



(51) International Patent Classification:
C01B 39/48 (2006.01)

(21) International Application Number:
PCT/US2017/015034

(22) International Filing Date:
26 January 2017 (26.01.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/325,510 21 April 2016 (21.04.2016) US

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR,
KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,

SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: SYNTHESIS OF ZEOLITE SSZ-31

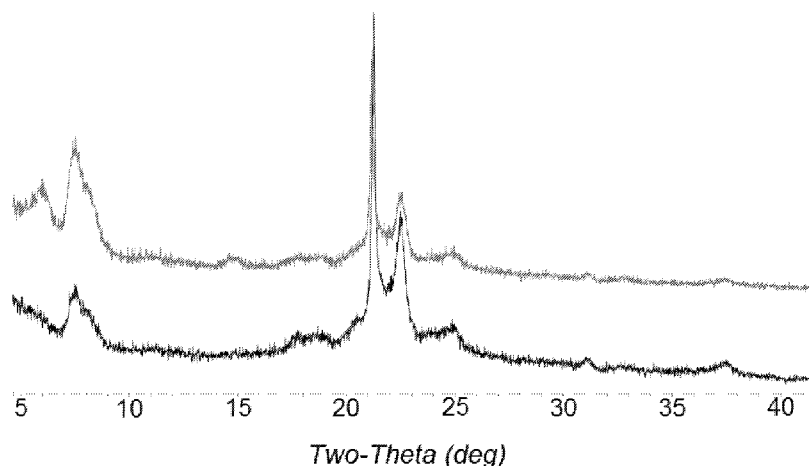


FIG. 1

(57) Abstract: A zeolite having the framework structure of SSZ-31 is synthesized using 1-cyclohexylmethyl-1-ethylpiperidinium cations as a structure directing agent.



SYNTHESIS OF ZEOLITE SSZ-31

TECHNICAL FIELD

[001] The present disclosure is to a method of synthesizing zeolite SSZ-31 using 1-cyclohexylmethyl-1-ethylpiperidinium cations as a structure directing agent.

BACKGROUND

[002] Molecular sieves are a commercially important class of crystalline materials. They have distinct crystal structures with ordered pore structures which are demonstrated by distinct X-ray diffraction patterns. The crystal structure defines cavities and pores which are characteristic of the different species. Molecular sieves such as zeolites have been used extensively to catalyze a number of chemical reactions in refinery and petrochemical reactions, and catalysis, adsorption, separation, and chromatography.

[003] SSZ-31 is a high-silica molecular sieve material with a large one-dimensional pore system. The pore apertures are elliptical with a dimension of approximately $8.6 \times 5.7 \text{ \AA}$. The structure of SSZ-31 is highly faulted and can be described as an intergrowth of four different but structurally related polymorphs.

[004] The framework structure of SSZ-31 has been assigned the three letter code *STO by the Structure Commission of the International Zeolite Association.

[005] The composition and characterizing powder X-ray diffraction pattern of SSZ-31 are disclosed in U.S. Patent No. 5,106,801, which also describes the synthesis of the borosilicate form of the zeolite in the presence of a structure directing agent selected from one or more of *N,N,N*-trimethylammonium-8-tricyclo[5.2.1.0]decane, 4-trimethylammonium-2,2,6,6-tetramethylpiperidine, *N,N*-dimethyl-3-azonium bicyclo[3.2.2]nonane, *N,N,N*-trimethylammonium-2-bicyclo[3.2.1]octane, *N,N*-dimethyl-6-azonium-1,3,3-trimethylbicyclo[3.2.1]octane, and 1,1,3,5,5-pentamethyl azonium cycloheptane. An all-silica form of SSZ-31 was also synthesized using *N,N,N*-trimethylammonium-8-tricyclo[5.2.1.0]decane as a structure directing agent.

[006] Due to the very large pore diameter of SSZ-31, aluminum-containing forms of SSZ-31 are of interest for shape-selective catalysis, such as alkylation of

relatively bulky aromatic compounds. Aluminosilicate SSZ-31 may be prepared from borosilicate SSZ-31 by heteroatom lattice substitution techniques such as described in U.S. Patent Nos. 6,468,501 and 6,790,433.

