



(51) International Patent Classification:
C01B 39/02 (2006.01)

(21) International Application Number:
PCT/US2017/066009

(22) International Filing Date:
13 December 2017 (13.12.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/446,979 17 January 2017 (17.01.2017) US

(71) Applicant: CHEVRON U.S.A. INC. [US/US]; 6001
Bollinger Canyon Road, San Ramon, California 94583
(US).

(72) Inventor: XIE, Dan; 6001 Bollinger Canyon Road, San
Ramon, California 94583 (US).

(74) Agent: FLAHERTY, Terrence M. et al.; Chevron Corpo-
ration, Law Department, Post Office Box 6006, San Ramon,
California 94583-0806 (US).

(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, JO, 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: MOLECULAR SIEVE SSZ-108, ITS SYNTHESIS AND USE

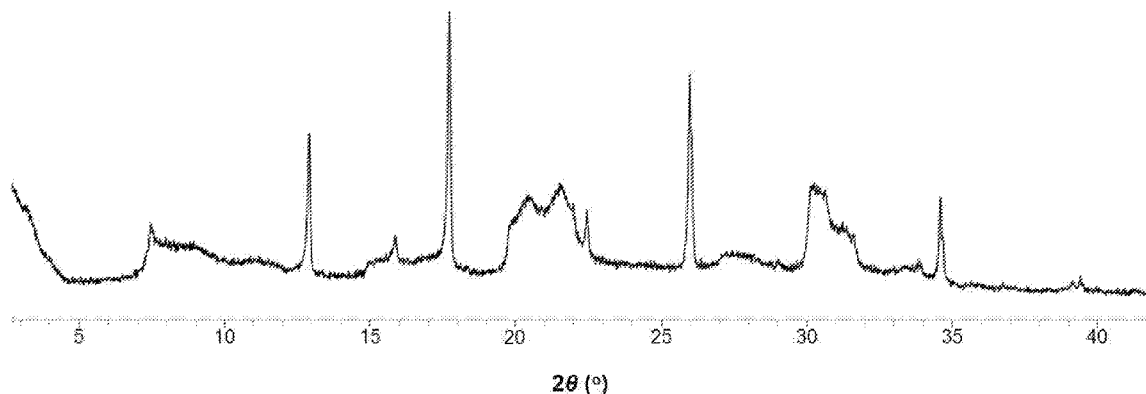


FIG. 1

(57) Abstract: A novel synthetic crystalline molecular sieve designated as SSZ-108 is disclosed. SSZ-108 may be synthesized using a structure directing agent comprising one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-methylpiperidinium cations. Molecular sieve SSZ-108 may be used in catalytic and sorptive processes.



MOLECULAR SIEVE SSZ-108, ITS SYNTHESIS AND USE**CROSS-REFERENCE TO RELATED APPLICATIONS**

[001] This application claims priority to U.S. Provisional Application Ser. No. 62/446,979, filed on January 17, 2017, the disclosure of which is fully incorporated herein by reference.

TECHNICAL FIELD

[002] This disclosure relates to a novel synthetic crystalline molecular sieve designated SSZ-108, its synthesis, and its use in sorption and catalytic processes.

BACKGROUND

[003] Molecular sieve materials, both natural and synthetic, have been demonstrated in the past to be useful as adsorbents and to have catalytic properties for various types of organic conversion reactions. Certain molecular sieves, such as zeolites, aluminophosphates, and mesoporous materials, are ordered, porous crystalline materials having a definite crystalline structure as determined by X-ray diffraction. Within the crystalline molecular sieve material there are a large number of cavities which may be interconnected by a number of channels or pores. These cavities and pores are uniform in size within a specific molecular sieve material. Because the dimensions of these pores are such as to accept for adsorption molecules of certain dimensions while rejecting those of larger dimensions, these materials have come to be known as "molecular sieves" and are utilized in a variety of industrial processes.

[004] Although many different crystalline molecular sieves have been discovered, there is a continuing need for new molecular sieves with desirable properties for gas separation and drying, chemical conversion reactions, and other applications.

[005] According to the present disclosure, a new molecular sieve, designated SSZ-108 and having a unique X-ray diffraction pattern, has now been synthesized using one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-methylpiperidinium cations as a structure directing agent.

SUMMARY

[006] In one aspect, there is provided a molecular sieve having, in its as-synthesized form, an X-ray diffraction pattern including the peaks listed in Table 2.

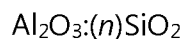
[007] In its as-synthesized and anhydrous form, the molecular sieve has a chemical composition comprising the following molar relationship:

	Broad	Exemplary
SiO ₂ /Al ₂ O ₃	5 to 25	5 to 15
Q/SiO ₂	>0 to 0.1	>0 to 0.1
M/SiO ₂	>0 to 0.1	>0 to 0.1

wherein Q comprises one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-methylpiperidinium cations; and M is a Group 1 or Group 2 metal.

