MOLECULAR SIEVE SSZ-87 COMPOSITION OF MATTER AND SYNTHESIS THEREOF

FIELD

[001] This disclosure is directed to a new crystalline molecular sieve designated SSZ-87synthesized using an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication as a structure directing agent.

BACKGROUND

[002] 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. Although many different crystalline molecular sieves have been disclosed, there is a continuing need for new molecular sieves with desirable properties for gas separation and drying, hydrocarbon and chemical conversions, and other applications. New molecular sieves can contain novel internal pore architectures, providing enhanced selectivities in these processes.

SUMMARY

[003] The present disclosure is directed to a new family of crystalline molecular sieves with unique properties, referred to herein as "molecular sieve SSZ-87" or simply "SSZ-87."

In one aspect, there is provided a molecular sieve having a mole ratio of 10 or greater of (1) at least one oxide of at least one tetravalent element to (2) optionally, one or more oxides selected from the group consisting of oxides of trivalent elements, pentavalent elements, and mixtures thereof, and having, in its calcined form, the powder X-ray diffraction (XRD) lines of Table 4. It should be noted that the phrase "mole ratio of 10 or greater" includes the case where there is no oxide (2), i.e., the mole ratio of oxide (1) to oxide (2) is infinity. In that case, the molecular sieve is comprised of essentially all of the oxide of one or more tetravalent elements.

[004a] In another aspect, there is provided a molecular sieve having a mole ratio of 10 or greater of (1) at least one oxide of at least one tetravalent element to (2) optionally, one or more oxides selected from the group consisting of oxides of trivalent elements, pentavalent elements, and mixtures thereof, and having, in its calcined form, an X-ray diffraction pattern

substantially as shown in the following table:

2-Theta	d-Spacing, nm	Relative Intensity
7.09 ± 0.20	1.245	VS
8.78 ± 0.20	1.006	S
9.95 ± 0.20	0.889	W
13.36 ± 0.20	0.662	W
16.04 ± 0.20	0.553	W
16.88 ± 0.20	0.525	W
17.51 ± 0.20	0.506	W
19.48 ± 0.20	0.455	VS
21.65 ± 0.20	0.410	VS
22.24 ± 0.20	0.399	M
24.52 ± 0.20	0.363	M
25.17 ± 0.20	0.354	W
26.17 ± 0.20	0.340	M
26.87 ± 0.20	0.331	M
28.28 ± 0.20	0.315	W
28.58 ± 0.20	0.312	W
29.94 ± 0.20	0.298	M

wherein the molecular sieve has a mole ratio of 10 or greater of (1) silicon oxide to (2) an oxide selected from boron oxide, aluminum oxide, and mixtures thereof.

[005] In another aspect, there is provided a method for preparing a molecular sieve by contacting under crystallization conditions (1) at least one source of silicon; (2) at least one source of boron; (3) fluoride ions; and (4) an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication.

[006] In yet another aspect, there is provided a process for preparing a molecular sieve having, in its calcined form, the powder XRD lines of Table 4, by: (a) preparing a reaction mixture containing: (1) at least one source of silicon; (2) at least one source of boron; (3) fluoride ions; (4) an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication; and (5) water; and (b) maintaining the reaction mixture under conditions sufficient to form crystals of the molecular sieve.

[006a] In another aspect, there is provided a method of preparing the molecular sieve as described herein comprising contacting under crystallization conditions (1) at least one source of silicon; (2) at least one source of boron; (3) fluoride ions; and (4) an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication (Q); and (5) water;

wherein the molecular sieve is prepared from a reaction mixture comprising, in terms of mole ratios, the following:

SiO_2/B_2O_3	5 to 100
Q/SiO_2	0.05 to 0.5
F/SiO_2	0.05 to 0.5
H_2O/SiO_2	10 to 100

[007] Where the molecular sieve formed is an intermediate material, the process disclosed herein includes a further post-crystallization processing step in order to achieve the target molecular sieve (e.g., by post-crystallization heteroatom lattice substitution or acid leaching).

[008] There is also provided a novel molecular sieve designated SSZ-87 having a composition, as-synthesized and in its anhydrous state, in terms of mole ratios, as follows:

	Broad	Secondary
SiO_2/B_2O_3	10 to 200	10 to 100
Q/SiO_2	0.015 to 0.06	0.025 to 0.06

wherein Q is an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication.

BRIEF DESCRIPTION OF THE DRAWINGS

[009] FIG. 1 shows the powder XRD pattern of the as-synthesized borosilicate SSZ-87 product of Example 1.

[010] FIG. 2 shows the powder XRD pattern of the calcined borosilicate SSZ-87 product of Example 4.

[011] FIG. 3 shows the scanning electron microscopy (SEM) image of the calcined borosilicate SSZ-87 product of Example 4.