[007] U.S. Patent No. 6,471,940 discloses the direct synthesis of aluminosilicate SSZ-31 by a dry gel conversion method using a structure directing agent selected from one of more of *N,N'*-bis-triethyl-1,6-hexanediyl-diammonium dihydroxide, *N,N'*-bis-triethyl-1,7-heptanediyl-diammonium dihydroxide, *N,N'*-bis-triethyl-1,8-octanediyl-diammonium dihydroxide, *N,N'*-bis-triethyl-1,9-nonanediyl-diammonium dihydroxide, and *N,N'*-bis-triethyl-1,10-decanediyl-diammonium dihydroxide.

[008] According to the present disclosure, it has now been found that 1-cyclohexylmethyl-1-ethylpiperidinium cations are effective as structure directing agent in the direct synthesis of all-silica and aluminosilicate forms of zeolite SSZ-31.

SUMMARY

[009] In one aspect, there is provided a method of synthesizing a zeolite having the framework structure of SSZ-31, the method comprising: (a) preparing a reaction mixture comprising: (1) a source of silicon oxide; (2) optionally, a source of aluminum oxide; (3) a structure directing agent comprising 1-cyclohexylmethyl-1-ethylpiperidinium cations; (4) hydroxide ions; and (5) water; and (b) subjecting the reaction mixture to crystallization condition sufficient to form crystals of the zeolite.

[010] In another aspect, there is provided a zeolite having the framework structure of SSZ-31 and comprising 1-cyclohexylmethyl-1-ethylpiperidinium cations in its pores.

[011] In its as-synthesized and anhydrous form, the zeolite has a chemical composition comprising the following molar relationship:

	Embodiment 1	Embodiment 2
$\text{SiO}_2/\text{Al}_2\text{O}_3$	≥ 50	100 to 500
Q/SiO_2	>0 to 0.2	>0 to 0.1

wherein Q comprises 1-cyclohexylmethyl-1-ethylpiperidinium cations.

BRIEF DESCRIPTION OF THE DRAWINGS

[012] FIG. 1 compares the powder X-ray diffraction (XRD) patterns of the zeolite product of Example 1 in its-as-synthesized form (bottom pattern) and in its calcined form (top pattern).

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

DETAILED DESCRIPTION

Introduction

[014] The term "as-synthesized" is employed herein to refer to the zeolite in its form after crystallization, prior to removal of the structure directing agent.

[015] The term "anhydrous" is employed herein to refer to a zeolite substantially devoid of both physically adsorbed and chemically adsorbed water.

[016] As used herein, the numbering scheme for the Periodic Table Groups is as disclosed in *Chem. Eng. News* 1985, 63(5), 26-27.

Reaction Mixture

[017] All-silica and aluminosilicate forms of zeolite SSZ-31 can be directly synthesized from an aqueous reaction mixture comprising 1-cyclohexylmethyl-1-ethylpiperidinium cations, as described herein below. The term "directly synthesized" in the context of the present disclosure means that the zeolite is formed from the reaction mixture described below, as opposed to forming a zeolite containing silicon oxide and another oxide (e.g., boron oxide) and then subjecting the thus-formed zeolite to a post-synthesis treatment to create an all-silica or aluminosilicate SSZ-31 zeolite.

[018] In general, the present zeolite is synthesized by: (a) preparing a reaction mixture comprising (1) a source of silicon oxide; (2) optionally, a source of aluminum oxide; (3) a structure directing agent (Q) comprising 1-cyclohexylmethyl-1-ethylpiperidinium cations; (4) hydroxide ions; and (5) water; and (b) subjecting the reaction mixture to crystallization conditions sufficient to form crystals of the zeolite.

[019] The composition of the reaction mixture from which the zeolite is formed, in terms of mole ratios, is identified in Table 1 below:

TABLE 1

Reactants	Useful	Exemplary
SiO ₂ /Al ₂ O ₃	≥50	100 to 500
Q/SiO ₂	0.05 to 0.50	0.10 to 0.45
OH/SiO ₂	0.05 to 0.50	0.20 to 0.45
H ₂ O/SiO ₂	10 to 60	15 to 50

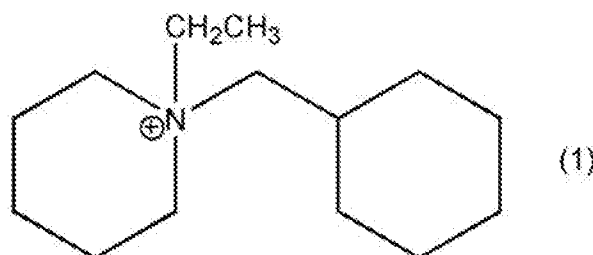
wherein Q and M are as described herein above.