[008] In another aspect, there is provided a molecular sieve having, in its calcined form, an X-ray diffraction pattern including the peaks listed in Table 3.

[009] In its calcined form, the molecular sieve has a chemical composition comprising the following molar relationship:



wherein n has a value of from 5 to 25.

[010] In a further aspect, there is provided a method of synthesizing the molecular sieve described herein, the method comprising (a) preparing a reaction mixture comprising: (1) a source of silicon oxide; (2) a source of aluminum oxide; (3) a source of a Group 1 or Group 2 metal; (4) a structure directing agent comprising one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-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.

[011] In yet a further aspect, there is provided an organic compound conversion process comprising contacting an organic compound under organic compound conversion conditions with a catalyst comprising an active form of the molecular sieve described herein.

[012] In still yet a further aspect, there is provided a process of selectively reducing nitrogen oxides (NO_x) comprising contacting a gas stream containing nitrogen oxides, with a catalyst comprising the molecular sieve described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[013] FIG. 1 shows the powder X-ray diffraction (XRD) pattern of the as-synthesized molecular sieve of Example 1.

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

[015] FIG. 3 shows the powder XRD pattern of the calcined molecular sieve of Example 6.

DETAILED DESCRIPTION

Introduction

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

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

[018] 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

[019] In general, the present molecular sieve is synthesized by: (a) preparing a reaction mixture comprising (1) a source of silicon oxide; (2) a source of aluminum oxide; (3) a source of a Group 1 or Group 2 metal (M); (4) a structure directing agent (Q) comprising one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-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

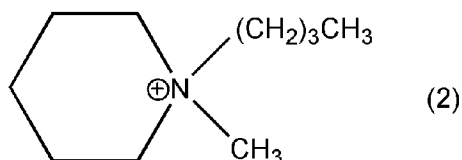
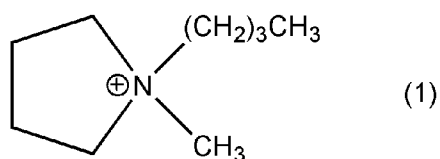
Reactants	Broad	Exemplary
SiO ₂ /Al ₂ O ₃	10 to 100	15 to 80
M/SiO ₂	0.05 to 1.00	0.10 to 0.60
Q/SiO ₂	0.05 to 0.50	0.10 to 0.35
OH/SiO ₂	0.10 to 1.00	0.40 to 0.80
H ₂ O/SiO ₂	10 to 60	15 to 40

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

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

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

[024] The structure directing agent (Q) comprises one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-methylpiperidinium cations, represented by the following structures (1) and (2), respectively:



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

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

[027] The reaction mixture may contain seeds of a molecular sieve material, such as SSZ-108 crystals from a previous synthesis, 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.

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

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

Crystallization and Post-Synthesis Treatment

[030] 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 120°C to 200°C for a time sufficient for crystallization to occur at the temperature used, e.g., from 1 to 15 days. Crystallization is usually carried out in a closed system under autogenous pressure.

[031] 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.

[032] 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.

[033] The molecular sieve described herein may be subjected to subsequent treatment to remove part or all of the 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. The thermal treatment can be performed at a temperature up to 925°C. 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. Additionally or alternatively, the 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).

[034] The original Group 1 or 2 metal cations (e.g., Na⁺) in 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 chemical conversion reactions. These include hydrogen, rare earth metals and metals of Groups 2 to 15 of the Periodic Table of the Elements.

[035] It may be desirable to incorporate the present molecular sieve with another component resistant to the temperatures and other conditions employed in organic conversion processes. Such components can include active and inactive materials and synthetic or naturally occurring zeolites, as well as inorganic materials such as clays, silica, and/or metal oxides such as alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and other metal oxides. Use of a material in conjunction with SSZ-108 (i.e., combined therewith or present during synthesis of the crystalline material, which can be in its active state) can tend to change the level of conversion and/or selectivity of the catalyst in certain chemical conversion processes. Inactive materials can suitably serve as diluents, e.g., to control the amount of conversion in a given process, so that products can be obtained in an economic and orderly manner, such as without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays (e.g., bentonite and/or kaolin) to improve the crush strength of the catalyst under commercial operating conditions. These materials (i.e., clays, oxides, etc.) can function as binders for the

catalyst. It can be desirable to provide a catalyst having good crush strength, because, in commercial use, it can be desirable to prevent/limit the catalyst from breaking down into powder-like materials (fines). These clay and/or oxide binders can be employed, for example, solely to improve the crush strength of the catalyst.

[036] Naturally occurring clays that can be composited with SSZ-108 can include the montmorillonite and kaolin families, which families include the sub-bentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays, as well as others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays can be used in the raw state (as originally mined) and/or initially subjected to calcination, acid treatment, and/or chemical modification. Binders useful for compositing with SSZ-108 can additionally or alternately include inorganic oxides, such as silica, zirconia, titania, magnesia, beryllia, alumina, and mixtures thereof.

