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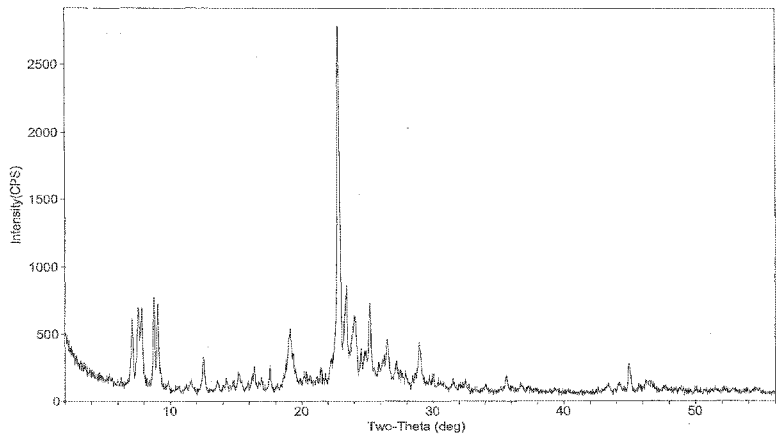


FIG. 1

(57) Abstract: A new family of coherently grown composites of TUN and IMF zeotypes has been synthesized and shown to be effective catalysts for dehydrocyclodimerization reactions. These zeolites are represented by the empirical formula. $Na_nM_m^{n+}R_rQ_qAl_{1-x}E_xSi_yO_z$ where M represents zinc or a metal or metals from Group 1, Group 2, Group 3 or the lanthanide series of the periodic table, R is an A,Ω-dihalosubstituted paraffin such as 1,4-dibromobutane, Q is a neutral amine containing 5 or fewer carbon atoms such as 1-methylpyrrolidine and E is a framework element such as gallium. The process involves contacting at least one aliphatic hydrocarbon having from 2 to 6 carbon atoms per molecule with the coherently grown composites of TUN and IMF zeotypes to produce at least one aromatic hydrocarbon.

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DEHYDROCYCLODIMERIZATION USING UZM-39 ALUMINOSILICATE ZEOLITE

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 61/736,296 which was filed December 12, 2012, the contents of which are hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to using a new family of aluminosilicate zeolites designated UZM-39 as the catalytic composite for dehydrocyclodimerization reactions. The zeolite family is represented by the empirical formula of:

$$Na_nM_m^{k+}T_tAl_{1-x}E_xSi_yO_z$$

where M represents a metal or metals from zinc or Group 1 (IUPAC 1), Group 2 (IUPAC 2), Group 3 (IUPAC 3) or the lanthanide series of the periodic table, T is the organic directing agent derived from reactants R and Q where R is an A,Ω-dihalosubstituted alkane such as 1,4-dibromobutane and Q is at least one neutral amine having 6 or fewer carbon atoms such as 1-methylpyrrolidine. E is a framework element such as gallium.

BACKGROUND OF THE INVENTION

[0003] Zeolites are crystalline aluminosilicate compositions which are microporous and which are formed from corner sharing AlO_2 and SiO_2 tetrahedra. Numerous zeolites, both naturally occurring and synthetically prepared, are used in various industrial processes. Synthetic zeolites are prepared via hydrothermal synthesis employing suitable sources of Si, Al and structure directing agents such as alkali metals, alkaline earth metals, amines, or organoammonium cations. The structure directing agents reside in the pores of the zeolite and are largely responsible for the particular structure that is ultimately formed. These species balance the framework charge associated with aluminum and can also serve as space fillers. Zeolites 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 zeolite crystal structure. Zeolites 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.

[0004] One particular zeolite, designated TNU-9, was first disclosed by Hong et al. in 2004, (*J. Am. Chem. Soc.* 2004, *126*, 5817-26) and then in a Korean Patent granted in 2005, KR 480229. This report and patent was followed by a full report of the synthesis in 2007 (*J. Am. Chem. Soc.* 2007, *129*, 10870-85). These papers describe the synthesis of TNU-9 from the flexible dicationic structure directing agent, 1,4-bis(N-methylpyrrolidinium)butane dibromide in the presence of sodium. After the structure of TNU-9 was solved (*Nature*, 2006, *444*, 79-81), the International Zeolite Association Structure Commission gave the code of TUN to this zeolite structure type, see Atlas of Zeolite Framework Types, which is maintained by the International Zeolite Association Structure Commission at http://www.iza-structure.org/databases/. The TUN structure type was found to contain 3 mutually orthogonal sets of channels in which each channel is defined by a 10-membered ring of tetrahedrally coordinated atoms. In addition, 2 different sizes of 10-membered ring channels exist in the structure.

