.g., 2 to 80 wt. %) of the total catalyst.

#### Characterization of the Molecular Sieve

[041] In its as-synthesized and anhydrous form, the present MTW framework type molecular sieve has a chemical composition, in terms of molar ratios, as shown in Table 2:

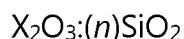
TABLE 2

	Broad	Exemplary
$\text{SiO}_2/\text{X}_2\text{O}_3$	10 to 250	15 to 150
$\text{Q}/\text{SiO}_2$	>0 to 0.1	>0 to 0.1
$\text{M}/\text{SiO}_2$	>0 to 0.1	>0 to 0.1

wherein X is a trivalent element (e.g., one or more of boron and aluminum), Q comprises 1,1-diethyl-4-methylpiperidinium cations, and M is Group 1 or Group 2 metal. The term "as-synthesized" is employed herein to refer to the molecular sieve in its form after crystallization, prior to removal of the structure directing agent. The term "anhydrous

form" is employed herein to refer to a molecular sieve substantially devoid of both physically adsorbed and chemically adsorbed water.

[042] In its calcined form, the present MTW framework type molecular sieve has a chemical composition comprising the following molar relationship:



wherein X is a trivalent element and *n* has a value of 10 to 250 (e.g., 10 to 150, 15 to 250, 15 to 150, 20 to 250, or 20 to 150).

[043] The MTW framework type molecular sieve prepared as described herein can form agglomerates of small crystals that may have crystallite sizes in a range of 10 to 250 nm (e.g., 25 to 200 nm, or 40 to 150 nm). These small crystals can be desirable for they generally lead to greater activity. Smaller crystals can mean greater surface area, which can lead to a greater number of active catalytic sites per given amount of catalyst. As used herein, the term "crystallite size" refers to the longest dimension of the crystal. Crystallite size can be determined by SEM analysis.

[044] The present MTW framework type molecular sieve is characterized by X-ray diffraction. Powder X-ray diffraction patterns representative of MTW framework type molecular sieves can be referenced in the *"Collection of Simulated XRD Powder Patterns for Zeolites,"* Fifth Revised Edition, 2007 of the International Zeolite Association. Minor variations in the diffraction pattern can result from variations in the mole ratios of the framework species of the particular sample due to changes in lattice constants. In addition, sufficiently small crystals will affect the shape and intensity of peaks, leading to significant peak broadening. Minor variations in the diffraction pattern can result from variations in the organic compound used in the preparation. Calcination can also cause minor shifts in the X-ray diffraction pattern.

[045] The powder X-ray diffraction patterns presented herein were collected by standard techniques. The radiation was  $CuK_{\alpha}$  radiation. The peak heights and the positions, as a function of  $2\theta$  where  $\theta$  is the Bragg angle, were read from the relative

intensities of the peaks, and  $d$ , the interplanar spacing corresponding to the recorded lines, can be calculated.

### EXAMPLES

[046] The following illustrative examples are intended to be non-limiting.

#### EXAMPLE 1

[047] 12.10 g of deionized water, 0.42 g of a 45% KOH solution, 3.55 g of a 24.39% 1,1-diethyl-4-methylpiperidinium hydroxide solution, 0.103 g of boric acid and 5.00 g of LUDOX<sup>®</sup> AS-40 colloidal silica were mixed together in a Teflon liner. The gel was stirred until it became homogeneous. The liner was then capped and placed within a Parr Steel autoclave reactor. The autoclave was then put in an oven heated at 170°C for 9 days. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[048] FIG. 1 compares the powder X-ray diffraction patterns of the as-synthesized borosilicate product of Example 1 in FIG 1(a) and a conventional MTW framework type molecular sieve in FIG. 1(b). As depicted in FIG. 1, the powder XRD pattern of the as-synthesized product showed the typical phase of MTW topology and also indicated decreased crystal size as inferred from the peak broadening in the XRD pattern.

[049] FIG. 2 is a SEM image of the as-synthesized product and showed that the material was composed of agglomerates of plate-like crystals with an average length of about 100 nm and average width of about 60 nm.

[050] The product had a SiO<sub>2</sub>/B<sub>2</sub>O<sub>3</sub> molar ratio of 38.7, as determined by ICP elemental analysis.

#### EXAMPLE 2

[051] 4.84 g of deionized water, 0.17 g of a 45% KOH solution, 1.42 g of a 24.39% 1,1-diethyl-4-methylpiperidinium hydroxide solution, 0.017 g of boric acid and 2.00 g of LUDOX<sup>®</sup> AS-40 colloidal silica were mixed together in a Teflon liner. The

resulting gel was stirred until it became homogeneous. The liner was then capped and placed within a Parr Steel autoclave reactor. The autoclave was then put in an oven heated at 170°C for 7 days. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[052] The resulting product was identified by powder XRD and SEM as a pure borosilicate MTW-type molecular sieve. The crystal sizes of the product were about the same as the product of Example 1.

