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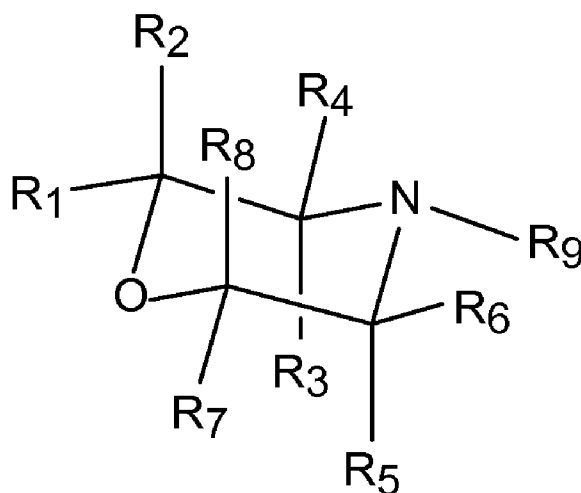
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(54) Title: ZEOLITES USING AN ORGANO-1-OXA-4-AZONIUMCYCLOHEXANE COMPOUND

**FIG. 1**

(57) **Abstract:** A method for synthesizing a zeolite is described. The method may include the steps of: (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon, and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound; (d) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution; and (e) heating the reaction mixture to form the zeolite.

ZEOLITES USING AN
ORGANO-1-OXA-4-AZONIUMCYCLOHEXANE COMPOUND

STATEMENT OF PRIORITY

5 This application claims priority to U.S. Application No. 14/561,112 which was filed December 04, 2012, the contents of which are hereby incorporated by reference in its entirety.

TECHNICAL FIELD OF THE INVENTION

10 This invention relates to novel organo-1-oxa-4-azonium cyclohexane compounds, a process for preparing the quaternary ammonium salts, and the use of the quaternary ammonium salts in the synthesis of zeolitic molecular sieves. The process involves forming 1-oxa-4-azoniumcyclohexane compounds from suitable reagents such as a substituted alkane and 1-oxa-4-azacyclohexane derivatives.

BACKGROUND OF THE INVENTION

15 Classes of molecular sieves include crystalline aluminophosphate, silicoaluminophosphate, or metalloaluminophosphate compositions which are microporous and which are formed from corner sharing $\text{AlO}_{4/2}$ and $\text{PO}_{4/2}$ tetrahedra. This class is described by Lok and coworkers in US 4,440,871. Other classes of molecular sieves include crystalline
20 aluminosilicate or silicate compositions, often referred to as zeolites. These are formed from corner sharing $\text{SiO}_{4/2}$ and $\text{AlO}_{4/2}$ tetrahedra. Numerous molecular sieves, both naturally occurring and synthetically prepared, are used in various industrial processes. Synthetically, these molecular sieves are prepared via hydrothermal synthesis employing suitable sources of Si, Al, P, and structure directing agents such as alkali metals, alkaline earth metals, amines,
25 or organoammonium cations. The structure directing agents reside in the pores of the molecular sieve and are largely responsible for the particular structure that is ultimately formed. These species may balance the framework charge associated with silicon or other metals such as Zn in the aluminophosphate compositions or aluminum in the silicate compositions and can also serve as space fillers to stabilize the tetrahedral network
30 framework. Molecular sieves are characterized by having pore openings of uniform dimensions, having a significant ion exchange capacity, and being capable of reversibly

desorbing an adsorbed phase which is dispersed throughout the internal voids of the crystal without significantly displacing any atoms which make up the permanent molecular sieve crystal structure. Molecular sieves can be used as catalysts for hydrocarbon conversion reactions, which can take place on outside surfaces as well as on internal surfaces within the pore.

Synthesis of molecular sieve materials often relies on the use of organoammonium templates known as organic structure directing agents (OSDAs). While simple OSDAs such as tetramethylammonium, tetraethylammonium and tetrapropylammonium are commercially available, often, OSDAs are complicated molecules that are difficult and expensive to synthesize; however, their importance lies in their ability to impart aspects of their structural features to the molecular sieve to yield a desirable pore structure. For example, the synthesis of N,N,N,-trimethylmyrtanylammonium derivatives allowed the synthesis of CIT-1, a member of the CON zeotype (Lobo and Davis *J. Am. Chem. Soc.* 1995, 117, 3766-79), the synthesis of a methyl substituted N,N,N',N'-tetraethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-dipyrrolidinium diiodide enabled the synthesis of ITQ-37, the member of the ITV zeotype (Sun, et.al. *Nature*, 2009, 458, 1154-7) and synthesis of the trans isomer of N,N-diethyl-2-methyldecahydroquinolinium iodide (Elomari, et.al. *Micro. Meso. Mater.* 2009, 118, 325-33) allowed synthesis of SSZ-56, the member of the SFS zeotype. The use of 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane as OSDA has been shown to allow synthesis of STA-7, an aluminophosphate based material of the SAV zeotype (Wright, et.al. *J. Chem. Soc., Dalton Trans.*, 2000, 1243-1248).

The art clearly shows that use of complex organoammonium SDAs often results in new molecular sieve materials. However, the synthesis of these complicated organoammonium compounds is quite lengthy and requires many steps, often in an organic solvent, thereby hindering development of the new molecular sieve material. Frequently, even for simple, commercially available OSDAs, the OSDA is the most costly ingredient used in synthesizing molecular sieve materials. Consequently, it would be economically advantageous to synthesize new molecular sieves from either commercially available organoammonium SDAs or SDAs which may be readily synthesized from commercially available starting materials.

The simple, commercially available, amine morpholine (tetrahydro-1,4-oxazine has been previously utilized in aluminophosphate based molecular sieve synthesis

and has been shown to yield CHA-type molecular sieves (Marchese, et.al. *Micro.Meso.Mater.* 1999, 30, 145-53; Ito, et.al. *Acta Cryst.* 1985, C41, 1698-1700) in aluminophosphate based syntheses, but has not yet been shown to yield other structure type molecular sieves. Additionally, the vapor pressure of morpholine is relatively high, making
5 its use on commercial scale troublesome as low vapor pressure organoammonium SDAs are preferred.

The complicated OSDA(s) discussed previously were synthesized *ex-situ* and added to the reaction mixture at several points. However, one drawback of *ex-situ* synthesis is the process is typically carried out in the presence of an organic solvent, which necessitates
10 at least one undesirable purification step to recover the SDA from the unwanted organic material.

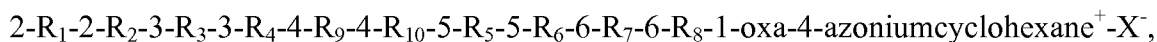
Therefore, what is needed in the art are novel organo-1-oxa-4-azonium cyclohexane compounds. It would be desirable for these organo-1-oxa-4-azonium cyclohexane compounds to be useful as SDAs for aluminosilicate, silicate,
15 aluminophosphate, or silicoaluminophosphate compositions.

SUMMARY OF THE INVENTION

The present invention discloses a process for preparing a pre-reacted aqueous solution of substituted hydrocarbons and amines essentially incapable of undergoing
20 pyramidal inversion, which overcomes the aforementioned difficulties. The inventors have made the surprising discovery that a substituted hydrocarbon and amine may be reacted in an aqueous solution at (or slightly above) room temperature to yield an aqueous solution comprising the OSDA. This process is disclosed for a broad class of amines in US Application Serial No. 14/552,654, herein incorporated by reference. This solution may then
25 be used without purification in the synthesis of molecular sieves. This procedure thereby allows the preparation of SDAs, such as unusual quaternary ammonium salts, from readily available starting reagents in a facile and practical manner.

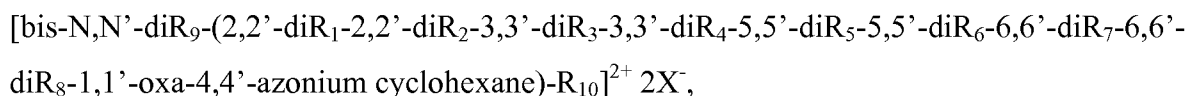
OSDAs prepared by the methods of the present invention are in aqueous solution and do not pose odor and flashpoint concerns. The result is the unprecedented
30 ability to remove the cooling step typically required in the preparation of *in-situ* zeolite reaction mixtures and to avoid purification steps such as evaporation of organic solvent typically required in *ex-situ* preparation methods.

One aspect of the invention are novel morpholinium compounds comprising 1-oxa-4-azonium cyclohexane salts. In one version, the 1-oxa-4-azonium cyclohexane salts have the structure of Formula 1:



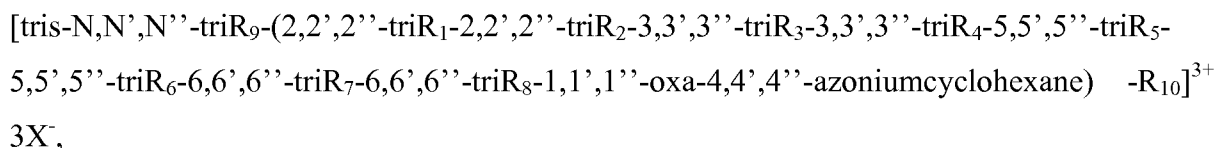
wherein $\text{R}_1\text{-R}_8$ are independently selected from H or an alkyl group having the formula $\text{C}_n\text{H}_{2n+1}$ where n is in the range from 1 to 4; R_9 and R_{10} form a cyclic alkyl group having the formula C_mH_{2m} forming a heterocycle of ring size q, where m is in the range from 4 to 8, and q is in the range of 5 to m+1; X is a halide or hydroxide; and the total number of C atoms in the molecule is in a range of 8 to 17.

Another version of the 1-oxa-4-azonium cyclohexane salts have the structure of Formula 2:



wherein $\text{R}_1\text{-R}_9$ are independently selected from H or an alkyl group having the formula $\text{C}_n\text{H}_{2n+1}$, where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C atoms in the molecule is in the range of 11 to 24, and R_{10} is an alkyl group having the formula C_mH_{2m} , where m is in the range from 3 to 8 and is connected to the 4 and 4' N atoms at positions x and y of the alkyl chain where x and y are independently selected from 1 to m.

Yet another version of the 1-oxa-4-azonium cyclohexane salts have the structure of Formula 3:



wherein $\text{R}_1\text{-R}_9$ are independently selected from H or an alkyl group having the formula $\text{C}_n\text{H}_{2n+1}$, where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C atoms in the molecule is the range of 15 to 36, and R_{10} is an alkyl group having the formula $\text{C}_m\text{H}_{2m-1}$, where m is in the range from 3 to 8 and is connected to the 4, 4' and 4'' N atoms at positions x, y and z of the alkyl chain where x, y and z are independently selected from 1 to m.

Still another version of the 1-oxa-4-azonium cyclohexane salts have the structure of Formula 4:

2-R₁-2-R₂-3-R₃-3-R₄-4-R₉-4-R₁₀-5-R₅-5-R₆-6-R₇-6-R₈-1-oxa-4-azoniumcyclohexane⁺-X⁻,

wherein R₁-R₉ are independently selected from H or an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4, R₁₀ is selected from an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4, benzyl, 1-methylnaphthalene, 2-methylnaphthalene and a non-olefinic alkyl group having the formula C_pH_{2p-1} where p is in the range from 4 to 10, X is halide or hydroxide, and the total number of C atoms in the molecule is in the range of 4 to 16.

In another aspect, the invention provides a method for synthesizing a 1-oxa-4-azonium cyclohexane compound. The method includes the steps of: (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; and (c) obtaining a solution comprising the organo-1-oxa-4-azoniumcyclohexane compound, wherein the mixture and the solution are essentially free of aluminum and silicon. In one version of the method, the solution is essentially free of aluminum, silicon and phosphorous. In one version of the method, the solution is essentially free of aluminum and phosphorous. Essentially free of is meant to indicate that the element described was not intentionally added to the mixture or solution. Adventitious amounts of the element may be permitted, whether coming from dissolution of reactor walls, impurities in the starting materials or other causes. Essentially free of may signify that less than 1 wt% or less than 0.5 wt% or less than 0.1 wt% of the element is present.

In one version of the method, the step of reacting the aqueous mixture occurs at a temperature from 0°C to 125°C, and for a time from 15 min to 72 hours. In another version of the method, the organo-1-oxa-4-azoniumcyclohexane product is used as a structure directing agent in the synthesis of a molecular sieve. In another version of the method, the 1-oxa-4-azacyclohexane derivative is essentially incapable of undergoing pyramidal inversion.

In another version of the method, the organo-1-oxa-4-azoniumcyclohexane compound is a structure directing agent in the synthesis of zeolites, aluminophosphates, or silicoaluminophosphates.