[037] Additionally or alternatively to the foregoing materials, as desired, SSZ-108 can be composited with a porous matrix material, such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, silica-magnesia-zirconia, and mixtures thereof.

[038] The relative proportions of SSZ-108 and inorganic oxide matrix may vary widely, with the SSZ-108 content typically ranging from 1 to 90 wt. % (e.g., 2 to 80 wt. %), based on the total composite weight.

Characterization of the Molecular Sieve

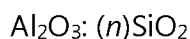
[039] In its as-synthesized and anhydrous form, the present molecular sieve has a chemical composition comprising the following molar relationship:

	Broad	Exemplary
$\text{SiO}_2/\text{Al}_2\text{O}_3$	5 to 25	5 to 15
Q/SiO_2	>0 to 0.1	>0 to 0.1
M/SiO_2	>0 to 0.1	>0 to 0.1

wherein compositional variables Q and M are as described herein above.

[040] It should be noted that the as-synthesized form of the present molecular sieve may have molar ratios different from the molar ratios of reactants of the reaction mixture used to prepare the as-synthesized form. This result may occur due to incomplete incorporation of 100% of the reactants of the reaction mixture into the crystals formed (from the reaction mixture).

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



wherein n has a value of from 5 to 25 (e.g., 5 to 20, or 5 to 15).

[042] The novel molecular sieve structure SSZ-108 is characterized by a powder X-ray diffraction pattern, which in the as-synthesized form of the molecular sieve, includes at least the lines listed in Table 2 below and which, in the calcined form of the molecular sieve, includes at least the peaks listed in Table 3 below.

TABLE 2
Characteristic Peaks for As-Synthesized SSZ-108

2-Theta ^(a)	<i>d</i> -Spacing, nm	Relative Intensity ^(b)	Peak Broadening ^(c)
7.46	1.184	M	B
9.02	0.980	M	B
11.24	0.787	W	B
12.90	0.686	M	Sh
15.25	0.581	W	B
15.86	0.558	W	Sh
17.72	0.500	VS	Sh
20.43	0.434	VS	B
21.58	0.412	VS	B
22.44	0.396	W	Sh
25.97	0.343	S	Sh
27.62	0.323	W	B
30.45	0.293	VS	B
31.23	0.286	S	B
33.85	0.265	W	Sh
34.59	0.259	M	Sh

^(a) ±0.20

^(b) The powder XRD 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).

- (c) Peak broadening is characterized by the Full-Width at Half Maximum (FWHM) of the XRD peak. Based on the FWHM values, the peaks are classified as: Sh=sharp (≤2×smallest FWHM); B=broad (>2×smallest FWHM).

TABLE 3
Characteristic Peaks for Calcined SSZ-108

2-Theta ^(a)	d-Spacing, nm	Relative Intensity ^(b)	Peak Broadening ^(c)
7.51	1.176	W	B
9.11	0.971	M	B
12.90	0.686	S	Sh
15.92	0.556	W	Sh
17.74	0.500	S	Sh
20.43	0.434	VS	B
21.60	0.411	VS	B
26.03	0.342	S	Sh
27.70	0.322	W	B
30.53	0.293	VS	B
31.38	0.285	S	B
34.65	0.259	W	Sh

(a) ±0.20

- (b) The powder XRD 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).

- (c) Peak broadening is characterized by the Full-Width at Half Maximum (FWHM) of the XRD peak. Based on the FWHM values, the peaks are classified as: Sh=sharp (≤2×smallest FWHM); B=broad (>2×smallest FWHM).

[043] 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 (adjusting for background), and d , the interplanar spacing corresponding to the recorded lines, can be calculated.

[044] 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 disordered materials and/or small crystals will affect the shape and intensity of peaks, leading to significant peak broadening. Minor variations in the diffraction pattern can also result from variations in the organic compound used in the preparation. Calcination can also cause minor shifts in the XRD pattern. Notwithstanding these minor perturbations, the basic crystal lattice structure remains unchanged.

Sorption and Catalysis

[045] The present molecular sieve may be used as a sorbent or a catalyst for a variety of chemical reactions. The present molecular sieve is particularly suited for use as a catalyst for organic conversion processes and for the reduction of nitrogen oxides in a gas stream. Examples of organic conversion processes which may be catalyzed by the present molecular sieve include, but are not limited to, animating lower alcohols and converting organic oxygenates to one or more olefins. Such reactions may be catalyzed by contacting the respective feedstock with a catalyst comprising SSZ-108 under conditions sufficient to affect the named transformation.

[046] The present molecular sieve may be used in the catalytic conversion of organic oxygenates to one or more olefins, particularly ethylene and propylene. The term "organic oxygenates" is defined herein to include aliphatic alcohols, ethers, carbonyl compounds (e.g., aldehydes, ketones, carboxylic acids, carbonates, and the like), and also compounds containing hetero-atoms, such as, halides, mercaptans, sulfides, amines, and mixtures thereof. The aliphatic moiety normally contains from 1 to 10 carbon atoms (e.g., 1 to 4 carbon atoms).