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

[021] Suitable sources of aluminum oxide include hydrated alumina and water-soluble aluminum salts (e.g., aluminum nitrate).

[022] 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).

[023] The organic structure directing agent (Q) comprises 1-cyclohexylmethyl-1-ethylpiperidinium cations, represented by the following structure (1):



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

[025] The reaction mixture also contains a source of hydroxide ions, for example, an alkali metal hydroxide (e.g., NaOH or KOH). Hydroxide can also be present as a counter ion of the structure directing agent.

[026] The reaction mixture may also contain seeds of a molecular sieve material, such as SSZ-31, from a previous synthesis, desirably in an amount of from

0.01 to 10,000 ppm by weight (e.g., from 100 to 5000 ppm by weight) of the reaction mixture.

[027] 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.

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

Crystallization and Post-Synthesis Treatment

[029] Crystallization of the zeolite 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 1 day to 28 days. Crystallization is usually carried out in closed system under autogenous pressure.

[030] Once the zeolite 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 zeolite crystals. The drying step is typically performed at a temperature of less than 200°C.

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

[032] The as-synthesized zeolite described may be subjected to treatment to remove part or all of the organic structure directing agent (Q) used in its synthesis. This is conveniently effected by thermal treatment in which the as-synthesized material is heated at a temperature of at least about 370°C for at least 1 minute and generally not longer than 20 hours. The thermal treatment can be performed at a

temperature up to about 925°C. While sub-atmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. 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).

[033] To the extent desired and depending on the SiO₂/Al₂O₃ mole ratio of the material, any cations in the as-synthesized zeolite can be replaced in accordance with techniques well known in the art by ion exchange with other cations. Illustrative examples of suitable replacing cations include metal ions, hydrogen ions, hydrogen precursor ions (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.

Characterization of the Zeolite

[034] In its as-synthesized and anhydrous form, the zeolite prepared by the method described herein has a chemical composition comprising the following molar relationship:

	Embodiment 1	Embodiment 2
SiO ₂ /Al ₂ O ₃	≥ 50	100 to 500
Q/SiO ₂	>0 to 0.2	>0 to 0.1

wherein Q comprises 1-cyclohexylmethyl-1-ethylpiperidinium cations. In some embodiments, the zeolite has a SiO₂/Al₂O₃ molar ratio of at least 100 (e.g., at least 200, 100 to 1000, 100 to 300, 200 to 1000, 200 to 500, or 200 to 300). It will appreciate from the permitted values for the SiO₂/Al₂O₃ molar ratio that the zeolite can be synthesized in a totally siliceous form (i.e., an "all-silica" form) in which aluminum oxide is absent or essentially absent.

[035] As taught by U.S. Patent No. 5,106,801, zeolite SSZ-31 has, in its as-synthesized form, an X-ray diffraction pattern which includes at least the peaks set forth in Table 2 below.

TABLE 2

Characteristic Peaks for As-Synthesized SSZ-31

2-Theta ^(a)	<i>d</i> -spacing (nm)	Relative Intensity ^(b)
6.10	1.449	W
7.38	1.198	M
8.18	1.081	W
20.30	0.437	W
21.12	0.421	VS
22.25	0.399	VS
24.73	0.360	M
30.90	0.289	W

^(a) ±0.20

^(b) The powder X-ray diffraction patterns provided are based on a relative intensity scale in which the strongest line in the XRD pattern is assigned a value of 100: W=weak (>0 to ≤20); M=medium (>20 to ≤40); S=strong (>40 to ≤60); VS=very strong (>60 to ≤100).

[036] The powder X-ray diffraction patterns presented herein were collected by standard techniques. The radiation was CuK_α radiation. The peak heights and the positions, as a function of 2θ where θ 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.

[037] 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.

EXAMPLES

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

EXAMPLE 1

Synthesis of All-Silica SSZ-31

[039] 6.29 g of deionized water, 5.64 g of a 20.12% 1-cyclohexylmethyl-1-ethylpiperidinium hydroxide solution (SACHEM, Inc.) and 3.00 g of LUDOX[®] 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 9 days with tumbling at 43 rpm. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[040] A portion of the resultant product was calcined according to the following procedure. The zeolite was calcined inside a muffle furnace under a flow of air heated to 595°C at a rate of 1°C/minute and maintained at 595°C for 5 hours.