It is therefore an advantage of the present invention to provide a system and method for preparing structure directing agents in an aqueous mixture wherein the structure directing agents are prepared in the absence of Si and Al reactive sources. Furthermore, the

aqueous mixture is capable of forming an organo-1-oxa-4-azoniumcyclohexane halogen salt such as a bromide salt, in order to ultimately provide a solution including a quaternary organoammonium compound. The organoammonium bromide salt can be ion-exchanged, either by reaction with Ag_2O or by anion exchange resins to yield the hydroxide form of the organo-1-oxa-4-azoniumcyclohexane compound or used as the halogen salt directly. Finally, the resultant organoammonium compound can be used for the synthesis of a zeolite or molecular sieve.

In one version of the process, an organic solvent is not used in obtaining the structure directing agent.

In one aspect, the invention provides a method for synthesizing a zeolite. The method may include the steps of: (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon, and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound; (d)) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution,; and (e) heating the reaction mixture to form the zeolite.

In another version of the method, step (d) comprises forming a first mixture of the reactive sources of M, Al, Si and the optional seeds of a material L, and adding the solution to the first mixture without cooling the first mixture, wherein M is a metal.

In one version of the method, the step of reacting the aqueous mixture occurs at a temperature from 0°C to 125°C , and for a time from 15 min to 72 hours.

In another aspect, the invention provides a zeolite prepared by a process comprising the steps of: (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon, and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; (c) obtaining a solution comprising a structure directing agent comprising an organo-1-oxa-4-azoniumcyclohexane compound; (d) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution; and (e) heating the reaction mixture to form the zeolite.

In one version of the method, the aqueous mixture and the solution are essentially free of aluminum and silicon.

In another version of the method, the 1-oxa-4-azacyclohexane derivative is essentially incapable of undergoing pyramidal inversion.

These and other features, aspects, and advantages of the present invention will become better understood upon consideration of the following detailed description, drawings and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustration of the 1-oxa-4-azacyclohexane derivative.

Fig. 2 is an illustration of the class of 1-oxa-4-azonium cyclohexane salts having the structure of Formula 1.

Fig. 3 is an illustration of the class of 1-oxa-4-azonium cyclohexane salts having the structure of Formula 2.

Fig. 4 is an illustration of the class of 1-oxa-4-azonium cyclohexane salts having the structure of Formula 3.

Fig. 5 is an illustration of the class of 1-oxa-4-azonium cyclohexane salts having the structure of Formula 4.

Figs. 6A-B are illustrations of substituted amine compounds undergoing pyramidal inversion.

Figs. 7A-D are illustrations of quaternary ammonium compounds formed from 1-oxa-4-azacyclohexane derivatives.

Fig. 8 shows the x-ray diffraction pattern of the Example 15 product.

DETAILED DESCRIPTION OF THE INVENTION

The present invention deals with an aqueous process for preparing novel 1-oxa-4-azonium cyclohexane salts and their use in zeolite synthesis. These compounds can be used as an organic structure directing agent (OSDA), and they overcome many of the typical problems associated with OSDA synthesis and subsequent zeolite synthesis. Embodiments of the present invention cover methods for synthesis of the 1-oxa-4-azonium cyclohexane salts from a variety of starting materials.

In a typical method for preparing the 1-oxa-4-azonium cyclohexane salts of the present invention, a substituted hydrocarbon is added to water to form a mixture. The 1-oxa-4-azacyclohexane derivative, as shown in Fig. 1, may then be added and the reaction mixture stirred until a solution containing the 1-oxa-4-azonium cyclohexane salt is observed.

If the solution is cooled to room temperature, the product is stably maintained as an aqueous solution for later use.

In certain embodiments, the precursor reagents (*e.g.*, the substituted alkane and 1-oxa-4-azacyclohexane derivative) may be added separately or together to form the reaction mixture at a number of points in the process. The precursors may be reacted together at temperatures ranging from 0°C to 125°C. Preferably the precursors are reacted at room temperature or at a slightly elevated temperature such as temperatures ranging from 5°C to 100°C. More preferably, the precursors are reacted at temperatures from 20°C to 120°C, or 20°C to 80°C.

The reaction time varies from 5 minutes to 72 hr or from 15 minutes to 48hr or from 0.5 hr to 48 hr.

The resulting solution may be cooled to room temperature or used as is. Other known techniques require the use of purification steps such as distillation, crystallization, chromatography and removal of a component via vacuum. A benefit of the instant method is that the solution of the organo-1-oxa-4-azoniumcyclohexane salt is prepared without additional purification steps occurring prior to use of the solution to make zeolites and molecular sieves. Some small laboratory scale procedures may involve removal of unreacted reactants; however, in commercial embodiments, it is most likely to react to completion. Ion-exchange as described below does not purify the solution, but converts halide anions to hydroxide ions and thus is not a purification step. The resulting solution may be cooled to room temperature or used as is. However, no purification steps occur prior to use of the solution.

The methods of the present invention may be carried out in preparation of zeolitic molecular sieves. In one aspect, the invention provides a method for synthesizing a zeolite. The method may include the steps of: (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound; (d) forming a molecular sieve reaction mixture comprising reactive sources of the elements in the framework and the solution; and (e) heating the reaction mixture to form the molecular sieve.

In one aspect of the present invention, the 1-oxa-4-azonium cyclohexane salts are prepared from a substituted hydrocarbon and a 1-oxa-4-azacyclohexane derivative.

Suitable substituted hydrocarbons include halogen substituted alkanes having between 2 and 8 carbon atoms, benzyl halides, 1-halomethane naphthalene, 2-halomethane naphthalene, halo-substituted non-olefinic alkyl groups having the formula C_pH_{2p-1} where p is in the range from 4 to 10, α,ω -dihalogen substituted alkanes having between 3 and 6 carbon atoms, di-
5 halogen substituted alkanes having between 3 and 8 carbon atoms, tri-halogen substituted alkanes having between 3 and 8 carbons, and combinations thereof. Halogens include chlorine, bromine and iodine. In an aspect, the halogen is bromine or iodine. In another aspect, the halogen is bromine. In an aspect, the identity of the halogen substitutions on a substituted hydrocarbon may be all different, all the same, or any combination thereof.

10 Suitable halogen substituted alkanes having between 2 and 8 carbon atoms include, but are not limited to, bromoethane, iodoethane, chloropropane, bromopropane, iodopropane, chlorobutane, 1-bromobutane, 2-bromobutane, iodobutane, 1-bromo-2-methylpropane, 2-bromo-2-methylpropane, chloropentane, bromopentane, iodopentane, 2-bromopentane, chlorohexane, bromohexane, iodohexane, benzyl bromide, 1-chloro-2-
15 phenylethane, 1-bromo-2-phenylethane, and 1-iodo-2-phenylethane.

α,ω -dihalogen substituted alkanes having between 3 and 6 carbon atoms include, but are not limited to, 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane, 1,3-dibromopropane, 1,4-dibromobutane, 1,4-dibromo-2-methylbutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,3-diiodopropane, 1,4-diiodobutane,
20 1,5-diiodopentane, 1,6-diiodohexane and combinations thereof.

Di-halogen substituted alkanes having between 3 and 8 carbon atoms suitably include, but are not limited to, 1,2-dibromopropane, 1,3-dibromobutane, 1,3-dibromopentane, 1,4-dibromopentane, 2,4-dibromopentane, 1,5-dibromohexane, 1,4-dibromohexane, 1,3-dibromohexane, 2,4-dibromohexane, 2,5-dibromohexane, 2,5-dibromo-3-methylhexane, 2,5-
25 dibromo-3,3-dimethylhexane, 1,4-dibromo-2-ethylbutane, and 1,2-dibromo-2-phenylethane. Halogen substitutions may be chlorine, bromine or iodine, but are illustrated for bromine. In an aspect, the two halogen substitutions may be the same or different.

Tri-halogen substituted alkanes having between 3 and 8 carbons suitably include, but are not limited to, 1,2,3-tribromopropane, 1,2,4-tribromobutane, 1,2,3-
30 tribromobutane, 1,3,5-tribromopentane, 1,2,4-tribromopentane, 1,2,3-tribromopentane, 1,3,6-tribromohexane, 1,2,4-tribromohexane, 1,2,5-tribromohexane, 1,2,6-tribromohexane, 1,3,4-tribromohexane, and 1,3,5-tribromohexane.

Halogen substitutions may be chlorine, bromine or iodine, but are illustrated for bromine. In an aspect, the identity of the three halogen substitutions on the substituted hydrocarbon may be all different, all the same, or any combination thereof.

In an aspect, the mole ratio of the 1-oxa-4-azacyclohexane derivative to the substitution is from 1:1 to 2:1 and is preferably from 1:1 to 1.5:1. Typically, the mole ratio of 1-oxa-4-azacyclohexane derivative to substitution is 1. Thus, when butylbromide is used as the substituted hydrocarbon, 1 equivalent of 1-oxa-4-azacyclohexane derivative is typically used, whereas when 1,4-dibromobutane is used as the substituted hydrocarbon, 2 equivalents of 1-oxa-4-azacyclohexane derivative are typically used.

Suitable 1-oxa-4-azacyclohexane derivatives include those for which at least one conformer is essentially incapable of undergoing pyramidal inversion. The IUPAC definition of pyramidal inversion is given as, "a polytopal rearrangement in which the change in bond directions to a three-coordinate central atom having a pyramidal arrangement of bonds (tripodal arrangement) causes the central atom (apex of the pyramid) to appear to move to an equivalent position on the other side of the base of the pyramid. If the three ligands to the central atom are different pyramidal inversion interconverts enantiomers." The tripodal nature of many nitrogen compounds result in the ability of these compounds to undergo pyramidal inversion. Typically, the energy barrier to inversion is low for unconstrained molecules. For example, ammonia (NH_3) has an inversion barrier of 24.5 kJ mol^{-1} , with an observed inversion frequency of $2.4 \times 10^{10} \text{ s}^{-1}$, dimethylamine has an inversion barrier of 18 kJ mol^{-1} , triisopropylamine has an inversion barrier of $6\text{--}8 \text{ kJ mol}^{-1}$ and dimethylethylamine has an inversion barrier of 22 kJ mol^{-1} . However, inversion barrier energy can become very high when the nitrogen substituents are part of a small ring or other rigid molecule as in the case of 1-methylpyrrolidine. Molecules defined as essentially incapable of undergoing pyramidal inversion have an inversion barrier energy of at least 28 kJ mol^{-1} and more preferably of at least 30 kJ mol^{-1} . A discussion of pyramidal inversion may be found in Rauk, A., *et al.*, (1970), Pyramidal Inversion. *Angew. Chem. Int. Ed. Engl.*, 9: 400–414, with further discussion specifically for amines found in "Inorganic Chemistry" edited by Arnold F. Holleman, *et al.*, Academic Press, 2001. Furthermore, Figs. 6A-B illustrate substituted amine compounds undergoing pyramidal inversion. Molecules may exist in many conformers or folding patterns. For example, it is well known that both chair and boat forms of cyclohexane

exist and interconvert between the two different conformers. In an aspect of the invention, at least one conformer of the amine is essentially incapable of undergoing pyramidal inversion.

Table 1: Molecules generally incapable of undergoing pyramidal inversion.

Molecule Name	Inversion Barrier (kJ mol ⁻¹)
N-methylhomopiperidine	28-29
1-methyl-4-piperidone	30.7
Trimethylamine	31-35
1,3,3-trimethylpyrrolidine	31
N-methylpyrrolidine	31-35
3-methyl-1-thia-3-azacyclopentane	33
9-methyl-9-azabicyclo[3.3.1]nonane	34
N-methyl piperidine (equatorial)	36.4
1,2,2,6-tetramethylpiperidine (axial)	38
2-methyl-dihydro-2-azaphenalene	40.5
Methylazetidione	42
1,2,2,6-tetramethylpiperidine (equatorial)	46
4-methyl-1-oxa-4-azacyclohexane	
AKA methylmorpholine	48
2-methyl-1-oxa-2-azacyclohexane (equatorial)	57
2-methyl-1-oxa-2-azacyclopentane	65
Methylaziridine	80-90

5

The 1-oxa-4-azacyclohexane derivative is illustrated in Fig. 1 and has the structure of formula 5:

2-R₁-2-R₂-3-R₃-3-R₄-4-R₅-5-R₅-5-R₆-6-R₇-6-R₈-1-oxa-4-azacyclohexane,

wherein R₁-R₉ are independently selected from H or an alkyl group having the formula C_nH_{2n+1}, and the total number of C atoms in the molecule is in the range of 4 to 12.

10

In some versions, R₁-R₉ are H.