[0005] Another particular zeolite, IM-5 was first disclosed by Benazzi, et al. in 1996 (FR96/12873; WO98/17581) who describe the synthesis of IM-5 from the flexible dicationic structure directing agent, 1,5-bis(N-methylpyrrolidinium)pentane dibromide or 1,6-bis(N-methylpyrrolidinium)hexane dibromide in the presence of sodium. After the structure of IM-5 was solved by Baerlocher et al. (Science, 2007, 315, 113-6), the International Zeolite Structure Commission gave the code of IMF to this zeolite structure type, see Atlas of Zeolite Framework Types. The IMF structure type was also found to contain three mutually orthogonal sets of channels in which each channel is defined by a 10-membered ring of tetrahedrally coordinated atoms, however, connectivity in the third dimension is interrupted every 2.5nm, therefore diffusion is somewhat limited. In addition, multiple different sizes of 10-membered ring channels exist in the structure.

[0006] Applicants have successfully prepared a new family of materials designated UZM-39. The topology of the materials is similar to that observed for TNU-9 and IM-5. The materials are prepared via the use of a mixture of simple commercially available structure directing agents, such as 1,4-dibromobutane and 1-methylpyrrolidine, in concert with Na^+

using the Layered Material Conversion approach to zeolite synthesis (described below). This type of zeolite may be used as a catalyst in dehydrocyclodimerization reactions where aliphatic hydrocarbons containing from 2 to 6 carbon atoms per molecule are reacted over a catalyst to produce a high yield of aromatics and hydrogen, with a light ends byproduct and a C_2-C_4 recycle product. Processes for dehydrocyclodimerization are known and described in detail in US 4,654,455 and US 4,746,763 which are incorporated by reference.

SUMMARY OF THE INVENTION

[0007] As stated, the present invention relates to using a new catalytic composite comprising a coherently grown composite of TUN and IMF zeotypes designated UZM-39 as at least a portion of the catalytic composite in a process for dehydrocyclodimerization. One embodiment of the invention uses a microporous crystalline zeolite having a three-dimensional framework of at least AlO_2 and SiO_2 tetrahedral units and an empirical composition in the as synthesized and anhydrous basis expressed by an empirical formula of:

$$Na_nM_m^{k+}T_tAl_{1-x}E_xSi_yO_z$$

where "n" is the mole ratio of Na to (Al + E) and has a value from 0.05 to 0.5, M represents at least one metal selected from the group consisting of zinc, Group 1 (IUPAC 1), Group 2 (IUPAC 2), Group 3 (IUPAC 3), and the lanthanide series of the periodic table, and any combination thereof, "m" is the mole ratio of M to (Al + E) and has a value from 0 to 0.5, "k" is the average charge of the metal or metals M, T is the organic structure directing agent or agents derived from reactants R and Q where R is an A,Ω-dihalogen substituted alkane having from 3 to 6 carbon atoms and Q is at least one neutral monoamine having 6 or fewer carbon atoms, "t" is the mole ratio of N from the organic structure directing agent or agents to (Al + E) and has a value of from 0.5 to 1.5, E is an element selected from the group consisting of gallium, iron, boron and combinations thereof, "x" is the mole fraction of E and has a value from 0 to 1.0, "y" is the mole ratio of Si to (Al + E) and varies from greater than 9 to 25 and "z" is the mole ratio of O to (Al + E) and has a value determined by the equation:

$$z = (n + k \bullet m + 3 + 4 \bullet y)/2$$

and is characterized in that it has TUN regions and IMF regions that are coherently aligned so that the $[010]_{TUN}$ zone axis and the $[001]_{IMF}$ zone axis are parallel to each other and there is

continuity of crystal planes of type $(002)_{TUN}$ and $(060)_{IMF}$, where the indexing is referred to monoclinic $C_{2/m}$ and orthorhombic C_{mcm} unit cells for TUN and IMF respectively.