[053] The product had a  $\text{SiO}_2/\text{B}_2\text{O}_3$  molar ratio of 82.3, as determined by ICP elemental analysis.

#### EXAMPLE 3

[054] 7.26 g of deionized water, 0.25 g of a 45% KOH solution, 2.13 g of a 24.39% 1,1-diethyl-4-methylpiperidinium hydroxide solution, 0.012 g of boric acid and 3.00 g of LUDOX<sup>®</sup> AS-40 colloidal silica were mixed together in a Teflon liner. The resulting gel was stirred until it became homogeneous. The liner was then capped and placed within a Parr Steel autoclave reactor. The autoclave was then put in an oven heated at 170°C for 7 days. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[055] The resulting product was identified by powder XRD and SEM as a pure borosilicate MTW-type molecular sieve. The crystal sizes of the product were about the same as the product of Example 1.

[056] The product had a  $\text{SiO}_2/\text{B}_2\text{O}_3$  molar ratio of 114.6, as determined by ICP elemental analysis.

#### EXAMPLE 4

[057] 26.68 g of deionized water, 1.00 g of a 45% KOH solution, 18.39 g of a 11.38% 1,1-diethyl-4-methylpiperidinium hydroxide solution and 5.00 g of CBV760 Y-zeolite powder (Zeolyst International,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio=60) were mixed together in a Teflon liner. The resulting gel was stirred until it became homogeneous. The liner was

then capped and placed within a Parr Steel autoclave reactor. The autoclave was then put in an oven heated at 160°C for 6 days. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[058] The resulting product was identified by powder XRD and SEM as a pure aluminosilicate MTW-type molecular sieve. The crystal sizes of the product are about the same as the product of Example 1.

[059] The product had a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 29.2, as determined by ICP elemental analysis.

#### EXAMPLE 5

[060] The as-synthesized molecular sieve product of Example 1 was calcined inside a muffle furnace under a flow of air heated to 595°C at a rate of 1°C/minute and held at 595°C for 5 hours, cooled and then analyzed by powder XRD. The powder XRD data indicated that the material remains stable after calcination to remove the structure directing agent.

[061] 1.5 g of calcined molecular sieve was then added to 32 mL of a 1M solution of aluminum nitrate in a Teflon liner. The liner was capped and placed within a Parr Steel autoclave reactor. The autoclave was then put in an oven heated at 160°C for 15 hours. The solid products were recovered from the cooled reactor by filtration, washed with deionized water.

[062] The dry product was identified by powder XRD as a pure MTW-type molecular sieve. The powder XRD data showed that the diffraction peaks were shifted to lower angles compared to the XRD data collected from the initial calcined sample, these shifts are consistent with expansion of the molecular sieve lattice when aluminum is inserted into the framework.

**CLAIMS**

1. A method of synthesizing a molecular sieve of MTW framework type, the method comprising:

(a) preparing a reaction mixture comprising:

- (1) a source of silicon oxide;
- (2) a source of an oxide of a trivalent element (X);
- (3) a source of Group 1 or 2 metal (M);
- (4) a structure directing agent (Q) comprising 1,1-diethyl-4-methylpiperidinium

cations;

(5) hydroxide ions; and

(6) water; and

(b) subjecting the reaction mixture to crystallization condition sufficient to form crystals of the molecular sieve.

2. The method of claim 1, wherein the reaction mixture has a composition, in terms of molar ratios, as follows:

$\text{SiO}_2/\text{X}_2\text{O}_3$	10 to 250
$\text{M}/\text{SiO}_2$	0.05 to 0.30
$\text{Q}/\text{SiO}_2$	0.05 to 0.40
$\text{OH}/\text{SiO}_2$	0.10 to 0.50
$\text{H}_2\text{O}/\text{SiO}_2$	10 to 60.

3. The method of claim 1, wherein the reaction mixture has a composition, in terms of molar ratios, as follows:

$\text{SiO}_2/\text{X}_2\text{O}_3$	15 to 150
$\text{M}/\text{SiO}_2$	0.05 to 0.20
$\text{Q}/\text{SiO}_2$	0.10 to 0.30
$\text{OH}/\text{SiO}_2$	0.20 to 0.45
$\text{H}_2\text{O}/\text{SiO}_2$	15 to 40.