In some versions, at least one of R₁-R₉ is an alkyl group. In some versions, at least two of R₁-R₉ are alkyl groups. In some versions, when at least two of R₁-R₉ are alkyl groups, two of the alkyl groups are on the same C atom (e.g., R₁ and R₂, or R₃ and R₄, or R₅ and R₆, or R₇ and R₈).

15

Where more than one alkyl group is present, the alkyl groups can be the same group or they can be different. Most commonly, the alkyl groups are methyl or ethyl groups.

Suitable 1-oxa-4-azacyclohexane derivatives include, but are not limited to, 4-butylmorpholine, 4-propylmorpholine, 4-ethylmorpholine, 4-methylmorpholine, morpholine, 2-methylmorpholine, 2,4-dimethylmorpholine, 4-ethyl-2-methylmorpholine, 4-propyl-2-methylmorpholine, 3-methylmorpholine, 3,4-dimethylmorpholine, 4-ethyl-3-methylmorpholine, 4-propyl-3-methylmorpholine, 5-methylmorpholine, 2,5-dimethylmorpholine, 4-ethyl-5-methylmorpholine, 4-propyl-5-methylmorpholine, 5-ethyl-2-methylmorpholine, 6-methylmorpholine, 4,6-dimethylmorpholine, 4-ethyl-6-methylmorpholine, 4-propyl-6-methylmorpholine, 2,6-dimethylmorpholine, 2,4,6-trimethylmorpholine, 4-ethyl-2,6-dimethylmorpholine, 2,3-dimethylmorpholine, 2,3,4-trimethylmorpholine, 4-ethyl-2,3-dimethylmorpholine, 2,5-dimethylmorpholine, 2,4,5-trimethylmorpholine, 4-ethyl-2,5-dimethylmorpholine, 2,2-dimethylmorpholine, 2,2,4-trimethylmorpholine, 4-ethyl-2,2-dimethylmorpholine, 3,3-dimethylmorpholine, 3,3,4-trimethylmorpholine, 4-ethyl-3,3-dimethylmorpholine, 5,5-dimethylmorpholine, 4,5,5-trimethylmorpholine, 4-ethyl-5,5-dimethylmorpholine, 6,6-dimethylmorpholine, 4,6,6-trimethylmorpholine, 4-ethyl-6,6-dimethylmorpholine, 5-ethyl-2-methylmorpholine and combinations thereof. Butyl may indicate n-butyl, sec-butyl, isobutyl or tert-butyl. Propyl may indicate n-propyl or isopropyl.

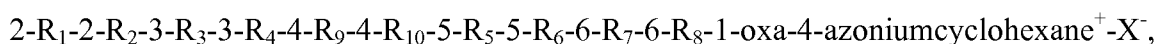
When the substituted hydrocarbon is an α,ω -dihalogen substituted alkane having between 3 and 6 carbon atoms, or a di-halogen substituted alkanes having between 3 and 8 carbon atoms, the 1-oxa-4-azonium cyclohexane salts may have the structure of either Formula 1 or Formula 2. When R_9 is an alkyl group, the structure of Formula 2 may be obtained. When R_9 is H, the structure of Formula 1 may be obtained.

When the substituted hydrocarbon is a tri-halogen substituted alkane having between 3 and 8 carbons, the 1-oxa-4-azonium cyclohexane salts may have the structure of Formula 3.

When the substituted hydrocarbon is a halogen substituted alkane having between 2 and 8 carbon atoms, benzyl halides, 1-halomethane naphthalene, 2-halomethane naphthalene, or a halo-substituted non-olefinic alkyl group having the formula C_pH_{2p-1} where p is in the range from 4 to 10, the 1-oxa-4-azonium cyclohexane salts may have the structure of Formula 4.

The 1-oxa-4-azacyclohexane derivative includes R_1 - R_9 , and at least R_{10} is from the substituted hydrocarbon. In some versions, the substituents at R_1 - R_8 of the 1-oxa-4-azacyclohexane derivative and the substituents at R_1 - R_8 of the 1-oxa-4-azoniumcyclohexane salt are the same. In some versions, the substituents at R_1 - R_9 of the 1-oxa-4-azacyclohexane derivative and the substituents at R_1 - R_9 of the 1-oxa-4-azoniumcyclohexane salt are the same.

One class of 1-oxa-4-azoniumcyclohexane salts have the structure of Formula 1:



wherein R_1 - R_8 are independently selected from H or an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4; R_9 and R_{10} form a cyclic alkyl group having the formula C_mH_{2m} forming a heterocycle of ring size q, where m is in the range from 4 to 8, and q is in the range of 5 to m+1; X is a halide or hydroxide; and the total number of C atoms in the molecule is in a range of 8 to 17.

In some versions, when R_1 - R_8 are H, and m is 4, X is hydroxide. In some versions, when R_1 - R_8 are H, m is in the range from 5 to 8.

In some versions, X is hydroxide.

The cyclic alkyl group can have from 4 to 8 carbons, and the heterocycle ring has a ring size of 5 to m+1. Most commonly, the heterocycle ring has 5 or 6 members. In some versions, q is 5. In some versions q is 6. In some versions, q is 5 or 6.

In some versions, R_{10} can be a straight chain alkyl group or a branched alkyl group. When R_{10} is a branched alkyl group, the heterocycle ring can have one or more alkyl substituents. For example, the use of 1,4-dibromo-4,4-dimethylbutane would yield a 5 member heterocycle ring with 2 methyl groups on the carbon adjacent to the nitrogen atom and the cyclic alkyl group has the formula C_6H_{12} .

In some versions, R_1 - R_8 are H.

In some versions, at least one of R_1 - R_8 is an alkyl group. In some versions, at least two of R_1 - R_8 are alkyl groups. In some versions, when at least two of R_1 - R_8 are alkyl groups, two of the alkyl groups are on the same C atom (e.g., R_1 and R_2 , or R_3 and R_4 , or R_5 and R_6 , or R_7 and R_8).

Where more than one alkyl group is present, the alkyl groups can be the same group or they can be different. Most commonly, the alkyl groups are methyl or ethyl groups.

In one version, the cyclic alkyl group has 5 carbons, q is 6, R₁-R₈ are H, and X is a halide.

As an example, Fig. 7A shows the 3-oxa-6-azonia-8,8-dimethylspiro[5.5]undecane product formed from the reaction of 1,5-dibromo-2,2-dimethylpentane with morpholine.

Another class of 1-oxa-4-azonium cyclohexane salts have the structure of Formula 2:

[bis-N,N'-diR₉-(2,2'-diR₁-2,2'-diR₂-3,3'-diR₃-3,3'-diR₄-5,5'-diR₅-5,5'-diR₆-6,6'-diR₇-6,6'-diR₈-1,1'-oxa-4,4'-azonium cyclohexane)-R₁₀]²⁺ 2X⁻,

wherein R₁-R₉ are independently selected from H or an alkyl group having the formula C_nH_{2n+1}, where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C atoms in the molecule is in the range of 11 to 24, and R₁₀ is an alkyl group having the formula C_mH_{2m}, where m is in the range from 3 to 8 and is connected to the 4 and 4' N atoms at positions x and y of the alkyl chain where x and y are independently selected from 1 to m.

In some versions, when R₁-R₈ are H, R₉ is CH₃, R₁₀ is C₄H₈, x is 1, and y is 4, X is hydroxide; or when R₁-R₈ are H, R₉ is CH₃, R₁₀ is C₅H₁₀, x is 1, and y is 5, X is hydroxide; or when R₁-R₈ are H, R₉ is CH₃, R₁₀ is C₆H₁₂, x is 1, and y is 6, X is hydroxide; or when R₁-R₈ are H, R₉ is CH₃, R₁₀ is C₇H₁₄, x is 1, and y is 7, X is hydroxide; or when R₁-R₈ are H, R₉ is C₂H₅, R₁₀ is C₆H₁₂, x is 1, and y is 6, X is hydroxide.

In some versions, when R₁-R₈ are H and R₉ is CH₃ or C₂H₅, then X is hydroxide. In some versions, when R₁-R₈ are H and R₉ is CH₃, then m is 3 or 8. In some versions, when R₁-R₈ are H and R₉ is C₂H₅, then m is 3, 4, 5, 7, or 8. In some versions, when R₁-R₈ are H and R₉ is CH₃, then y is not equal to m. In some versions, when R₁-R₈ are H and R₉ is C₂H₅, then y is not equal to m. In some versions, when R₁-R₈ are H and R₉ is an alkyl group, then y is not equal to m.

In some versions, when R₉ is CH₃ or C₂H₅, then X is hydroxide. In some versions, when R₉ is CH₃, then m is 3 or 8. In some versions, when R₉ is C₂H₅, then m is 3, 4, 5, 7, or 8. In some versions, when R₉ is CH₃, then y is not equal to m. In some versions, when R₉ is C₂H₅, then y is not equal to m. In some versions, when R₉ is an alkyl group, then y is not equal to m.

In some versions, X is hydroxide.

In some versions, R₁₀ is a straight chain alkyl group (i.e., x is 1 and y is m).

In some versions, when R₉ is an alkyl group, X is hydroxide.

In some versions, R₉ is a methyl group. In some versions, R₉ is a methyl group and R₁₀ has 4 carbons. In some versions, R₉ is a methyl group, R₁₀ has 4 carbons, and
 5 R₁₀ is attached at the end of the chain to the two morpholine rings (i.e., x is 1, and y is 4). In some versions, the compound is a dihalide or a dihydroxide of 1,4-bis(4-methylmorpholinium)butane.

In some versions, R₁-R₈ are H. In some versions, when R₁-R₈ are H, R₉ is an alkyl group. In some versions, when R₁-R₈ are H, R₉ is H. In some versions, when R₁-R₈ are
 10 H and R₉ is CH₃, y and m do not have the same value. In some versions, when R₁-R₈ are H and R₉ is C₂H₅, m is selected from the group consisting of 3, 4, 5, 7, and 8. In some versions, at least one of R₁-R₈ is an alkyl group. In some versions when at least one of R₁-R₈ is an alkyl group, R₉ is an alkyl group. In some versions, when at least one of R₁-R₈ is an alkyl group, R₉ is H.

15 In some versions, at least two of R₁-R₈ are alkyl groups. In some versions, when at least two of R₁-R₈ are alkyl groups, two of the alkyl groups are on the same C atom (e.g., R₁ and R₂, or R₃ and R₄, or R₅ and R₆, or R₇ and R₈).

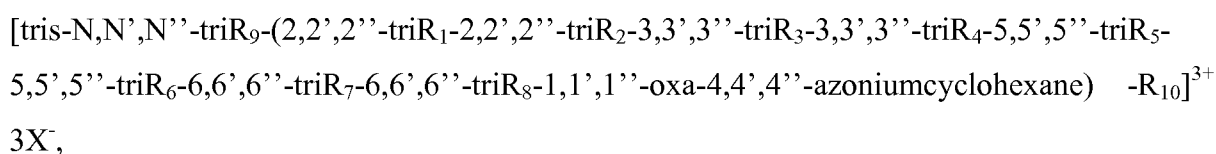
Where more than one of R₁-R₉ is an alkyl group, the alkyl groups can be the same group or they can be different. Most commonly, the alkyl groups are methyl or ethyl
 20 groups.

In some versions, the 1-oxa-4-azonium cyclohexane salt comprises at least one of the di-halides or di-hydroxides of bis-: 4-butylmorpholine, 4-propylmorpholine, 4-ethylmorpholine, 4-methylmorpholine, morpholine, 2-methylmorpholine, 2,4-dimethylmorpholine, 4-ethyl-2-methylmorpholine, 4-propyl-2-methylmorpholine,
 25 3-methylmorpholine, 3,4-dimethylmorpholine, 4-ethyl-3-methylmorpholine, 4-propyl-3-methylmorpholine, 5-methylmorpholine, 2,5-dimethylmorpholine, 4-ethyl-5-methylmorpholine, 4-propyl-5-methylmorpholine, 5-ethyl-2-methylmorpholine, 6-methylmorpholine, 4,6-dimethylmorpholine, 4-ethyl-6-methylmorpholine, 4-propyl-6-methylmorpholine, 2,6-dimethylmorpholine, 2,4,6-trimethylmorpholine, 4-ethyl-2,6-
 30 dimethylmorpholine, 2,3-dimethylmorpholine, 2,3,4-trimethylmorpholine, 4-ethyl-2,3-dimethylmorpholine, 2,5-dimethylmorpholine, 2,4,5-trimethylmorpholine, 4-ethyl-2,5-dimethylmorpholine, 2,2-dimethylmorpholine, 2,2,4-trimethylmorpholine, 4-ethyl-2,2-

dimethylmorpholine, 3,3-dimethylmorpholine, 3,3,4-trimethylmorpholine, 4-ethyl-3,3-dimethylmorpholine, 5,5-dimethylmorpholine, 4,5,5-trimethylmorpholine, 4-ethyl-5,5-dimethylmorpholine, 6,6-dimethylmorpholine, 4,6,6-trimethylmorpholine, 4-ethyl-6,6-dimethylmorpholine, 5-ethyl-2-methylmorpholine and combinations thereof. Butyl may indicate n-butyl, sec-butyl, isobutyl or tert-butyl. Propyl may indicate n-propyl or isopropyl.