[041] The calcined sample was subjected to a micropore volume analysis using N₂ as adsorbate and via the B.E.T. method. The zeolite exhibited a micropore volume of 0.12 cm³/g.

[042] FIG. 1 compares the powder XRD patterns of the as-synthesized and calcined products.

[043] FIG. 2 shows a SEM image of the as-synthesized product and indicates a uniform field of crystals.

EXAMPLE 2

Synthesis of All-Silica SSZ-31

[044] 10.72 g of deionized water, 40.63 g of a 20.12% 1-cyclohexylmethyl-1-ethylpiperidinium hydroxide solution (SACHEM, Inc.) and 12.00 g of LUDOX[®] 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 8 days with tumbling at 43 rpm. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[045] The resulting zeolite product was identified by powder XRD and SEM as a pure silicate SSZ-31 zeolite.

EXAMPLE 3

Synthesis of Aluminosilicate SSZ-31

[046] 20.68 g of deionized water, 36.29 g of a 20.12% 1-cyclohexylmethyl-1-ethylpiperidinium hydroxide solution (SACHEM, Inc.), 13.64 g of LUDOX[®] AS-40 colloidal silica and 0.08 g of CBV600 Y-zeolite (Zeolyst International, SiO₂/Al₂O₃ molar ratio=5.1) 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 14 days with tumbling at 43 rpm. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[047] The resulting zeolite product was identified by powder XRD and SEM as a pure aluminosilicate SSZ-31 zeolite.

[048] The product had a SiO₂/Al₂O₃ molar ratio of 273, as determined by ICP elemental analysis.

EXAMPLE 4

Synthesis of Aluminosilicate SSZ-31

[049] 1.58 g of deionized water, 2.72 g of a 20.12% 1-cyclohexylmethyl-1-ethylpiperidinium hydroxide solution (SACHEM, Inc.), 0.98 g of LUDOX[®] AS-40 colloidal silica and 0.03 g of CBV600 Y-zeolite (Zeolyst International, SiO₂/Al₂O₃ molar ratio=5.1) 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 16 days with tumbling at 43 rpm. The solid products were recovered from the cooled reactor by centrifugation, washed with deionized water and dried at 95°C.

[050] The resulting zeolite product was identified by powder XRD and SEM as aluminosilicate SSZ-31 zeolite with a trace amount of amorphous material.

CLAIMS

1. A method of synthesizing a zeolite having the structure of SSZ-31, the method comprising:

(a) preparing a reaction mixture comprising:

(1) a source of silicon oxide;

(2) optionally, a source of aluminum oxide;

(3) a structure directing agent (Q) comprising 1-cyclohexylmethyl-1-ethylpiperidinium cations;

(4) hydroxide ions; and

(5) water; and

(b) subjecting the reaction mixture to crystallization conditions sufficient to form crystals of the zeolite.

2. The method of claim 1, wherein the reaction mixture comprises, in terms of molar ratios, the following:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	≥ 50
Q/SiO_2	0.05 to 0.50
OH/SiO_2	0.05 to 0.50
$\text{H}_2\text{O}/\text{SiO}_2$	10 to 60.

3. The method of claim 1, wherein the reaction mixture comprises, in terms of molar ratios, the following:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	100 to 500
Q/SiO_2	0.10 to 0.45
OH/SiO_2	0.20 to 0.45
$\text{H}_2\text{O}/\text{SiO}_2$	15 to 50.

4. The method of claim 1, wherein the crystallization conditions include a temperature of from 125°C to 200°C.

5. A zeolite having the structure of SSZ-31 and comprising 1-cyclohexylmethyl-1-ethylpiperidinium cations in its pores.

6. The zeolite of claim 5, wherein the zeolite has, in its as-synthesized and anhydrous form, a composition comprising the following molar relationship:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	≥ 50
Q/SiO_2	>0 to 0.2