DETAILED DESCRIPTION

Introduction

[012] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

CLAIMS

1. A molecular sieve having a mole ratio of 10 or greater of (1) at least one oxide of at least one tetravalent element to (2) optionally, one or more oxides selected from the group consisting of oxides of trivalent elements, pentavalent elements, and mixtures thereof, and having, in its calcined form, an X-ray diffraction pattern substantially as shown in the following table:

2-Theta	d-Spacing, nm	Relative Intensity
7.09 ± 0.20	1.245	VS
8.78 ± 0.20	1.006	S
9.95 ± 0.20	0.889	W
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26.87 ± 0.20	0.331	M
28.28 ± 0.20	0.315	W
28.58 ± 0.20	0.312	W
29.94 ± 0.20	0.298	M.

2. The molecular sieve of claim 1, wherein the molecular sieve has a mole ratio of 10 or greater of (1) silicon oxide to (2) an oxide selected from boron oxide, aluminum oxide, gallium oxide, indium oxide, and mixtures thereof.

3. The molecular sieve of claim 2, wherein the oxides comprise silicon oxide and boron oxide.

4. The molecular sieve of claim 2, wherein the oxides comprise silicon oxide and aluminum oxide.

5. The molecular sieve of claim 2, wherein the molecular sieve comprises essentially all silicon oxide.

6. The molecular sieve of claim 1, wherein the molecular sieve has a composition, as-synthesized and in its anhydrous state, in terms of mole ratios as follows:

SiO_2/B_2O_3	10 to 200
Q/SiO_2	0.015 to 0.06

wherein Q is an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication.

7. The molecular sieve of claim 1, wherein the molecular sieve has a composition, as-synthesized and in its anhydrous state, in terms of mole ratios as follows:

SiO_2/B_2O_3	10 to 100
Q/SiO_2	0.025 to 0.06

wherein Q is an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication.

8. A method of preparing a molecular sieve comprising contacting under crystallization conditions (1) at least one source of silicon; (2) at least one source of boron; (3) fluoride ions; and (4) an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication;
wherein the molecular sieve has, in its calcined form, an X-ray diffraction pattern substantially as shown in the following table:

2-Theta	d-Spacing, nm	Relative Intensity
7.09 ± 0.20	1.245	VS
8.78 ± 0.20	1.006	S
9.95 ± 0.20	0.889	W
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26.17 ± 0.20	0.340	M
26.87 ± 0.20	0.331	M
28.28 ± 0.20	0.315	W
28.58 ± 0.20	0.312	W
29.94 ± 0.20	0.298	M.

9. The method of claim 8, wherein the molecular sieve is prepared from a reaction mixture comprising, in terms of mole ratios, the following:

SiO_2/B_2O_3	5 to 100
Q/SiO_2	0.05 to 0.5
F/SiO_2	0.05 to 0.5
H_2O/SiO_2	10 to 100

wherein Q is an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication.

10. The method of claim 8, wherein the molecular sieve is prepared from a reaction mixture comprising, in terms of mole ratios, the following:

SiO_2/B_2O_3	10 to 60
Q/SiO_2	0.1 to 0.4
F/SiO_2	0.1 to 0.4
H_2O/SiO_2	15 to 25

wherein Q is an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication.

11. The method of claim 8, wherein the molecular sieve has composition, as-synthesized and in its anhydrous state, in terms of mole ratios, as follows:

SiO_2/B_2O_3	10 to 200
Q/SiO_2	0.015 to 0.06.

12. The molecular sieve of claim 8, wherein the molecular sieve has a composition, as-synthesized and in its anhydrous state, in terms of mole ratios as follows:

SiO_2/B_2O_3	10 to 100
Q/SiO_2	0.025 to 0.06.

Claims

1. A molecular sieve having a mole ratio of 10 or greater of (1) at least one oxide of at least one tetravalent element to (2) optionally, one or more oxides selected from the group consisting of oxides of trivalent elements, pentavalent elements, and mixtures thereof, and having, in its calcined form, an X-ray diffraction pattern substantially as shown in the following table:

2-Theta	d-Spacing, nm	Relative Intensity
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28.58 ± 0.20	0.312	W
29.94 ± 0.20	0.298	M

wherein the molecular sieve has a mole ratio of 10 or greater of (1) silicon oxide to (2) an oxide selected from boron oxide, aluminum oxide, and mixtures thereof.

2. The molecular sieve of claim 1, wherein the oxides comprise silicon oxide and boron oxide.

3. The molecular sieve of claim 1, wherein the oxides comprise silicon oxide and aluminum oxide.

4. The molecular sieve of claim 1, wherein the molecular sieve comprises essentially all silicon oxide.

5. A method of preparing the molecular sieve of claim 2 comprising contacting under crystallization conditions (1) at least one source of silicon; (2) at least one source of boron; (3) fluoride ions; and (4) an N,N'-diisopropyl-N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication (Q); and (5) water;
wherein the molecular sieve is prepared from a reaction mixture comprising, in terms of mole ratios, the following:

SiO_2/B_2O_3	5 to 100
Q/SiO_2	0.05 to 0.5
F/SiO_2	0.05 to 0.5
H_2O/SiO_2	10 to 100

6. The method of claim 5, wherein the molecular sieve is prepared from a reaction mixture comprising, in terms of mole ratios, the following:

SiO_2/B_2O_3	10 to 60
Q/SiO_2	0.1 to 0.4
F/SiO_2	0.1 to 0.4
H_2O/SiO_2	15 to 25