As an example, Fig. 7B shows the 1,4-*bis*(4-ethylmorpholinium) butane dibromide product formed from the reaction of 1,4-dibromobutane with 4-ethylmorpholinium.

Another class of 1-oxa-4-azonium cyclohexane salts have the structure of Formula 3:



wherein R₁-R₉ are independently selected from H or an alkyl group having the formula C_nH_{2n+1}, where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C atoms in the molecule is the range of 15 to 36, and R₁₀ is an alkyl group having the formula C_mH_{2m-1}, where m is in the range from 3 to 8 and is connected to the 4, 4' and 4'' N atoms at positions x, y and z of the alkyl chain where x, y and z are independently selected from 1 to m.

In some versions, X is hydroxide.

In some versions, when R₉ is an alkyl group, X is hydroxide.

In some versions, R₉ is an alkyl group. In some versions, R₉ is a methyl or ethyl group.

In some versions, x is 1 and z is m. In some versions, x is 1 and z is m-1. In some versions, x is 1 and z is m-2. In some versions, m is in the range from 4 to 8 or from 4 to 7.

In some versions, R₁-R₈ are H. In some versions, when R₁-R₈ are H, R₉ is an alkyl group. In some versions, when R₁-R₈ are H, R₉ is a methyl or ethyl group. In some versions, when R₁-R₈ are H, R₉ is H.

In some versions, at least one of R₁-R₈ is an alkyl group. In some versions when at least one of R₁-R₈ is an alkyl group, R₉ is an alkyl group. In some versions when at

least one of R₁-R₈ is an alkyl group, R₉ is a methyl or ethyl group. In some versions when at least one of R₁-R₈ is an alkyl group, R₉ is H.

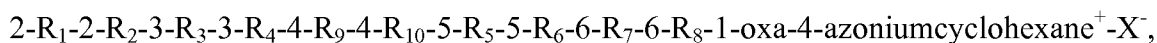
In some versions, at least two of R₁-R₈ are alkyl groups. In some versions, when at least two of R₁-R₈ are alkyl groups, two of the alkyl groups are on the same C atom (e.g., R₁ and R₂, or R₃ and R₄, or R₅ and R₆, or R₇ and R₈).

Where more than one alkyl group is present, the alkyl groups can be the same group or they can be different. Most commonly, the alkyl groups are methyl or ethyl groups.

In some versions, the 1-oxa-4-azoniumcyclohexane salt comprises at least one of the tri-halides or tri-hydroxides of tris-: 4-butylmorpholine, 4-propylmorpholine, 4-ethylmorpholine, 4-methylmorpholine, morpholine, 2-methylmorpholine, 2,4-dimethylmorpholine, 4-ethyl-2-methylmorpholine, 4-propyl-2-methylmorpholine, 3-methylmorpholine, 3,4-dimethylmorpholine, 4-ethyl-3-methylmorpholine, 4-propyl-3-methylmorpholine, 5-methylmorpholine, 2,5-dimethylmorpholine, 4-ethyl-5-methylmorpholine, 4-propyl-5-methylmorpholine, 5-ethyl-2-methylmorpholine, 6-methylmorpholine, 4,6-dimethylmorpholine, 4-ethyl-6-methylmorpholine, 4-propyl-6-methylmorpholine, 2,6-dimethylmorpholine, 2,4,6-trimethylmorpholine, 4-ethyl-2,6-dimethylmorpholine, 2,3-dimethylmorpholine, 2,3,4-trimethylmorpholine, 4-ethyl-2,3-dimethylmorpholine, 2,5-dimethylmorpholine, 2,4,5-trimethylmorpholine, 4-ethyl-2,5-dimethylmorpholine, 2,2-dimethylmorpholine, 2,2,4-trimethylmorpholine, 4-ethyl-2,2-dimethylmorpholine, 3,3-dimethylmorpholine, 3,3,4-trimethylmorpholine, 4-ethyl-3,3-dimethylmorpholine, 5,5-dimethylmorpholine, 4,5,5-trimethylmorpholine, 4-ethyl-5,5-dimethylmorpholine, 6,6-dimethylmorpholine, 4,6,6-trimethylmorpholine, 4-ethyl-6,6-dimethylmorpholine, 5-ethyl-2-methylmorpholine and combinations thereof.

As an example, Fig. 7C shows the 1,3,6-*tris*(4-methylmorpholinium) 4-methylhexane tribromide product formed from the reaction of 1,3,6-tribromo-4-methylhexane with 4-methylmorpholine.

Still another class of 1-oxa-4-azonium cyclohexane salts have the structure Formula 4:



wherein R₁-R₉ are independently selected from H or an alkyl group having the formula C_nH_{2n+1}, R₁₀ is selected from an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4, benzyl, 1-methylnaphthalene, 2-methylnaphthalene and a non-olefinic

alkyl group having the formula C_pH_{2p-1} where p is in the range from 4 to 10, X is halide or hydroxide, and the total number of C atoms in the molecule is in the range of 4 to 16.

In some versions, X is hydroxide.

In some versions, when R_9 is an alkyl group, X is hydroxide.

5 In some versions, R_9 is an alkyl group. In some versions, R_9 is a methyl or ethyl group.

In some versions, R_1 - R_9 are H.

10 In some versions, R_1 - R_8 are H. In some versions, when R_1 - R_8 are H, R_9 is an alkyl group. In some versions, when R_1 - R_8 are H, R_9 is a methyl or ethyl group. In some versions, when R_1 - R_8 are H, R_9 is H.

In some versions, at least one of R_1 - R_8 is an alkyl group. In some versions when at least one of R_1 - R_8 is an alkyl group, R_9 is an alkyl group. In some versions when at least one of R_1 - R_8 is an alkyl group, R_9 is a methyl or ethyl group. In some versions when at least one of R_1 - R_8 is an alkyl group, R_9 is H.

15 In some versions, at least two of R_1 - R_8 are alkyl groups. In some versions, when at least two of R_1 - R_8 are alkyl groups, two of the alkyl groups are on the same C atom (e.g., R_1 and R_2 , or R_3 and R_4 , or R_5 and R_6 , or R_7 and R_8).

Where more than one alkyl group is present, the alkyl groups can be the same group or they can be different. Most commonly, the alkyl groups are methyl or ethyl groups.

20 In some versions, when at least two of R_1 - R_8 are alkyl groups, at least one of R_9 and R_{10} is the alkyl group having the formula C_nH_{2n+1} .

In some versions R_{10} is the alkyl group having the formula C_nH_{2n+1} . In some versions, R_{10} is a propyl or butyl group. In some versions, the R_{10} alkyl group can be a straight chain alkyl group or a branched alkyl group.

25 In some versions, R_{10} is benzyl. In some versions, when R_{10} is benzyl, at least one of R_1 - R_8 is an alkyl group. In some versions, when R_{10} is benzyl, R_9 is an alkyl group. In some versions, when R_{10} is benzyl, R_9 is H.

30 In some versions, R_{10} is 1-methylnaphthalene or 2-methylnaphthalene. In some versions, when R_{10} is 1-methylnaphthalene or 2-methylnaphthalene, at least one of R_1 - R_8 is an alkyl group. In some versions, when R_{10} is 1-methylnaphthalene or

2-methylnaphthalene, R_9 is an alkyl group. In some versions, when R_{10} is 1-methylnaphthalene or 2-methylnaphthalene, R_9 is H.

In some versions, R_{10} is the non-olefinic alkyl group having the formula C_pH_{2p-1} where p is in the range from 4 to 10. In some versions, when R_{10} is the non-olefinic alkyl group, at least one of R_1 - R_8 is an alkyl group. In some versions, when R_{10} is the non-olefinic alkyl group, R_9 is an alkyl group. In some versions, when R_{10} is the non-olefinic alkyl group, R_9 is H. In some versions, R_{10} is selected from the group consisting of cyclobutyl, cyclopentyl, cyclohexyl, methylcyclopentyl, cycloheptyl, methylcyclohexyl, dimethylcyclopentyl, cyclooctyl and dimethylcyclohexyl. Suitable non-olefinic alkyl groups having the formula C_pH_{2p-1} where p is in the range from 4 to 10 include, but are not limited to cyclobutyl, cyclopentyl, cyclohexyl, methylcyclopentyl, cycloheptyl, methylcyclohexyl, dimethylcyclopentyl, cyclooctyl and dimethylcyclohexyl. In some versions, p is in the range from 5 to 8.

In some versions, the 1-oxa-4-azonium cyclohexane salt comprises at least one of the halides or hydroxides of: 4-butylmorpholine, 4-propylmorpholine, 4-ethylmorpholine, 4-methylmorpholine, morpholine, 2-methylmorpholine, 2,4-dimethylmorpholine, 4-ethyl-2-methylmorpholine, 4-propyl-2-methylmorpholine, 3-methylmorpholine, 3,4-dimethylmorpholine, 4-ethyl-3-methylmorpholine, 4-propyl-3-methylmorpholine, 5-methylmorpholine, 2,5-dimethylmorpholine, 4-ethyl-5-methylmorpholine, 4-propyl-5-methylmorpholine, 5-ethyl-2-methylmorpholine, 6-methylmorpholine, 4,6-dimethylmorpholine, 4-ethyl-6-methylmorpholine, 4-propyl-6-methylmorpholine, 2,6-dimethylmorpholine, 2,4,6-trimethylmorpholine, 4-ethyl-2,6-dimethylmorpholine, 2,3-dimethylmorpholine, 2,3,4-trimethylmorpholine, 4-ethyl-2,3-dimethylmorpholine, 2,5-dimethylmorpholine, 2,4,5-trimethylmorpholine, 4-ethyl-2,5-dimethylmorpholine, 2,2-dimethylmorpholine, 2,2,4-trimethylmorpholine, 4-ethyl-2,2-dimethylmorpholine, 3,3-dimethylmorpholine, 3,3,4-trimethylmorpholine, 4-ethyl-3,3-dimethylmorpholine, 5,5-dimethylmorpholine, 4,5,5-trimethylmorpholine, 4-ethyl-5,5-dimethylmorpholine, 6,6-dimethylmorpholine, 4,6,6-trimethylmorpholine, 4-ethyl-6,6-dimethylmorpholine, 5-ethyl-2-methylmorpholine and combinations thereof.

As an example, Fig. 7D shows the 4-isopropyl(4,6,6-trimethylmorpholinium) bromide product formed from the reaction of 2-bromopropane with 4,6,6-trimethylmorpholine.

The 1-oxa-4-azonium cyclohexane halide salt can be ion-exchanged, either by reaction with Ag_2O yielding AgX as a byproduct or by passage across anion exchange resins to yield the hydroxide form of the 1-oxa-4-azonium cyclohexane compound or used as the halogen salt directly.

5 The ion-exchange process may involve contacting the 1-oxa-4-azonium cyclohexane halide salt with an ion-exchange resin having hydroxide ions. A particular ion-exchange resin capable of converting halide ions to hydroxide ions is Dowex Monosphere 550A UPW, available from Dow Chemical. The ion exchange may take place at temperatures from 20°C to 85°C or from 20°C to 50°C or from 25°C to 40°C for times from 15 minutes to 8
10 hours or from 30 minutes to 6 hours or from 30 minutes to 3 hours. The ion exchange may be performed in continuous or batch mode or any combination thereof. Batch mode is preferred when using Ag_2O and continuous mode is preferred when using ion exchange resin. Individual 1-oxa-4-azonium cyclohexane halide salts may require different operating conditions for the ion exchange from halide to hydroxide. Depending on the interaction of
15 anion with the 1-oxa-4-azonium cyclohexane cation, ion-exchange may be difficult or impossible.

Comparing the ^{13}C chemical shifts for the bromide and hydroxide salts in Example 2 and Example 3 shows that the interaction of the 1-oxa-4-azonium cyclohexane salt with the anion varies with the identity of the anion. In particular, without wishing to be
20 bound to theory, the chemical potential of the C atom next to the cationic N center is particularly affected. The electron density of the salt can be greatly affected by the identity of the anion. This difference can greatly affect the ability of the 1-oxa-4-azonium cyclohexane anion salt to direct the synthesis of particular zeolites or molecular sieves. In molecular sieve synthesis, hydroxide is typically used as a mineralizing agent, so hydroxide SDA salts are
25 often preferred to halide SDA salts. Utilizing the 1-oxa-4-azonium cyclohexane anion salt as a hydroxide salt also allows the separation of hydroxide to T-atom ratio, an important molecular sieve synthesis parameter, from metal to T-atom ratio as metal ions such as sodium are no longer introduced on a 1:1 mole basis with hydroxide. T-atom is used to represent the elements in tetrahedral framework positions, typically silicon or aluminum.