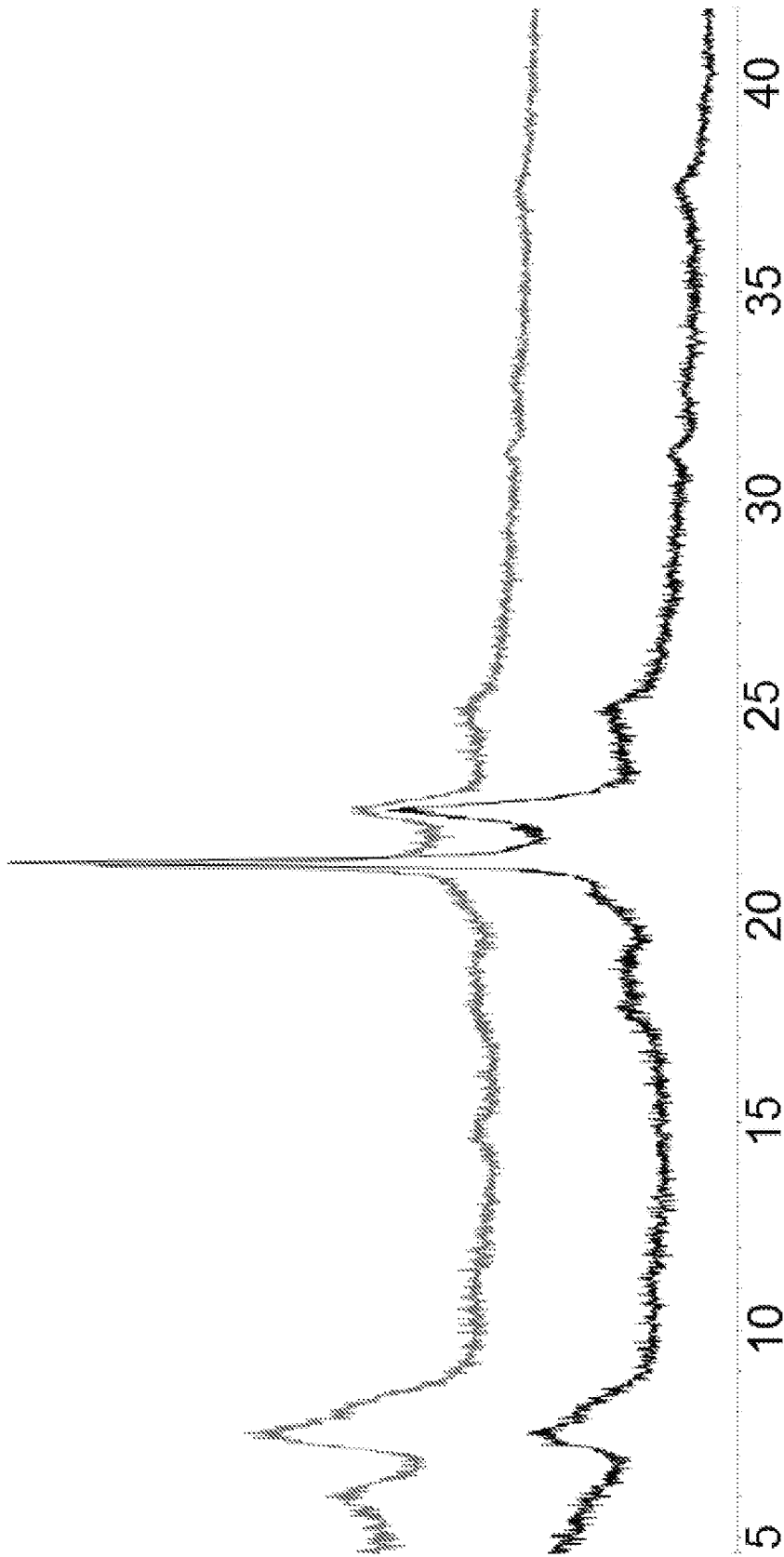
wherein Q comprises 1-cyclohexylmethyl-1-ethylpiperidinium cations.

7. The zeolite of claim 5, wherein the zeolite has, in its as-synthesized and anhydrous form, a composition comprising the following molar relationship:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	100 to 500
Q/SiO_2	>0 to 0.1

wherein Q comprises 1-cyclohexylmethyl-1-ethylpiperidinium cations.