[047] Representative organic oxygenates include lower straight chain or branched aliphatic alcohols, their unsaturated counterparts, and their nitrogen, halogen, and sulfur analogs. Examples of suitable organic oxygenate compounds include methanol; ethanol; *n*-propanol; isopropanol; C₄ to C₁₀ alcohols; methyl ethyl ether; dimethyl ether; diethyl ether; diisopropyl ether; formaldehyde; dimethyl

carbonate; acetone; acetic acid; *n*-alkyl amines, *n*-alkyl halides, *n*-alkyl sulfides having *n*-alkyl groups in a range of from 3 to 10 carbon atoms; and mixtures thereof. Particularly suitable oxygenate compounds are methanol, dimethyl ether, or combinations thereof, especially methanol.

[048] In the present oxygenate conversion process, a feedstock comprising an organic oxygenate, optionally, with one or more diluents, is contacted in the vapor phase in a reaction zone with a catalyst comprising the present molecular sieve at effective process conditions so as to produce the desired olefins. Alternatively, the process may be carried out in a liquid or a mixed vapor/liquid phase. When the process is carried out in the liquid phase or a mixed vapor/liquid phase, different conversion rates and selectivities of feedstock-to-product may result depending upon the catalyst and the reaction conditions.

[049] When present, the diluent is generally non-reactive to the feedstock or molecular sieve catalyst composition and is typically used to reduce the concentration of the oxygenate in the feedstock. Non-limiting examples of suitable diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, water, essentially non-reactive paraffins (especially alkanes such as methane, ethane, and propane), essentially non-reactive aromatic compounds, and mixtures thereof. The most preferred diluents are water and nitrogen, with water being particularly preferred. Diluent(s) may comprise from 1 to 99 mol % of the total feed mixture.

[050] The temperature employed in the oxygenate conversion process may vary over a wide range, such as from 200°C to 1000° C (e.g., 250°C to 800°C, 300°C to 650°C, or 400°C to 600°C).

[051] Light olefin products will form, although not necessarily in optimum amounts, at a wide range of pressures, including autogenous pressures and pressures in the range of from 0.1 kPa to 10 MPa (e.g., 7 kPa to 5 MPa, or 50 kPa to 1 MPa). The foregoing pressures are exclusive of diluent, if any is present, and refer to the partial pressure of the feedstock as it relates to oxygenate compounds and/or mixtures thereof. Lower and upper extremes of pressure may adversely affect

selectivity, conversion, coking rate, and/or reaction rate; however, light olefins such as ethylene and/or propylene may still may form.

[052] The oxygenate conversion process should be continued for a period of time sufficient to produce the desired olefin products. The reaction time may vary from tenths of seconds to a number of hours. The reaction time is largely determined by the reaction temperature, the pressure, the catalyst selected, the weight hourly space velocity, the phase (liquid or vapor), and the selected process design characteristics.

[053] A wide range of weight hourly space velocities (WHSV) can be used in the present oxygenate conversion process. WHSV is defined as weight of feed (excluding diluent) per hour per weight of a total reaction volume of molecular sieve catalyst (excluding inerts and/or fillers). The WHSV generally may be in the range of from 0.01 to 500 h⁻¹ (e.g., 0.5 to 300 h⁻¹, or 1 to 200 h⁻¹).

[054] The present molecular sieve may be used in the selective catalytic reduction (SCR) of nitrogen oxides. In this process, a gas stream comprising nitrogen oxides (NO_x) is selectively reduced in the presence of a reductant and a catalyst comprising the present molecular sieve. The nitrogen oxides (principally NO and NO₂) are reduced to N₂ while the reductant is oxidized. When ammonia is the reductant, N₂ is also an oxidation product. Ideally, the only reaction products are water and N₂, although some NH₃ is usually oxidized with air to NO or N₂O.

[055] To promote the catalytic activity, one more transition metals may be incorporated into the molecular sieve support. Any suitable transition metal may be selected. Transition metals particularly effective for use during selective catalytic reduction include one or more of Cr, Mn, Fe, Co, Ce, Ni, Cu, Mo, Ru, Rh, Pd, Ag, Re, Ir, and Pt. In one embodiment, the transition metal is selected from Fe and Cu. In an exemplary embodiment, the transition metal is Cu. Any suitable and effective amount of transition metal may be used in the catalyst. The total amount of the transition metal(s) that may be included in the molecular sieve may be from 0.01 to 20 wt. %

(e.g., 0.1 to 10 wt. %, 0.5 to 5 wt. %, or 1 to 2.5 wt. %) based on the total weight of the molecular sieve support.

[056] The molecular sieve catalyst may be used in any suitable form. For example, the molecular sieve catalyst may be used in powder form, as extrudates, as pellets, or in any other suitable form.