30 The methods of the present invention maybe carried out in preparation of zeolites. In one aspect, the invention provides a method for synthesizing a zeolite. The method may include the steps of: (a) preparing an aqueous mixture comprising water, a

substituted hydrocarbon, and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound; (d)) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution; and (e) heating the reaction mixture to form the zeolite.

5 In some versions of the method, step (d) comprises forming a first mixture of the reactive sources of M, Al, Si and the optional seeds of a material L, and adding the solution to the first mixture without cooling the first mixture, wherein M is a metal.

The step of forming a zeolite reaction mixture comprises forming a reaction mixture of a composition expressed in terms of mole ratios of the oxides of:

10 $m\text{MO}_{k/2} : t\text{T} : a\text{Al}_2\text{O}_3 : e\text{E}_2\text{O}_3 : \text{SiO}_2 : g\text{H}_2\text{O}$

where “m” has a value of 0 to 2, “k” has a value of 1 to 3, “t” has a value from 0.01 to 1, “a” has a value of 0 to 1, “e” has a value of 0 to 1, and “g” has a value of 5 to 4000. Additionally, the reaction mixture may comprise from 1 to 10 wt.-% of seed zeolite L based on the amount of SiO_2 in the reaction mixture, e.g., if there is 100 g of SiO_2 in the reaction mixture, from 1 to 10 g of seed zeolite L would be added to the reaction mixture. M represents at least one exchangeable cation of a metal or metals from Group 1 (IUPAC 1), Group 2 (IUPAC 2), Group 3 (IUPAC 3), or the lanthanide series of the periodic table and or zinc. Specific examples of M include but are not limited to lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, zinc, yttrium, lanthanum, gadolinium, and mixtures thereof. T represents the organo-1-oxa-4-azoniumcyclohexane compound, and E is an element selected from the group consisting of gallium, iron, boron and combinations thereof.

Sources of aluminum include, but are not limited to, aluminum alkoxides, precipitated aluminas, aluminum metal, aluminum hydroxide, sodium aluminate, aluminum salts and alumina sols. Specific examples of aluminum alkoxides include, but are not limited to, aluminum sec-butoxide and aluminum ortho isopropoxide. Sources of silica include but are not limited to tetraethylorthosilicate, colloidal silica, precipitated silica and alkali silicates. Sources of M include but are not limited to hydroxides, halides, nitrates, and sulfates.

30 The examples demonstrate a specific order of addition leading to the reaction mixtures from which the OSDAs described herein are formed. However, as there are a number of starting materials, many orders of addition are possible.

The zeolites prepared from the OSDAs of the process of this invention can be used as a catalyst or catalyst support in various hydrocarbon conversion processes. Hydrocarbon conversion processes are well known in the art and include cracking, hydrocracking, alkylation of aromatics or isoparaffins, isomerization of paraffin, olefins, or poly-alkylbenzene such as xylene, trans-alkylation of poly-alkylbenzene with benzene or mono-alkylbenzene, disproportionation of mono-alkylbenzene, polymerization, reforming, hydrogenation, dehydrogenation, transalkylation, dealkylation, hydration, dehydration, hydrotreating, hydrodenitrogenation, hydrodesulfurization, methanation and syngas shift process.

EXAMPLES

In order to more fully illustrate the invention, the following examples are set forth. It is to be understood that the examples are only by way of illustration and are not intended as a limitation on the broad scope of the invention as set forth in the appended claims.

EXAMPLE 1

422.44 g water was weighed into a 2 L Teflon bottle, and the bottle was placed in a 4 L beaker. Under constant stirring, 218.1 g 1,4 dibromobutane, 99% was added to the water. To this mixture, 204.34 g 4-Methylmorpholine, 99% was added. 1.5 L tap water was placed in the 4 L beaker surrounding the Teflon bottle to help control the heat of reaction. Low heat, 50°C, was used to warm up the mixture. Stirring was continued until a yellow solution was formed and no clear additional phase was present. ¹³C NMR of the solution showed a ratio of 1 mole methylmorpholine to 2.83 moles 1,4-bis(4-methylmorpholinium)butane dibromide.

EXAMPLE 2

413 g water was weighed into a 2L Teflon bottle. 474.1 g. 1,5 Dibromopentane, 97% (2 moles) was added. To this mixture, 176 g. Morpholine, 99% (4 moles) was added while stirring. The water and morpholine combined to form a cloudy phase while the denser dibromopentane remained on the bottom. The Teflon bottle was moved into a 4 liter beaker as secondary containment and placed under a high speed overhead stirrer for stirring at room temperature. 1-1.5 liters of cool water were added to the 4 liter beaker to disperse a strong exotherm should one occur. At 15 minutes, the mixture began to

turn yellow, indicating the reaction was beginning. The exotherm was mild. After an hour, the result was a clear light orange "solution". The remaining 413 g water was mixed in to make the final solution. ¹³C nuclear magnetic resonance (NMR) was used to confirm that the product comprises a 3-oxa-6-azoniaspiro[5.5]undecane bromide solution. Peaks for the spirocyclic compound were observed at 63.6, 59.9, 58.0, 21.0, and 18.9ppm with respect to tetramethylsilane. Resonances for morpholinium were present at 59.9 and 43.4ppm. The ratio of spirocyclic compound to morpholinium was 1:1. Variable temperature NMR, with C-N splitting is required to identify both compounds and acquire the proper integration ratios. The starting material 1,5-dibromopentane has peaks at 29.3, 34.4, and 36.2ppm with integral ratios of 1:2:2 respectively which is not observed in the final solution.

EXAMPLE 3

1150 grams of the solution from Example 2 was contacted with 336.4 grams of Ag₂O in a round-bottom flask, which combined to form a grey opaque solution. The flask was placed under a high speed overhead stirrer for stirring at room temperature (open system) for 1 day. The sample was filtered to remove the precipitated silver bromide and the final solution was sent for water analysis which showed that the sample was composed of 64.6% water. ¹³C nuclear magnetic resonance (NMR) was used to confirm that the product comprises a 3-oxa-6-azoniaspiro[5.5]undecane hydroxide solution. Peaks for the spirocyclic compound were observed at 67.1, 60.0, 57.9, 20.9, and 18.7ppm with respect to tetramethylsilane. Resonances for morpholinium were present at 59.8 and 44.7ppm. The ratio of spirocyclic compound to morpholinium was 1:1. Comparing the ¹³C chemical shifts for the bromide and hydroxide salts in Example 2 and Example 3 shows that the interaction of the 1-oxa-4-azonium cyclohexane salt with the anion varies with the identity of the anion. In particular, without wishing to be bound to theory, the chemical potential of the C atom next to the cationic N center is particularly affected. The electron density of the salt can be greatly affected by the identity of the anion.

EXAMPLE 4

88.65 g water was weighed into a 1L Teflon bottle. 141.33 g 1,4-Dibromobutane, 99% was added. To this mixture, 154 g 4-Ethylmorpholine, 97% was added. The water and ethylmorpholine combined to form a cloudy phase while the denser dibromobutane remained on the bottom. The Teflon bottle was moved into a 2 liter beaker as

secondary containment and placed under a high speed overhead stirrer for stirring at room temperature. The Teflon bottle was sealed and placed at 100°C overnight with no stirring. After the solution was cooled back down to room temperature, 88 g of deionized water was added to the solution. The solution was again placed at 100°C overnight with no stirring and
5 the result was a brown translucent solution which, by ¹³C NMR contained peaks for 1,4-bis(4-ethylmorpholinium) butane dication. The sample was sent for water analysis which showed that it was composed of 36.6 % water.

EXAMPLE 5

355.88 g water was weighed into a 2L glass beaker. 355.57 g 1,5-
10 Dibromopentane, 97% (1.5 moles) was added. To this mixture, 356.19 g 4-Ethylmorpholine, 97% (3 moles) was added. The water and ethylmorpholine combined to form a cloudy phase while the denser dibromopentane remained on the bottom. The glass beaker was moved onto a hot plate with low heat and placed under a high speed overhead stirrer for stirring at room temperature. The solution was then transferred into a 2L Teflon bottle, which was sealed and
15 placed at 100°C overnight with no stirring. After cooling, the solution as placed into a 2L Parr autoclave and heated to 100°C for 4 hours. 355.88 g of deionized water was then added to obtain a 50% solution.

EXAMPLE 6

196.5 g, water was weighed into a 2L Teflon bottle. 254.14 g 1,6-
20 Dibromohexane, 96% was added. To this mixture, 204.34 g 4-Methylmorpholine, 99% was added. The water and morpholine combined to form a cloudy phase while the denser dibromohexane remained on the bottom. The solution was put in a 4 liter beaker as secondary containment and placed under a high speed overhead stirrer for stirring at room temperature. The solution was then transferred into a 2L Parr autoclave, which was sealed
25 and placed at 125°C overnight with no stirring. 261.9 g deionized water was then added to obtain a 50% solution and the sample was placed back into the 2L Parr autoclave at 125°C overnight. The result was a brown clear solution. ¹³C NMR showed peaks at 65.5, 60.6, 59.7, 47.0, 25.3, and 21.1ppm in a 1:2:2:1:1:1 ratio for 1,6-bis (4-Methylmorpholinium)hexane dibromide and peaks at 64.9, 53.9, and 44.5ppm in a 2:2:1 ratio for starting material 4-
30 methylmorpholine. The ratio of diquaternary compound to amine was 1:0.9.

EXAMPLE 7

439 grams of the solution from Example 4 was contacted with 147.5 grams of Ag_2O in a round-bottom flask, which combined to form a grey opaque solution. The flask was placed under a high speed overhead stirrer for stirring at room temperature for 1 day.

5 The sample was filtered to remove the precipitated silver bromide and the final solution was sent for water analysis which showed that the sample was composed of 67.0% water.

EXAMPLE 8

1257 grams of the solution from Example 5 was contacted with 324.26 grams of Ag_2O in a round-bottom flask, which combined to form a grey opaque solution. The flask

10 was placed under a high speed overhead stirrer for stirring at room temperature for 1 day. The sample was filtered to remove the precipitated silver bromide and the final solution was sent for water analysis which showed that the sample was composed of 65.9% water.

EXAMPLE 9

1116 grams of the solution from Example 6 was contacted with 295.64 grams

15 of Ag_2O in a round-bottom flask, which combined to form a grey opaque solution. The flask was placed under a high speed overhead stirrer for stirring at room temperature for 1 day. The sample was filtered to remove the precipitated silver bromide and the final solution was sent for water analysis which showed that the sample was composed of 60.9% water.

EXAMPLE 10

20 25.73 g water was weighed into a 125 mL Teflon bottle. 12.57 g 1,4-Dibromobutane, 99% was added. To this mixture, 13.15 g 2,6-Dimethylmorpholine, 97.1% was added while stirring. The water and 2-6-dimethylmorpholine combined to form a cloudy phase while the denser dibromobutane remained on the bottom. The Teflon bottle was moved into a 400 mL beaker as secondary containment and placed on a hot plate for stirring

25 under low heat while sealed, 90°C. After two days, the result was a clear light yellow solution. The sample was sent for ^{13}C NMR. The 1-oxa-4-azonium cyclohexane derivative 2,6-dimethylmorpholine is comprised of two compounds, A having peaks at 75.5, 55.1, and 21.9ppm with 1:1:1 ratios and B having peaks at 69.1, 54.2, and 20.5ppm with 1:1:1 ratios. The ratio of the two compounds is 2.75A to 1B. The yellow solution has peaks at 16.4, 17.2,

30 17.3, 17.7, 20.6, 21.0, 21.7, 46.5, 47.2, 59.4, 61.7, 63.0, 63.9, 64.0, 65.7, 68.1, 68.3 and

69.8ppm with integral ratios of 1.25, 1.75, 3.7, 4, 1.2, 4.1, 2, 1.8, 4.35, 1.3, 1.5, 1.8, 4, 1.95, and 4 respectively. Without wishing to be bound by theory, it is believed that compounds A and B in the morpholine derivative are the cis and trans forms of the 2,6-dimethylmorpholine and peaks in the product are due to multiple conformers of cis and trans substituted
5 dimethylmorpholine based salts.