[0008] The microporous crystalline zeolite may also be described as having a three-dimensional framework of at least AlO_2 and SiO_2 tetrahedral units and an empirical composition in the as synthesized and anhydrous basis expressed by an empirical formula of:

$$Na_nM_m^{k+}T_tAl_{1-x}E_xSi_yO_z$$

where "n" is the mole ratio of Na to (Al + E) and has a value from 0.05 to 0.5, M represents a metal or metals from Group 1 (IUPAC 1), Group 2 (IUPAC 2), Group 3 (IUPAC 3), the lanthanide series of the periodic table or zinc, "m" is the mole ratio of M to (Al + E) and has a value from 0 to 0.5, "k" is the average charge of the metal or metals M, T is the organic structure directing agent or agents derived from reactants R and Q where R is an A,Ω-dihalogen substituted alkane having between 3 and 6 carbon atoms and Q is at least one neutral monoamine having 6 or fewer carbon atoms, "t" is the mole ratio of N from the organic structure directing agent or agents to (Al + E) and has a value of from 0.5 to 1.5, E is an element selected from the group consisting of gallium, iron, boron and combinations thereof, "x" is the mole fraction of E and has a value from 0 to 1.0, "y" is the mole ratio of Si to (Al + E) and varies from greater than 9 to 25 and "z" is the mole ratio of O to (Al + E) and has a value determined by the equation:

$$z = (n + k \bullet m + 3 + 4 \bullet y)/2$$

and the zeolite is characterized in that it has the x-ray diffraction pattern having at least the d-spacings and intensities set forth in Table A1

TABLE A1

2θ	d (Å)	I/Io %
7.17-7.21	12.25-12.31	vw-m
7.5-8.1*	11.78-10.91	w-m
8.88	9.95	m
9.17	9.63	w-m
12.47-12.62	7.09-7.00	w-m
17.7	5.01	vw-m
22.8-23.2	3.90-3.83	vs
23.39-23.49	3.80-3.78	m-s
25.01-25.31	3.56-3.52	m
28.74-29.25	3.10-3.05	w-m
45.08-45.29	2.01-2.00	w

*composite peak consisting of multiple overlapping reflections

The zeolite is thermally stable up to a temperature of greater than 600°C in one embodiment and at least 800°C in another embodiment.

[0009] The zeolite of the catalytic composite used in the process may be prepared by a process comprising forming a reaction mixture containing reactive sources of Na, R, Q, Al, Si, seeds of a layered material L and optionally E and/or M and heating the reaction mixture at a temperature of 150°C to 200°C, 155°C to 190°C, or 160°C to 180°C, for a time sufficient to form the zeolite. L does not have the same zeotype as the UZM-39 coherently grown composite. The reaction mixture has a composition expressed in terms of mole ratios of the oxides of:

$$a\text{-}b\ Na_2O : bM_{n/2}O : cRO : dQ : 1\text{-}eAl_2O_3 : eE_2O_3 : fSiO_2 : gH_2O$$

where "a" has a value of 10 to 30, "b" has a value of 0 to 30, "c" has a value of 1 to 10, "d" has a value of 2 to 30, "e" has a value of 0 to 1.0, "f" has a value of 30 to 100, "g" has a value of 100 to 4000. Additionally, the reaction mixture comprises 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. With this number of reactive reagent sources, many orders of addition can be envisioned. Typically, the aluminum reagent is dissolved in the sodium hydroxide prior to adding the silica reagents. As can be seen in the examples, reagents R and Q can be added together or separately in many different orders of addition.

[0010] The invention involves a process of dehydrocyclodimerization using the above-described zeolite as at least a portion of the catalytic composite. The process comprises reacting aliphatic hydrocarbons containing from 2 to 6 carbon atoms per molecule over a catalyst to produce a high yield of aromatics and hydrogen, with a light ends byproduct and a C_2-C_4 recycle product. The dehydrocyclodimerization reaction is carried out at temperatures in excess of 300°C (572°F), using the dual functional catalyst containing acidic and dehydrogenation components. At least the acidic function is provided by the zeolite described above which promotes the oligomerization and aromatization reactions. Optionally, a non-noble metal component may also be used to promote the dehydrogenation function.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG.1 is an XRD pattern of the UZM-39 zeolite formed in Example 1. This pattern shows the UZM-39 zeolite in the as-synthesized form.

[0012] FIG.2 is also an XRD pattern of the UZM-39 zeolite formed in Example 1. This pattern shows the UZM-39 zeolite after calcination.