[057] The molecular sieve catalyst for use in the reduction of nitrogen oxides may be coated on a suitable substrate monolith or can be formed as extruded-type catalysts, but is preferably used in a catalyst coating. In one embodiment, the molecular sieve catalyst is coated on a flow-through monolith substrate (i.e., a honeycomb monolithic catalyst support structure with many small, parallel channels running axially through the entire part) or filter monolith substrate, such as a wall-flow filter, etc. The molecular sieve catalyst for use herein may be coated (e.g., as a washcoat component) on a suitable monolith substrate, such as a metal or ceramic flow through monolith substrate or a filtering substrate, such as a wall-flow filter or sintered metal or partial filter. Alternatively, the molecular sieve may be synthesized directly onto the substrate and/or may be formed into an extruded-type flow through catalyst.

[058] The gas stream comprising nitrogen oxides may contain one or more of NO, NO₂, and N₂O in addition to other non-NO_x gases such as N₂, O₂, CO, CO₂, SO₂, HCl and H₂O. The gas stream may contain from 1 to 10,000 ppm (e.g., 10 to 1,000 ppm, or 50 to 500 ppm) of NO.

[059] The gas stream comprising nitrogen oxides may be an exhaust gas derived from a combustion process, such as from an internal combustion engine (whether mobile or stationary), a gas turbine or coal or oil fired plants.

[060] The reductant can be a nitrogen compound or a short-chain (e.g., C₁ to C₈) hydrocarbon. Preferably, the reductant is a nitrogen compound. Suitable nitrogen compounds include ammonia, hydrazine, and ammonia precursors (e.g., urea, ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate, and ammonium formate).

[061] The gas stream comprising nitrogen oxides can contact the catalyst at a gas hourly space velocity of from 5000 to 500,000 h⁻¹ (e.g., 10,000 to 200,000 h⁻¹).

[062] The reduction of nitrogen oxides may be carried out at a temperature within the range of 100°C to 650°C (e.g., 250°C to 600°C).

[063] The reduction of nitrogen oxides may be carried out in the presence of oxygen or in the absence of oxygen.

EXAMPLES

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

EXAMPLE 1

[065] 4.62 g of deionized water, 1.93 g of a 50% NaOH solution, 14.14 g of a 16.33% 1-butyl-1-methylpyrrolidinium hydroxide solution and 3.00 g of CBV760 Y-zeolite powder (Zeolyst International, SiO₂/Al₂O₃ molar 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 placed in an oven and the heated at 135°C for 4 days. The solid products were recovered by centrifugation, washed with deionized water and dried at 95°C.

[066] Powder XRD of the as-synthesized product gave the pattern indicated in FIG. 1 and showed the product to be a pure form of a new phase, designated SSZ-108. A SEM image of the as-synthesized product is shown in FIG. 2 indicating a uniform field of crystals.

[067] The as-synthesized product had a SiO₂/Al₂O₃ molar ratio of 8.82, as determined by ICP elemental analysis.

EXAMPLE 2

[068] 27.89 g of deionized water, 7.09 g of a 50% NaOH solution, 39.27 g of a 16.33% 1-butyl-1-methylpyrrolidinium hydroxide solution and 10.00 g of CBV760 Y-zeolite powder (Zeolyst International, SiO₂/Al₂O₃ molar 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 placed in an oven and the heated at 135°C for 4 days. The solid products were recovered by centrifugation, washed with deionized water and dried at 95°C.

[069] Powder XRD showed the product to be pure SSZ-108.

[070] The as-synthesized product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 8.24, as determined by ICP elemental analysis.

EXAMPLE 3

[071] 8.37 g of deionized water, 2.32 g of a 50% NaOH solution, 9.42 g of a 16.33% 1-butyl-1-methylpyrrolidinium hydroxide and 3.00 g of CBV720 Y-zeolite powder (Zeolyst International, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio=30) 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 placed in an oven and the heated at 135°C for 4 days. The solid products were recovered by centrifugation, washed with deionized water and dried at 95°C.

[072] Powder XRD showed the product to be a mixture of SSZ-108 and ANA framework type zeolite.

EXAMPLE 4

[073] 32.74 g of deionized water, 6.44 g of a 50% NaOH solution, 27.66 g of a 20.19% 1-butyl-1-methylpiperidinium hydroxide solution and 10.00 g of CBV760 Y-zeolite powder (Zeolyst International, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar 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 placed in an oven and the heated at 135°C for 5 days. The solid products were recovered by centrifugation, washed with deionized water and dried at 95°C.

[074] Powder XRD showed the product to be pure SSZ-108.

[075] The as-synthesized product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 7.95, as determined by ICP elemental analysis.

EXAMPLE 5

[076] 9.82 g of deionized water, 1.93 g of a 50% NaOH solution, 8.30 g of a 20.19% 1-butyl-1-methylpiperidinium hydroxide solution and 3.00 g of CBV780 Y-zeolite powder (Zeolyst International, SiO₂/Al₂O₃ molar ratio=80) 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 placed in an oven and the heated at 135°C for 4 days. The solid products were recovered by centrifugation, washed with deionized water and dried at 95°C.