4. The method of claim 1, wherein X comprises one or more of boron and aluminum.
5. The method of claim 1, wherein the crystallization conditions include a temperature of from 125°C to 200°C.
6. A molecular sieve of MTW framework type comprising 1,1-diethyl-4-piperidinium cations within its pore structure.
7. The molecular sieve of claim 6, and having a composition, in terms of molar ratios, as follows:

$\text{SiO}_2/\text{X}_2\text{O}_3$	10 to 250
$\text{M}/\text{SiO}_2$	>0 to 0.1
$\text{Q}/\text{SiO}_2$	>0 to 0.1

wherein X is a trivalent element, Q comprises 1,1-diethyl-4-methylpiperidinium cations, and M is Group 1 or Group 2 metal.

8. The molecular sieve of claim 6, and having a composition, in terms of molar ratios, as follows:

$\text{SiO}_2/\text{X}_2\text{O}_3$	15 to 150
$\text{M}/\text{SiO}_2$	>0 to 0.1
$\text{Q}/\text{SiO}_2$	>0 to 0.1

wherein X is a trivalent element, Q comprises 1,1-diethyl-4-methylpiperidinium cations, and M is Group 1 or Group 2 metal.

9. The molecular sieve of any one of claims 7 or 8, wherein X comprises one or more of boron and aluminum.

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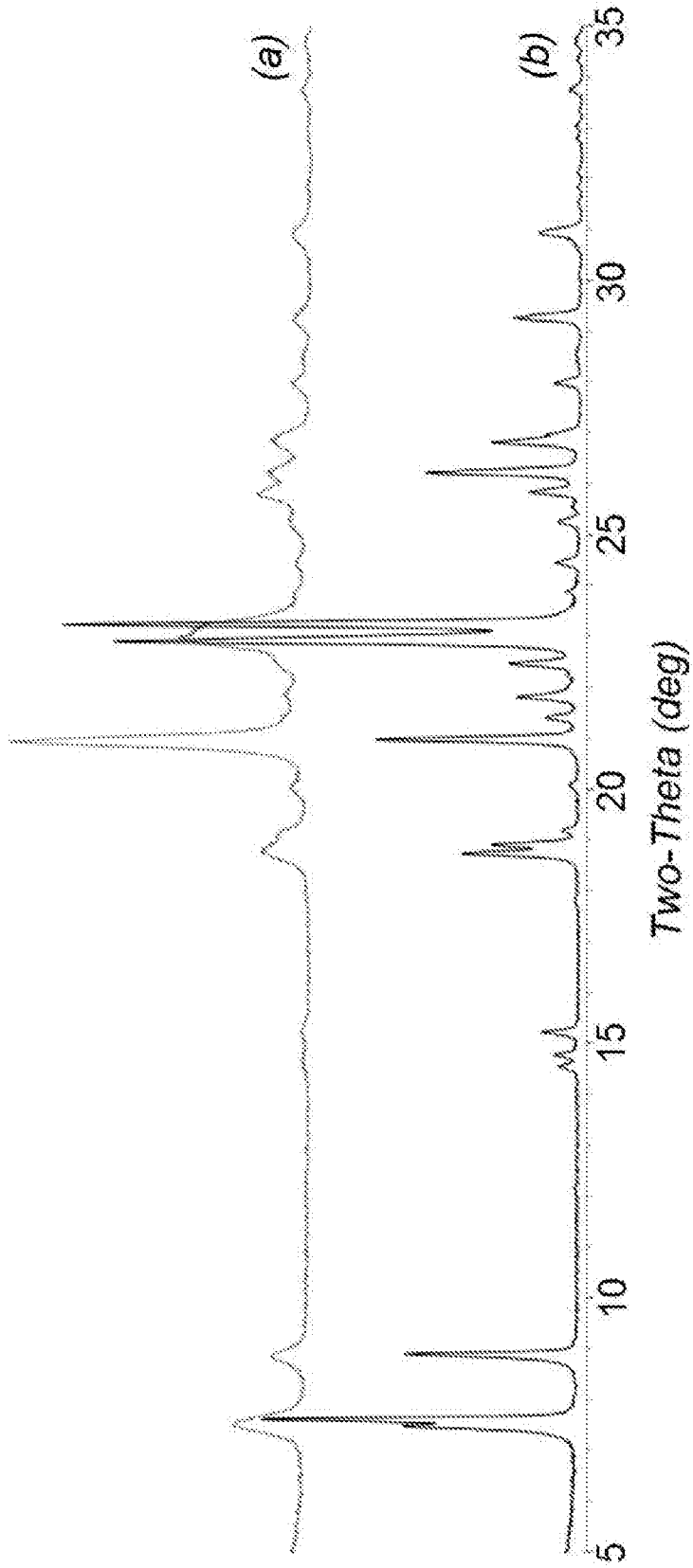