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Two-Theta (deg)

FIG. 1

2/2

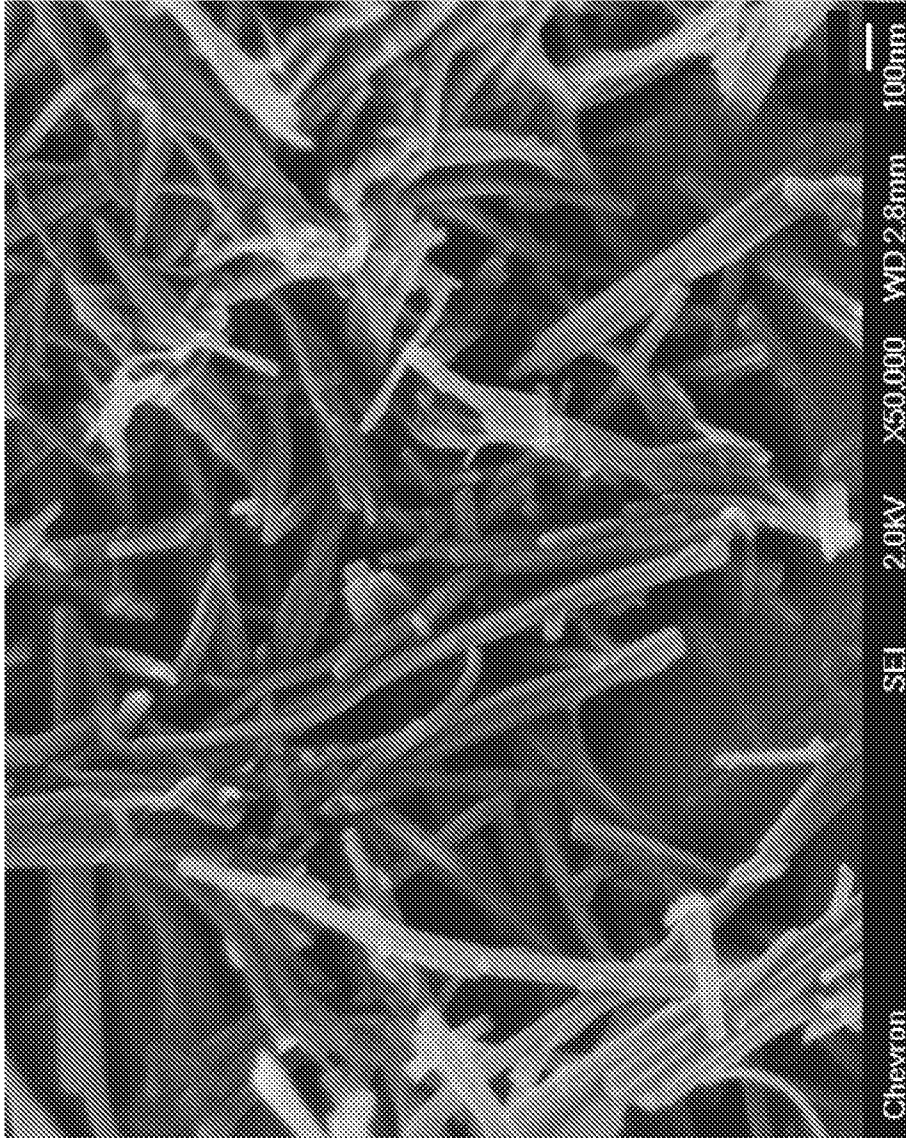


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/015034

A. CLASSIFICATION OF SUBJECT MATTER
INV. 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.
X	WO 2016/039807 A1 (CHEVRON USA INC [US]) 17 March 2016 (2016-03-17) claims 1,2,5,6; examples 1-2 -----	1-7
X	WO 2016/039825 A1 (CHEVRON USA INC [US]) 17 March 2016 (2016-03-17) claims 1,3, 6; example 5 -----	1-7
A	WO 94/00233 A1 (CHEVRON RES & TECH [US]) 6 January 1994 (1994-01-06) example 16 -----	1-7

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>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 24 February 2017	Date of mailing of the international search report 06/03/2017
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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 Bomm, Jana
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/015034

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016039807 A1	17-03-2016	US 2016068401 A1 WO 2016039807 A1	10-03-2016 17-03-2016

WO 2016039825 A1	17-03-2016	NONE	

WO 9400233 A1	06-01-1994	EP 0604597 A1 JP H07504396 A US 5281407 A WO 9400233 A1	06-07-1994 18-05-1995 25-01-1994 06-01-1994