[077] Powder XRD showed the product to be a mixture of SSZ-108 and ANA framework type zeolite.

EXAMPLE 6

[078] The as-synthesized molecular sieve product of Example 1 was calcined inside a muffle furnace under a flow of air heated to 540°C at a rate of 1°C/minute and held at 540°C for 5 hours, cooled and then analyzed by powder XRD.

[079] Powder XRD of the calcined product gave the pattern indicated in FIG. 3 and showed the material to be stable after calcination to remove the organic structure directing agent.

EXAMPLE 7

[080] The calcined molecular sieve material of Example 6 was treated with 10 mL (per g of molecular sieve) of a 1N ammonium nitrate solution at 90°C for 2 hours. The mixture was cooled, the solvent decanted off and the same process repeated.

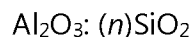
[081] After drying, the product (NH₄-SSZ-108) was subjected to micropore volume analysis using N₂ as adsorbate and via the B.E.T. method. The molecular sieve had a micropore volume of 0.15 cm³/g.

CLAIMS

1. A molecular sieve having, in its calcined form, an X-ray diffraction pattern including the peaks listed in the following Table:

2-Theta	<i>d</i> -Spacing, nm	Relative Intensity	Peak Broadening
7.51±0.20	1.176	W	B
9.11±0.20	0.971	M	B
12.90±0.20	0.686	S	Sh
15.92±0.20	0.556	W	Sh
17.74±0.20	0.500	S	Sh
20.43±0.20	0.434	VS	B
21.60±0.20	0.411	VS	B
26.03±0.20	0.342	S	Sh
27.70±0.20	0.322	W	B
30.53±0.20	0.293	VS	B
31.38±0.20	0.285	S	B
34.65±0.20	0.259	W	Sh.

2. The molecular sieve of claim 1, and having a composition comprising the molar relationship:



wherein *n* has a value of from 5 to 25.

3. A molecular sieve having, in its as-synthesized form, an X-ray diffraction pattern including the peaks listed in the following Table:

2-Theta	<i>d</i> -Spacing, nm	Relative Intensity	Peak Broadening
7.46±0.20	1.184	M	B
9.02±0.20	0.980	M	B
11.24±0.20	0.787	W	B
12.90±0.20	0.686	M	Sh
15.25±0.20	0.581	W	B
15.86±0.20	0.558	W	Sh
17.72±0.20	0.500	VS	Sh
20.43±0.20	0.434	VS	B
21.58±0.20	0.412	VS	B
22.44±0.20	0.396	W	Sh
25.97±0.20	0.343	S	Sh
27.62±0.20	0.323	W	B

30.45±0.20	0.293	VS	B
31.23±0.20	0.286	S	B
33.85±0.20	0.265	W	Sh
34.59±0.20	0.259	M	Sh.

4. The molecular sieve of claim 3, and having a composition comprising the molar relationship:

SiO ₂ /Al ₂ O ₃	5 to 25
Q/SiO ₂	>0 to 0.1
M/SiO ₂	>0 to 0.1

wherein Q comprises one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-methylpiperidinium cations; and M is a Group 1 or Group 2 metal.

5. The molecular sieve of claim 3, and having a composition comprising the molar relationship:

SiO ₂ /Al ₂ O ₃	5 to 15
Q/SiO ₂	>0 to 0.1
M/SiO ₂	>0 to 0.1

wherein Q comprises one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-methylpiperidinium cations; and M is a Group 1 or Group 2 metal.

6. A method of synthesizing the molecular sieve of claim 3, the method comprising:

(a) preparing a reaction mixture comprising:

- (1) a source of silicon oxide;
- (2) a source of aluminum oxide;
- (3) a source of a Group 1 or Group 2 metal (M);
- (4) a structure directing agent (Q) comprising one or more of 1-butyl-1-methylpyrrolidinium cations and 1-butyl-1-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.

7. The method of claim 6, wherein the reaction mixture has a composition, in terms of molar ratios, as follows:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	10 to 100
M/SiO_2	0.05 to 1.00
Q/SiO_2	0.05 to 0.50
OH/SiO_2	0.10 to 1.00
$\text{H}_2\text{O}/\text{SiO}_2$	10 to 60.

8. The method of claim 6, wherein the reaction mixture has a composition, in terms of mole ratios, as follows:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	15 to 80
M/SiO_2	0.10 to 0.60
Q/SiO_2	0.10 to 0.35
OH/SiO_2	0.40 to 0.80
$\text{H}_2\text{O}/\text{SiO}_2$	15 to 40.

9. The method of claim 6, wherein the crystallization conditions include a temperature of from 120°C to 200°C.

10. An organic compound conversion process comprising contacting an organic compound under organic compound conversion conditions with a catalyst comprising the molecular sieve of claim 1.

11. The organic compound conversion process of claim 10, wherein the organic compound comprises an organic oxygenate compound and the organic compound conversion process converts the organic oxygenate compound to a product comprising olefins.