FIG. 1



2/2

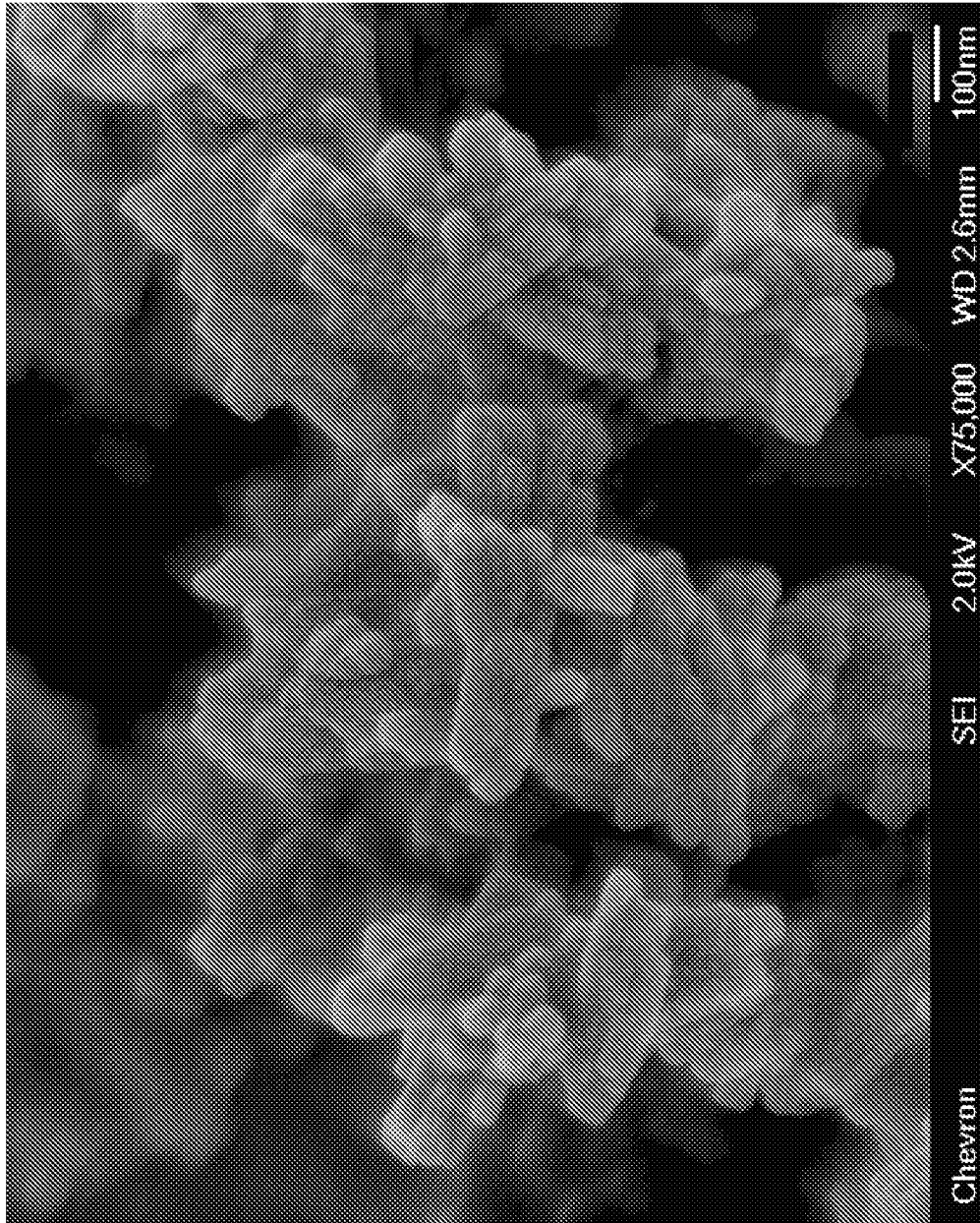


FIG. 2

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2017/050397

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C01B39/02 C01B39/48  
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 1 241 986 A (CHEVRON USA INC [US]) 19 January 2000 (2000-01-19) templates B3 and B4; example 1A	1-9
A	----- US 2008/045767 A1 (CAO GUANG [US] ET AL) 21 February 2008 (2008-02-21) claim 10	1-9
E	----- WO 2017/180222 A1 (CHEVRON USA INC [US]) 19 October 2017 (2017-10-19) claims 1-8; example 6	1-9
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  24 November 2017	Date of mailing of the international search report  08/12/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Mattheis, Chris
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/050397

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 1241986	A	19-01-2000	NONE
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US 2008045767	A1	21-02-2008	NONE
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			WO 2017180222 A1 19-10-2017
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