EXAMPLE 11

591.15 g water was weighed into a 2L Teflon bottle. 436.21 g 1,4-Dibromobutane, 99% (2 moles) was added. To this mixture, 352.0 g Morpholine, 99% (4 moles) was added while stirring. The water and morpholine combined to form a cloudy
10 phase while the denser dibromobutane remained on the bottom. The Teflon bottle was moved into a 4 liter beaker as secondary containment and placed under a high speed overhead stirrer for stirring at room temperature. 0.5-1 liters of cool water were added to the 4 liter beaker to disperse a strong exotherm should one occur. After 1.5-2.5 hours, the result was a clear light yellow solution. An additional 197.05 g water was mixed in to form the final
15 solution. ¹³C nuclear magnetic resonance (NMR) was used to confirm that the product was a 8-oxa-5-azoniaspiro[4.5]decane bromide solution. Peaks for the spirocyclic compound were observed at 63.3, 62.3, 59.2, and 21.4ppm with respect to tetramethylsilane with integral ratios of 2:2:2:2 respectively. Resonances for morpholinium were present at 63.9 and 43.5ppm with integral ratios of 2:2. The ratio of spirocyclic compound to morpholinium was
20 1:1. The presence of both compounds was confirmed by ion chromatography / mass spectrometry. The starting material 1,4-dibromobutane has peaks in the ¹³C NMR at 33.5 and 35.5ppm. Peaks due to the dibromobutane were not observed in the final solution.

EXAMPLE 12

1200 grams of the solution from Example 6 was contacted with 365.5 grams
25 of Ag₂O in a round-bottom flask, which combined to form a grey opaque solution. The flask was placed under a high speed overheard stirrer for stirring at room temperature for 1 day. The sample was filtered to remove the precipitated silver bromide and the final solution was sent for water analysis which showed that the sample was composed of 67.3% water.

EXAMPLE 13

48.45 g 1,4-bis (4-ethylmorpholinium) butane dihydroxide (33.0%) was combined with 0.16 g of $\text{Al}(\text{OH})_3$, (27.9 wt. - %Al). 25.00 g of Ludox AS-40 was added to the solution along with 65.44 g of de-ionized water. The alumino-silicate solution was then stirred vigorously for 1-2 hours. The final gel mixture was separated equally into 45-mL autoclaves and was digested at 175°C for 4 days under static conditions. The crystalline product was isolated via filtration and was shown by x-ray diffraction to be of the NON structure type. CHN analysis showed 2.51% C and 0.357% N.

EXAMPLE 14

48.94 g 1,5-bis (4-ethylmorpholinium) pentane dihydroxide (34.1%) was combined with 36.62 g tetramethylammonium hydroxide (25%). 1.62 g of $\text{Al}(\text{OH})_3$, (27.9 wt. - %Al) was then added to mixture of the two structure-determining agents. 50.00 g of Ludox AS-40 was added to the solution along with 136.46 g of de-ionized water. The alumino-silicate solution was then stirred vigorously for 1-2 hours. The final gel mixture was separated equally into 45-mL autoclaves and was digested at 150°C for 12 days under static conditions. The crystalline product was isolated via filtration and was shown by x-ray diffraction to be of the RUT structure type. CHN analysis showed 7.03% C and 2.16% N.

EXAMPLE 15

41.15 g. 1,6-bis (4-Methylmorpholinium)hexane dihydroxide (39.1%) was combined with 0.32 g. of $\text{Al}(\text{OH})_3$, (27.9 wt. - %Al). 25.00 g of Ludox AS-40 was added to the solution along with 49.52 g. of de-ionized water. The alumino-silicate solution was then stirred vigorously for an hour. 1.34 g. of NaOH, 10% was added dropwise. The final gel mixture was stirred vigorously for an hour. It was then separated equally into 45-mL autoclaves and was digested at 160°C for 6 days under static conditions. The crystalline product was isolated by centrifugation and was shown by x-ray diffraction to be of the MTW structure type. This pattern is shown in Figure 8.

Although the invention has been described in considerable detail with reference to certain embodiments, one skilled in the art will appreciate that the present invention can be practiced by other than the described embodiments, which have been presented for purposes of illustration and not of limitation. Therefore, the scope of the

appended claims should not be limited to the description of the embodiments contained herein.

SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

A first embodiment of the invention is a method for synthesizing a zeolite comprising (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon, and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound; (d) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution; and (e) heating the reaction mixture to form the zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the step of reacting the aqueous mixture occurs at a temperature between 20°C and 100°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the organo-1-oxa-4-azoniumcyclohexane compound is a structure directing agent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the substituted hydrocarbon is a halogen substituted alkane selected from the group consisting of bromoethane, iodoethane, chloropropane, bromopropane, iodopropane, chlorobutane, 1-bromobutane, 2-bromobutane, iodobutane, 1-bromo-2-methylpropane, 2-bromo-2-methylpropane, chloropentane, bromopentane, iodopentane, 2-bromopentane, chlorohexane, bromohexane, iodoheptane, benzyl halide, 1-chloro-2-phenylethane, 1-bromo-2-phenylethane, 1-iodo-2-phenylethane, 1-halomethane naphthalene, 2-halomethane naphthalene, and halo-substituted non-olefinic alkyl groups having the formula C_pH_{2p-1} where p is in the range from 4 to 10, and combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the substituted hydrocarbon is a dihalogen substituted alkane having between 2 and 8 carbon atoms selected from the group consisting of 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-

dibromohexane, 1,3-diiodopropane, 1,4-diiodobutane, 1,5-diiodopentane, 1,6-diiodohexane, 1,2-dibromopropane, 1,3-dibromobutane, 1,3-dibromopentane, 1,4-dibromopentane, 2,4-dibromopentane, 1,5-dibromohexane, 1,4-dibromohexane, 1,3-dibromohexane, 2,4-dibromohexane, 2,5-dibromohexane, 2,5-dibromo-3-methylhexane, 2,5-dibromo-3,3-

5 dimethylhexane, 1,4-dibromo-2-ethylbutane, and 1,2-dibromo-2-phenylethane, and combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the substituted hydrocarbon a tri-substituted alkane having from 3 to 8 carbon atoms selected from the group consisting of 1,2,3-tribromopropane, 1,2,4-tribromobutane, 1,2,3-

10 tribromobutane, 1,3,5-tribromopentane, 1,2,4-tribromopentane, 1,2,3-tribromopentane, 1,3,6-tribromohexane, 1,2,4-tribromohexane, 1,2,5-tribromohexane, 1,2,6-tribromohexane, 1,3,4-tribromohexane, and 1,3,5-tribromohexane, and combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the substituted hydrocarbon is an α,ω -dihalogen

15 substituted alkane. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the 1-oxa-4-azacyclohexane derivative has a structure of Formula 5 2-R1-2-R2-3-R3-3-R4-4-R9-5-R5-5-R6-6-R7-6-R8-1-oxa-4-azacyclohexane, wherein R1-R9 are independently selected from H or an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4 and the

20 total number of C atoms in the molecule is in the range of 4 to 10. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the 1-oxa-4-azacyclohexane derivative is selected from 4-butylmorpholine, 4-propylmorpholine, 4-ethylmorpholine, 4-methylmorpholine, morpholine, 2-methylmorpholine, 2,4-dimethylmorpholine, 4-ethyl-2-methylmorpholine, 4-

25 propyl-2-methylmorpholine, 3-methylmorpholine, 3,4-dimethylmorpholine, 4-ethyl-3-methylmorpholine, 4-propyl-3-methylmorpholine, 5-methylmorpholine, 2,5-dimethylmorpholine, 4-ethyl-5-methylmorpholine, 4-propyl-5-methylmorpholine, 5-ethyl-2-methylmorpholine, 6-methylmorpholine, 4,6-dimethylmorpholine, 4-ethyl-6-

30 methylmorpholine, 4-propyl-6-methylmorpholine, 2,6-dimethylmorpholine, 2,4,6-trimethylmorpholine, 4-ethyl-2,6-dimethylmorpholine, 2,3-dimethylmorpholine, 2,3,4-trimethylmorpholine, 4-ethyl-2,3-dimethylmorpholine, 2,5-dimethylmorpholine, 2,4,5-trimethylmorpholine, 4-ethyl-2,5-dimethylmorpholine, 2,2-dimethylmorpholine, 2,2,4-

trimethylmorpholine, 4-ethyl-2,2-dimethylmorpholine, 3,3-dimethylmorpholine, 3,3,4-trimethylmorpholine, 4-ethyl-3,3-dimethylmorpholine, 5,5-dimethylmorpholine, 4,5,5-trimethylmorpholine, 4-ethyl-5,5-dimethylmorpholine, 6,6-dimethylmorpholine, 4,6,6-trimethylmorpholine, 4-ethyl-6,6-dimethylmorpholine, 5-ethyl-2-methylmorpholine and

5 combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the 1-oxa-4-azacyclohexane derivative is essentially incapable of undergoing pyramidal inversion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the organo-1-oxa-4-
 10 azoniumcyclohexane compound has a structure of Formula 1 2-R1-2-R2-3-R3-3-R4-4-R9-4-R10-5-R5-5-R6-6-R7-6-R8-1-oxa-4-azoniumcyclohexane⁺-X⁻, wherein R1-R8 are independently selected from H or an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4; R9 and R10 form a cyclic alkyl group having the formula C_mH_{2m} forming a heterocycle of ring size q, where m is in the range from 4 to 8, and q is in the range
 15 of 5 to m+1; X is a halide or hydroxide; and the total number of C atoms in the molecule is in a range of 8 to 17; or Formula 2 [bis-N,N'-diR9-(2,2'-diR1-2,2'-diR2-3,3'-diR3-3,3'-diR4-5,5'-diR5-5,5'-diR6-6,6'-diR7-6,6'-diR8-1,1'-oxa-4,4'-azonium cyclohexane)-R10]₂⁺ 2X⁻, wherein R1-R9 are independently selected from H or an alkyl group having the formula C_nH_{2n+1}, where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C
 20 atoms in the molecule is in the range of 11 to 24, and R10 is an alkyl group having the formula C_mH_{2m}, where m is in the range from 3 to 8 and is connected to the 4 and 4' N atoms at positions x and y of the alkyl chain where x and y are independently selected from 1 to m; or Formula 3 [tris-N,N',N''-triR9-(2,2',2''-triR1-2,2',2''-triR2-3,3',3''-triR3-3,3',3''-triR4-5,5',5''-triR5-5,5',5''-triR6-6,6',6''-triR7-6,6',6''-triR8-1,1',1''-oxa-4,4',4''-
 25 azoniumcyclohexane)-R10]₃⁺ 3X⁻, wherein R1-R9 are independently selected from H or an alkyl group having the formula C_nH_{2n+1}, where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C atoms in the molecule is the range of 15 to 36, and R10 is an alkyl group having the formula C_mH_{2m-1}, where m is in the range from 3 to 8 and is connected to the 4, 4' and 4'' N atoms at positions x, y and z of the alkyl chain where x, y
 30 and z are independently selected from 1 to m; or Formula 4 2-R1-2-R2-3-R3-3-R4-4-R9-4-R10-5-R5-5-R6-6-R7-6-R8-1-oxa-4-azoniumcyclohexane⁺-X⁻, wherein R1-R9 are independently selected from H or an alkyl group having the formula C_nH_{2n+1}, R10 is

selected from an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4, benzyl, 1-methylnaphthalene, 2-methylnaphthalene and a non-olefinic alkyl group having the formula C_pH_{2p-1} where p is in the range from 4 to 10, X is halide or hydroxide, and the total number of C atoms in the molecule is in the range of 4 to 16; or combinations thereof.

5 An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein step (d) comprises forming a first mixture of the reactive sources of M, Al, Si, and optional seeds of a layered material L, and adding the solution to the first mixture without cooling the first mixture wherein M is a metal. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up
10 through the first embodiment in this paragraph wherein step (d) comprises forming a reaction mixture having a composition expressed in terms of mole ratios of the oxides of $mMO_k/2$ tT aAl_2O_3 eE_2O_3 SiO_2 gH_2O where “m” has a value of 0 to 2, “k” has a value of 1 to 3, “t” has a value from 0.01 to 1, “a” has a value of 0 to 1, “e” has a value of 0 to 1.0, and “g” has a value of 5 to 4000. An embodiment of the invention is one, any or all of prior embodiments
15 in this paragraph up through the first embodiment in this paragraph wherein the reaction mixture comprises from 1 to 10 wt.-% of seed zeolite L based on the amount of SiO_2 in the reaction mixture.