12. The organic compound conversion process of claim 11, wherein the organic oxygenate compound comprises methanol, dimethyl ether, or a combination thereof and the olefins comprise ethylene, propylene, or a combination thereof.
13. A process of selectively reducing nitrogen oxides (NO_x), comprising contacting a gas stream containing nitrogen oxides with a catalyst comprising the molecular sieve of claim 1.
14. The process of claim 13, wherein the catalyst further comprises a transition metal selected from or more of Cr, Mn, Fe, Co, Ce, Ni, Cu, Mo, Ru, Rh, Pd, Ag, Re, Ir, and Pt.
15. The process of claim 14, wherein the transition metal is present in an amount of 0.1 to 10 wt. %, based on the total weight of the molecular sieve.

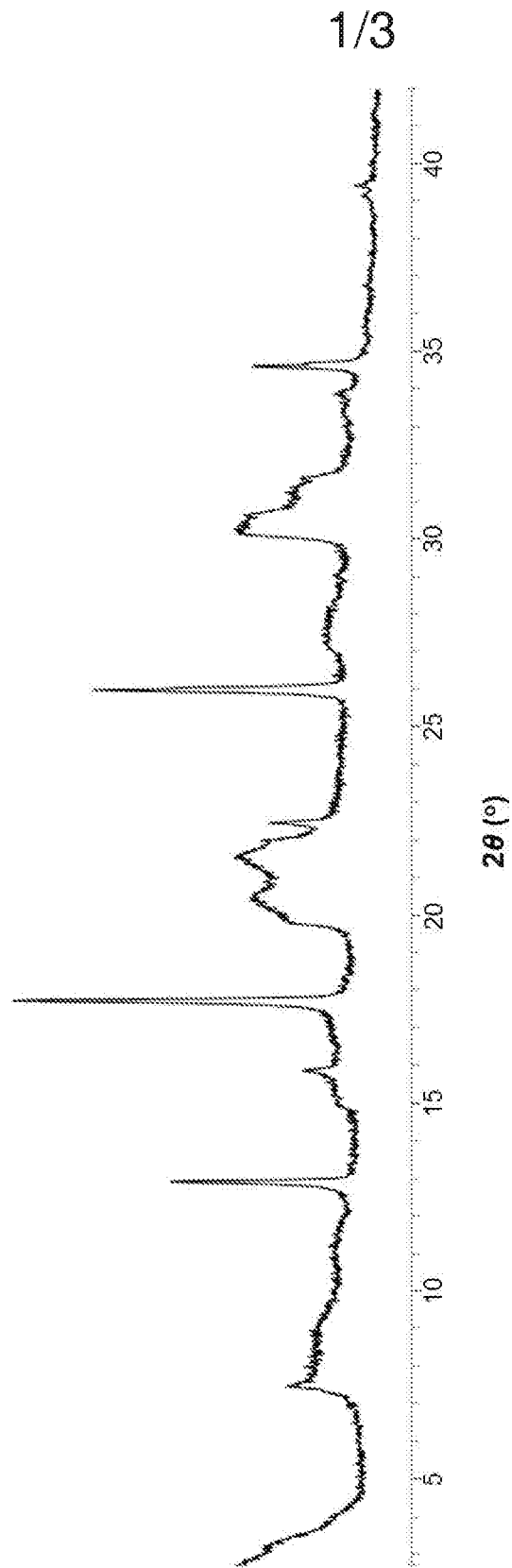


FIG. 1

2/3

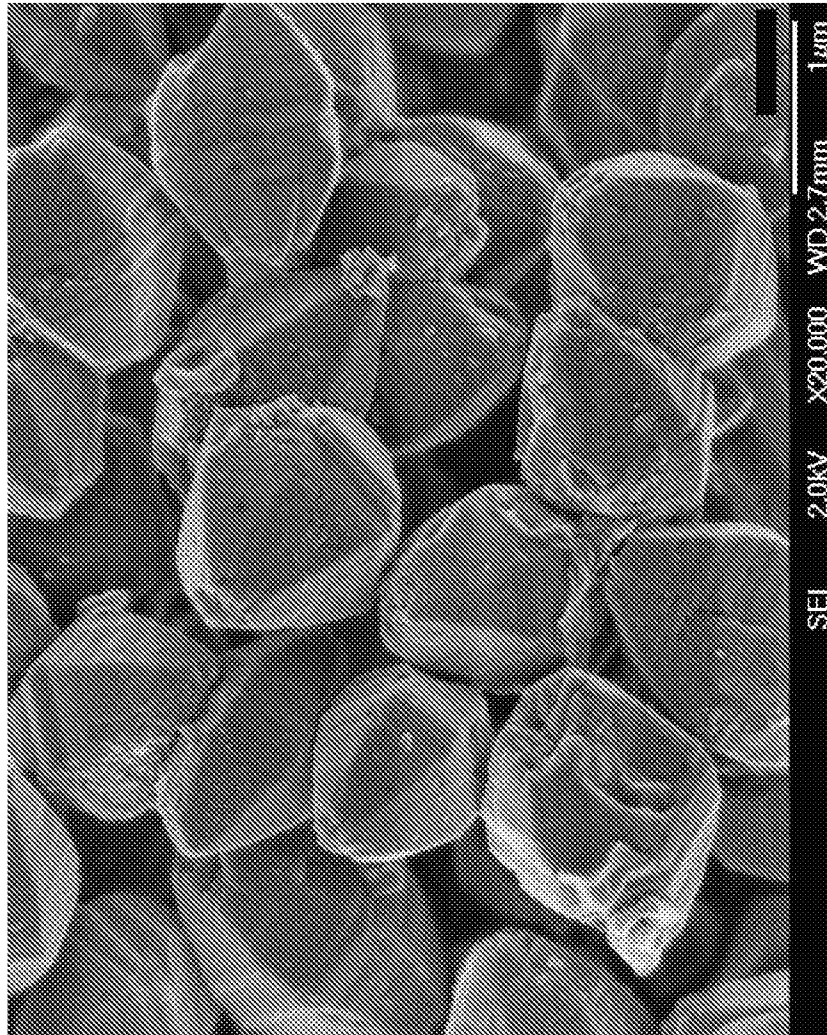


FIG. 2

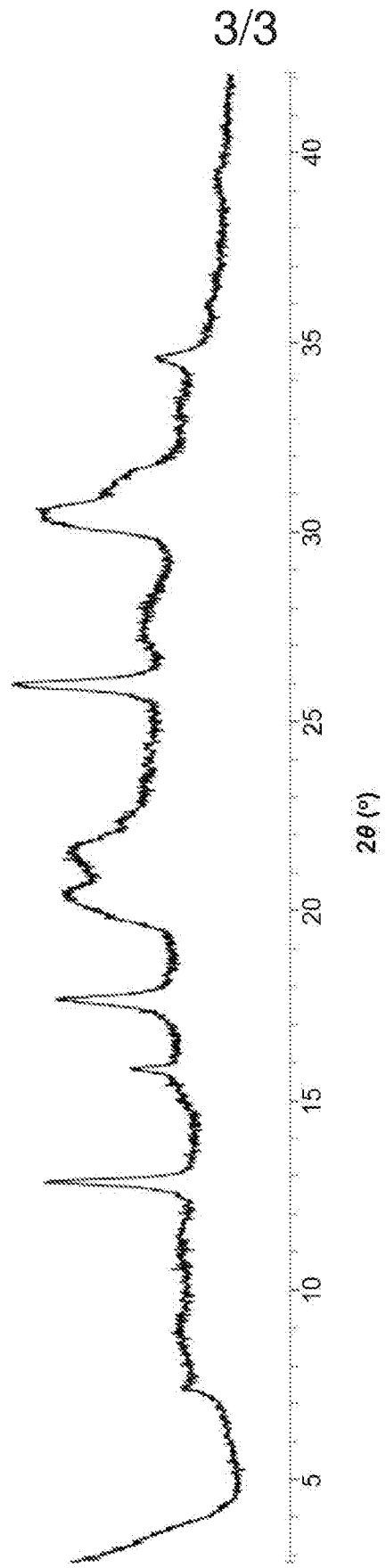


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/066009

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B39/02
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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/101985 A1 (BURTON ALLEN W [US] ET AL) 14 April 2016 (2016-04-14) example 5	1-15
X,P	WO 2017/180222 A1 (CHEVRON USA INC [US]) 19 October 2017 (2017-10-19) paragraph [0013] - paragraph [0032]; claims 1-8; examples 1,2, 9, 10	1-7,9
A	FR 2 953 509 A1 (INST FRANCAIS DU PETROLE [FR]) 10 June 2011 (2011-06-10) abstract page 3, line 1 - page 10, line 7	1-9
A	US 5 645 812 A (NAKAGAWA YUMI [US]) 8 July 1997 (1997-07-08) claims 1-29	1-9
	----- -/--	

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>
---	---

Date of the actual completion of the international search 14 March 2018	Date of mailing of the international search report 26/03/2018
--	--

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 Sevillano Rodriguez
--	---

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/066009

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 958 370 A (ZONES STACEY I [US] ET AL) 28 September 1999 (1999-09-28) claims 1-40 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/066009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016101985	A1	14-04-2016	CN 106794998 A
			EP 3206785 A1
			KR 20170070132 A
			SG 11201701991V A
			US 2016101985 A1
			US 2016102590 A1
			WO 2016060820 A1
			WO 2016060821 A1

WO 2017180222	A1	19-10-2017	US 2017291823 A1
			WO 2017180222 A1

FR 2953509	A1	10-06-2011	NONE

US 5645812	A	08-07-1997	AU 7963594 A
			EP 0721427 A1
			US 5645812 A
			US 6444191 B1
			WO 9509812 A1

US 5958370	A	28-09-1999	NONE