A second embodiment of the invention is a zeolite prepared by a process comprising the steps of (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon,
20 and a 1-oxa-4-azacyclohexane derivative; (b) reacting the aqueous mixture; (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound; (d) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution; and (e) heating the reaction mixture to form the zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph
25 wherein the organo-1-oxa-4-azoniumcyclohexane compound is a structure directing agent and an organic solvent is not used in obtaining the structure directing agent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the 1-oxa-4-azacyclohexane derivative is essentially incapable of undergoing pyramidal inversion. An embodiment of the invention is
30 one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein step (d) comprises forming a first mixture of the reactive sources of M, Al, Si, and seeds of a layered material L, and adding the solution to the first mixture

without cooling the first mixture, wherein M is a metal. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein step (d) comprises forming a reaction mixture having a composition expressed in terms of mole ratios of the oxides of $m\text{MO}_k/2$ $t\text{T}$ $a\text{Al}_2\text{O}_3$ $e\text{E}_2\text{O}_3$ SiO_2 $g\text{H}_2\text{O}$ where “m” has a value of 0 to 2, “k” has a value of 1 to 3, “t” has a value from 0.01 to 1, “a” has a value of 0 to 1, “e” has a value of 0 to 1, and “g” has a value of 5 to 4000. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the reaction mixture comprises from 1 to 10 wt.-% of seed zeolite L based on the amount of SiO_2 in the reaction mixture.

Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS

What Is Claimed Is:

1. A method for synthesizing a zeolite comprising:
 - 5 (a) preparing an aqueous mixture comprising water, a substituted hydrocarbon, and a 1-oxa-4-azacyclohexane derivative;
 - (b) reacting the aqueous mixture;
 - (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound;
 - 10 (d) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution; and
 - (e) heating the reaction mixture to form the zeolite.
2. The method of claim 1, wherein the step of reacting the aqueous
15 mixture occurs at a temperature between 20°C and 100°C.
3. The method of any of claims 1-2 wherein the substituted hydrocarbon is a halogen substituted alkane selected from the group consisting of bromoethane, iodoethane, chloropropane, bromopropane, iodopropane, chlorobutane, 1-bromobutane, 2-
20 bromobutane, iodobutane, 1-bromo-2-methylpropane, 2-bromo-2-methylpropane, chloropentane, bromopentane, iodopentane, 2-bromopentane, chlorohexane, bromohexane, iodohexane, benzyl halide, 1-chloro-2-phenylethane, 1-bromo-2-phenylethane, 1-iodo-2-phenylethane, 1-halomethane naphthalene, 2-halomethane naphthalene, and halo-substituted non-olefinic alkyl groups having the formula C_pH_{2p-1} where p is in the range from 4 to 10,
25 and combinations thereof.
4. The method any of claims 1-2 wherein the substituted hydrocarbon is a dihalogen substituted alkane having between 2 and 8 carbon atoms selected from the group consisting of 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-
30 dichlorohexane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,3-diiodopropane, 1,4-diiodobutane, 1,5-diiodopentane, 1,6-diiodohexane, 1,2-dibromopropane, 1,3-dibromobutane, 1,3-dibromopentane, 1,4-dibromopentane, 2,4-

dibromopentane, 1,5-dibromohexane, 1,4-dibromohexane, 1,3-dibromohexane, 2,4-dibromohexane, 2,5-dibromohexane, 2,5-dibromo-3-methylhexane, 2,5-dibromo-3,3-dimethylhexane, 1,4-dibromo-2-ethylbutane, and 1,2-dibromo-2-phenylethane, and combinations thereof.

5

5. The method of any of claims 1-2 wherein the substituted hydrocarbon a tri-substituted alkane having from 3 to 8 carbon atoms selected from the group consisting of 1,2,3-tribromopropane, 1,2,4-tribromobutane, 1,2,3-tribromobutane, 1,3,5-tribromopentane, 1,2,4-tribromopentane, 1,2,3-tribromopentane, 1,3,6-tribromohexane, 1,2,4-tribromohexane, 1,2,5-tribromohexane, 1,2,6-tribromohexane, 1,3,4-tribromohexane, and 1,3,5-tribromohexane, and combinations thereof.

10

6. The method of any of claims 1-2, wherein the 1-oxa-4-azacyclohexane derivative has a structure of:

15

Formula 5:

2-R₁-2-R₂-3-R₃-3-R₄-4-R₉-5-R₅-5-R₆-6-R₇-6-R₈-1-oxa-4-azacyclohexane,

wherein R₁-R₉ are independently selected from H or an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4 and the total number of C atoms in the molecule is in the range of 4 to 10.

20

7. The method of any of claims 1-2 wherein the organo-1-oxa-4-azoniumcyclohexane compound has a structure of:

Formula 1:

2-R₁-2-R₂-3-R₃-3-R₄-4-R₉-4-R₁₀-5-R₅-5-R₆-6-R₇-6-R₈-1-oxa-4-azoniumcyclohexane⁺-X⁻,

25

wherein R₁-R₈ are independently selected from H or an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4; R₉ and R₁₀ form a cyclic alkyl group having the formula C_mH_{2m} forming a heterocycle of ring size q, where m is in the range from 4 to 8, and q is in the range of 5 to m+1; X is a halide or hydroxide; and the total number of C atoms in the molecule is in a range of 8 to 17;

30

or Formula 2:

[bis-N,N'-diR₉-(2,2'-diR₁-2,2'-diR₂-3,3'-diR₃-3,3'-diR₄-5,5'-diR₅-5,5'-diR₆-6,6'-diR₇-6,6'-diR₈-1,1'-oxa-4,4'-azonium cyclohexane)-R₁₀]²⁺ 2X⁻,

wherein R_1 - R_9 are independently selected from H or an alkyl group having the formula C_nH_{2n+1} , where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C atoms in the molecule is in the range of 11 to 24, and R_{10} is an alkyl group having the formula C_mH_{2m} , where m is in the range from 3 to 8 and is connected to the 4 and 4' N atoms at positions x and y of the alkyl chain where x and y are independently selected from 1 to m;

or Formula 3:

[tris-N,N',N''-tri R_9 -(2,2',2''-tri R_1 -2,2',2''-tri R_2 -3,3',3''-tri R_3 -3,3',3''-tri R_4 -5,5',5''-tri R_5 -5,5',5''-tri R_6 -6,6',6''-tri R_7 -6,6',6''-tri R_8 -1,1',1''-oxa-4,4',4''-azoniumcyclohexane) $-R_{10}]^{3+} 3X^-$,

wherein R_1 - R_9 are independently selected from H or an alkyl group having the formula C_nH_{2n+1} , where n is in the range from 1 to 4, X is halide or hydroxide, the total number of C atoms in the molecule is the range of 15 to 36, and R_{10} is an alkyl group having the formula C_mH_{2m-1} , where m is in the range from 3 to 8 and is connected to the 4, 4' and 4'' N atoms at positions x, y and z of the alkyl chain where x, y and z are independently selected from 1 to m;

or Formula 4:

2- R_1 -2- R_2 -3- R_3 -3- R_4 -4- R_9 -4- R_{10} -5- R_5 -5- R_6 -6- R_7 -6- R_8 -1-oxa-4-azoniumcyclohexane $^+-X^-$,

wherein R_1 - R_9 are independently selected from H or an alkyl group having the formula C_nH_{2n+1} , R_{10} is selected from an alkyl group having the formula C_nH_{2n+1} where n is in the range from 1 to 4, benzyl, 1-methylnaphthalene, 2-methylnaphthalene and a non-olefinic alkyl group having the formula C_pH_{2p-1} where p is in the range from 4 to 10, X is halide or hydroxide, and the total number of C atoms in the molecule is in the range of 4 to 16;

or combinations thereof.

8. The method of any of claims 1-2, wherein step (d) comprises forming a first mixture of the reactive sources of M, Al, Si, and optional seeds of a layered material L, and adding the solution to the first mixture without cooling the first mixture wherein M is a metal.

9. The method of any of claims 1-2 wherein step (d) comprises forming a reaction mixture having a composition expressed in terms of mole ratios of the oxides of:

$m\text{MO}_{k/2} : t\text{T} : a\text{Al}_2\text{O}_3 : e\text{E}_2\text{O}_3 : \text{SiO}_2 : g\text{H}_2\text{O}$

where “m” has a value of 0 to 2, “k” has a value of 1 to 3, “t” has a value from 0.01 to 1, “a” has a value of 0 to 1, “e” has a value of 0 to 1.0, and “g” has a value of 5 to 4000.

5

10. A zeolite prepared by a process comprising the steps of:

(a) preparing an aqueous mixture comprising water, a substituted hydrocarbon, and a 1-oxa-4-azacyclohexane derivative;

(b) reacting the aqueous mixture;

10 (c) obtaining a solution comprising an organo-1-oxa-4-azoniumcyclohexane compound;

(d) forming a reaction mixture comprising reactive sources of Al, and Si, and the solution; and

(e) heating the reaction mixture to form the zeolite.

15

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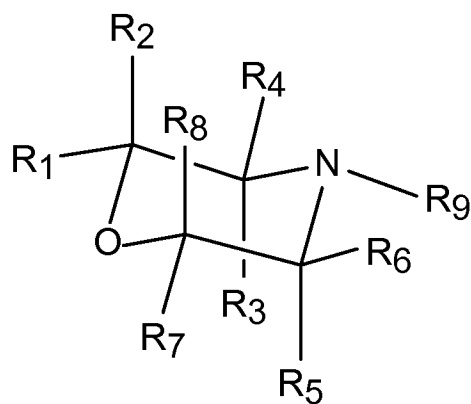


FIG. 1

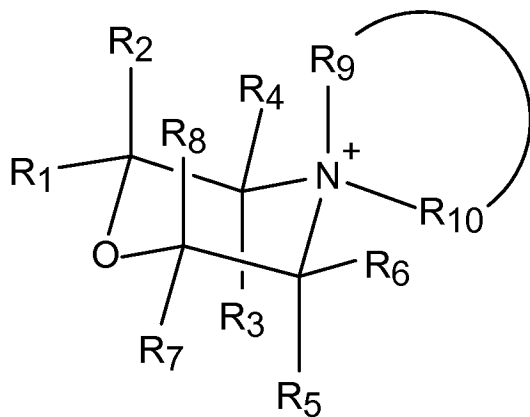


FIG. 2

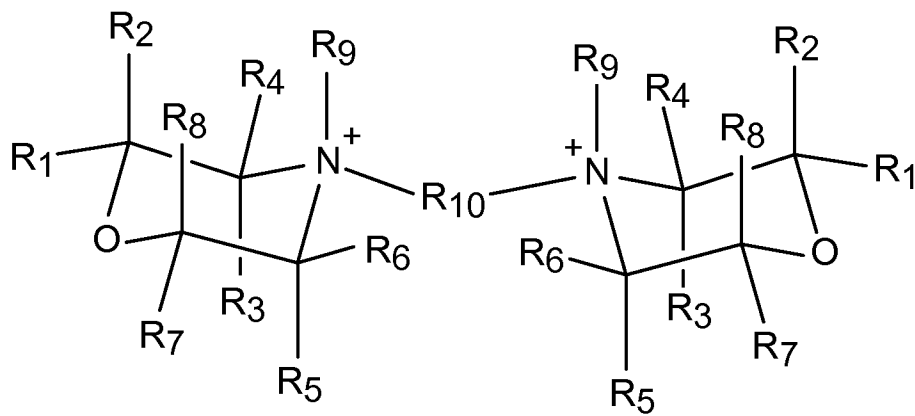


FIG. 3

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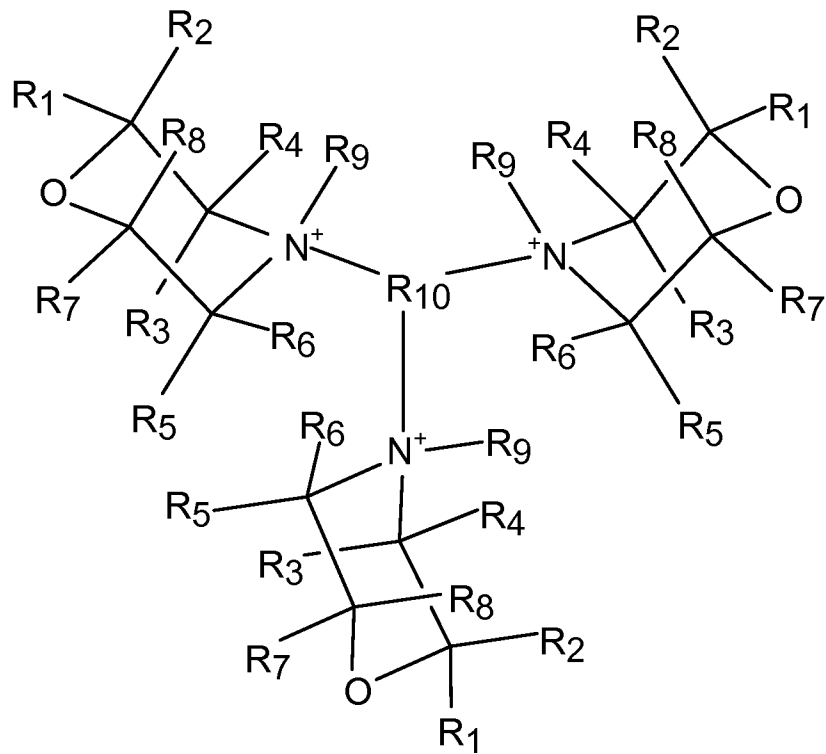


FIG. 4

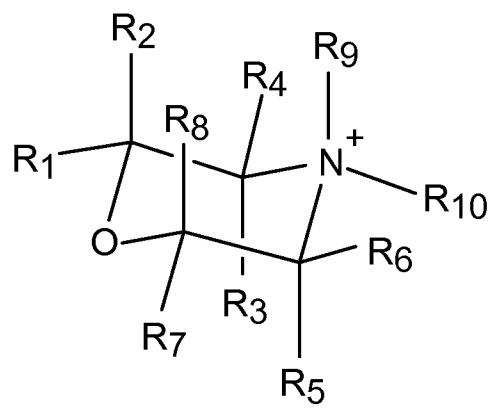


FIG. 5

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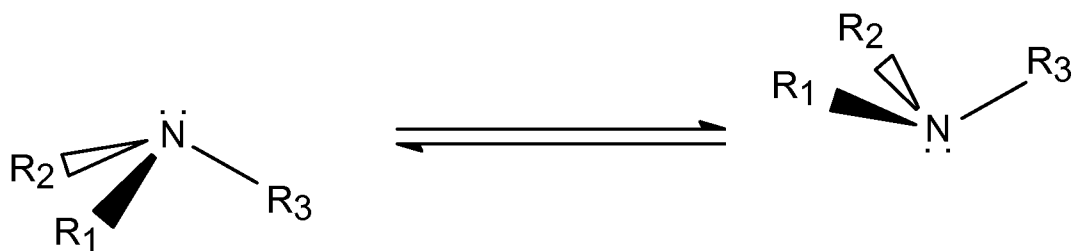


FIG. 6A

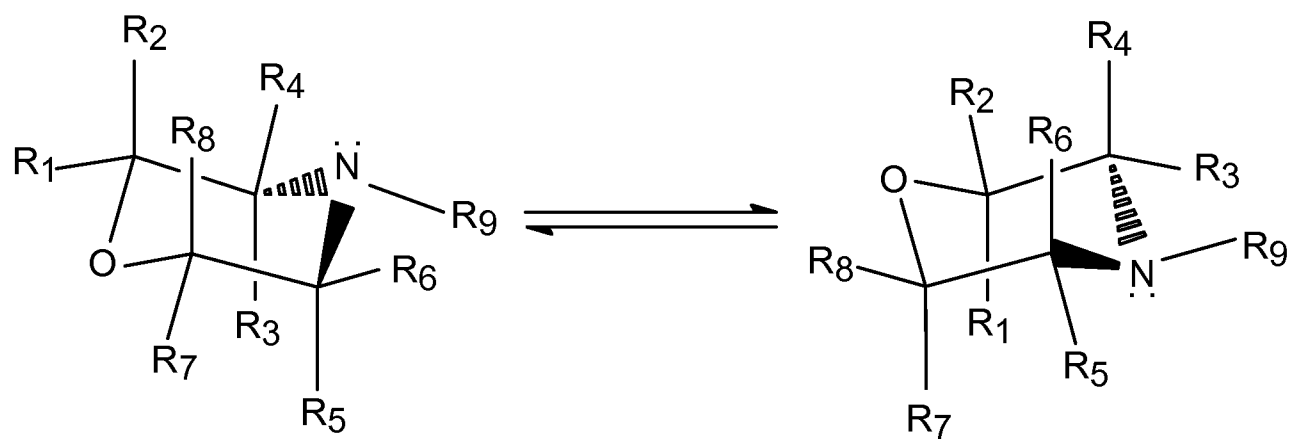


FIG. 6B

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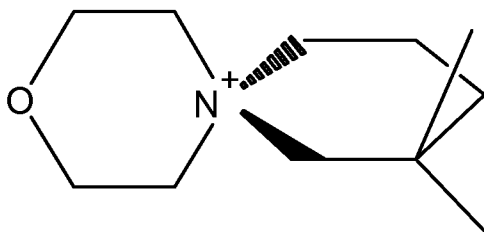


FIG. 7A

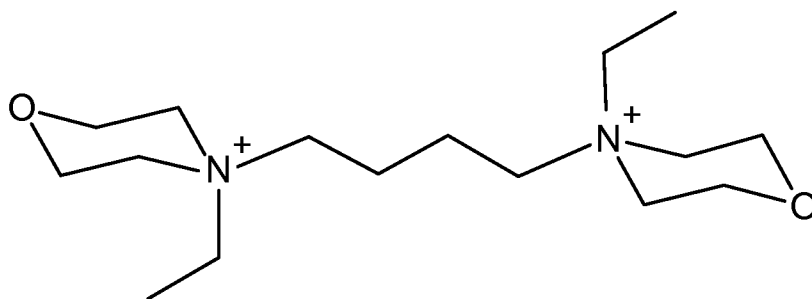


FIG. 7B

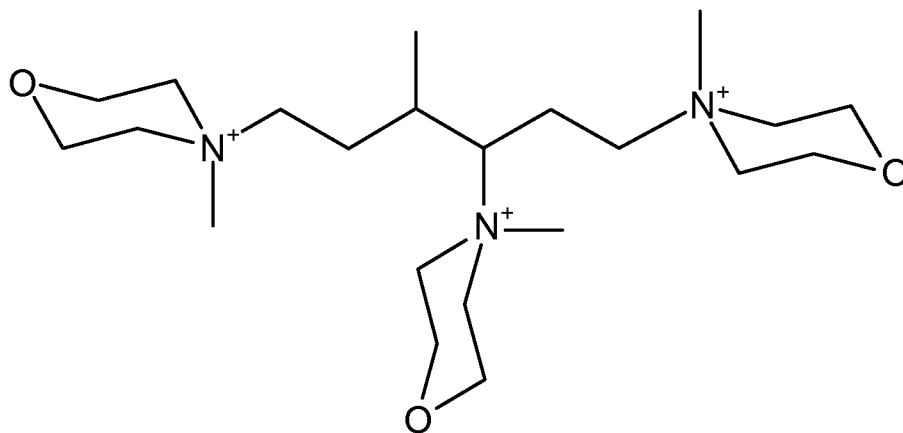


FIG. 7C

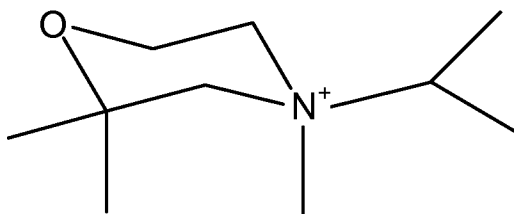


FIG. 7D

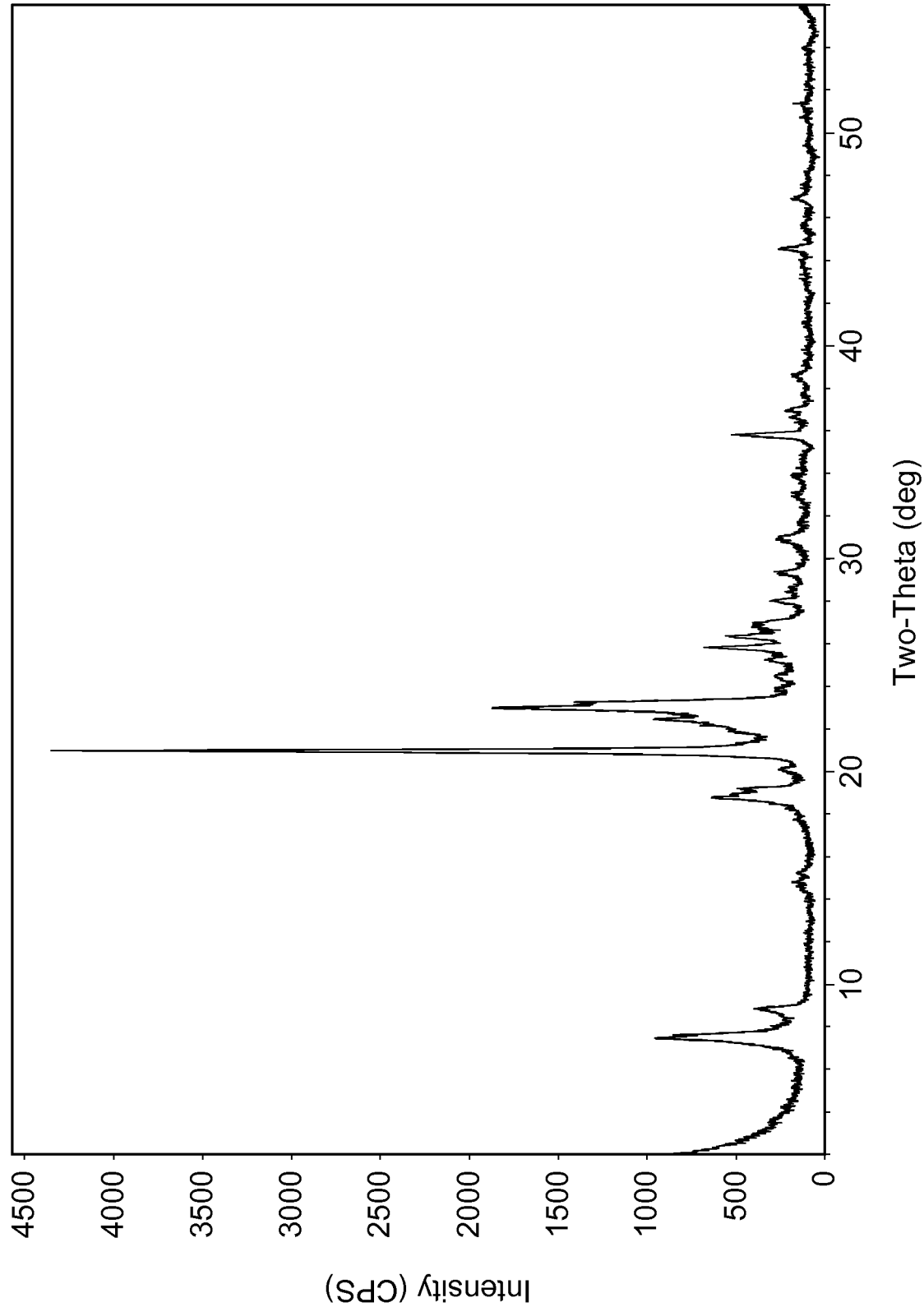


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2015/062919

A. CLASSIFICATION OF SUBJECT MATTER																						
<i>C01B 39/04 (2006.01)</i> <i>C07D 265/28 (2006.01)</i> <i>C07D 295/037 (2006.01)</i> <i>C07D 211/06 (2006.01)</i> <i>C07D 207/04 (2006.01)</i>																						
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 39/00-39/54, C07D 265/28, 295/037, 211/06, 207/04																						
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)																						
PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
A	US 5173281 A (MOBIL OIL CORP.) 22.12.1992	1-10																				
A	WO 1994/025539 A1 (MOBIL OIL CORPORATION) 10.11.1994	1-10																				
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.																						
* Special categories of cited documents: <table border="0"> <tr> <td>“A”</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>“T”</td> <td>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</td> </tr> <tr> <td>“E”</td> <td>earlier document but published on or after the international filing date</td> <td>“X”</td> <td>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</td> </tr> <tr> <td>“L”</td> <td>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)</td> <td>“Y”</td> <td>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</td> </tr> <tr> <td>“O”</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>“&”</td> <td>document member of the same patent family</td> </tr> <tr> <td>“P”</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			“A”	document defining the general state of the art which is not considered to be of particular relevance	“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	“E”	earlier document but published on or after the international filing date	“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	“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)	“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	“O”	document referring to an oral disclosure, use, exhibition or other means	“&”	document member of the same patent family	“P”	document published prior to the international filing date but later than the priority date claimed		
“A”	document defining the general state of the art which is not considered to be of particular relevance	“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																			
“E”	earlier document but published on or after the international filing date	“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																			
“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)	“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																			
“O”	document referring to an oral disclosure, use, exhibition or other means	“&”	document member of the same patent family																			
“P”	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search		Date of mailing of the international search report																				
29 January 2016 (29.01.2016)		10 March 2016 (10.03.2016)																				
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer T. Chilikina Telephone No. 499-240-25-91																				