[0013] FIG.3 is an XRD pattern of the UZM-39 zeolite formed in Example 16. This pattern shows the UZM-39 zeolite in the as-synthesized form.

[0014] FIG.4 is also an XRD pattern of the UZM-39 zeolite formed in Example 16. This pattern shows the UZM-39 zeolite in the H^+ form.

[0015] FIG.5 is an XRD pattern of the UZM-39 zeolite formed in Example 28. This pattern shows the UZM-39 zeolite in the as-synthesized form.

[0016] FIG.6 is also an XRD pattern of the UZM-39 zeolite formed in Example 28. This pattern shows the UZM-39 zeolite in the H^+ form.

[0017] FIG. 7 shows the results of high-resolution scanning electron microscopy characterization of the UZM-39 product of Example 1. The electron micrograph shows that UZM-39 forms in lathes which assemble into rectangular rod particles, often with a starburst cluster arrangement. The starburst cluster rods of UZM-39 can be seen in the scanning electron microscopy results of FIG. 7.

[0018] FIG. 8 shows the results of high-resolution scanning electron microscopy characterization of a different UZM-39, that of the product of Example 18. The electron micrograph also shows lathes assembled into rectangular rod particles with a number of starburst cluster arrangements.

[0019] FIG. 9 shows a wireframe representation of the TUN framework in the AC plane (left). Each vertex is a T-site and in the middle of each stick is an oxygen atom. A wireframe representation of the IMF framework in the AB plane is shown to the right. Along these projections, both the TUN and IMF frameworks contain nearly identical projections of chains of 5-rings connected by 6-rings and 10-ring channels.

[0020] FIG. 10 shows the results of transmission electron microscopy characterization of the UZM-39 product of Example 17 using high resolution imaging and computed optical diffractograms. The results show that UZM-39 is comprised of a coherently grown composite structure of TUN and IMF zeotypes.

[0021] FIG. 11 is an electron diffraction analysis of the cross sectioned rod particle of FIG. 10 and shows that from what appears to be a single-crystalline zeolite particle, areas that index to [010] zone axis of TUN and to [001] zone axis of IMF are found. The TUN regions and IMF regions are coherently aligned.

[0022] FIG. 12 is a plot of the low angle region in XRD analysis of materials showing that small percentages of IMF can be determined in samples largely consisting of TUN.

[0023] FIG. 13 is a plot of the low angle region in XRD analysis of materials showing that small percentages of TUN can be determined in samples largely consisting of IMF.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Applicants have prepared a catalytic component suitable for catalyzing dehydrocyclodimerization reactions where at least a portion of the catalytic component is an aluminosilicate zeolite whose topological structure is related to TUN as described in Atlas of Zeolite Framework Types, which is maintained by the International Zeolite Association Structure Commission at http://www.iza-structure.org/databases/, the member of which has been designated TNU-9. As will be shown in detail, UZM-39 is different from TNU-9 in a number of its characteristics including its x-ray diffraction pattern (XRD). UZM-39 is also related to IMF as described in the Atlas of Zeolite Framework Types, the member of which has been designated IM-5. As will be shown in detail, UZM-39 is different from TNU-9 and IM-5 in a number of its characteristics including its x-ray diffraction pattern. The instant microporous crystalline zeolite (UZM-39) has an empirical composition in the as synthesized and anhydrous basis expressed by an empirical formula of:

$$Na_nM_m^{k+}T_tAl_{1-x}E_xSi_yO_z$$

where "n" is the mole ratio of Na to (Al + E) and has a value from 0.05 to 0.5, M represents a metal or metals selected from the group consisting of zinc, Group 1 (IUPAC 1), Group 2 (IUPAC 2), Group 3 (IUPAC 3), the lanthanide series of the periodic table, and any combination thereof, "m" is the mole ratio of M to (Al + E) and has a value from 0 to 0.5, "k" is the average charge of the metal or metals M, T is the organic structure directing agent or agents derived from reactants R and Q where R is an A,Ω-dihalogen substituted alkane having between 3 and 6 carbon atoms and Q is at least one neutral monoamine having 6 or fewer carbon atoms, "t" is the mole ratio of N from the organic structure directing agent or agents to (Al + E) and has a value

of from 0.5 to 1.5, E is an element selected from the group consisting of gallium, iron, boron and combinations thereof, "x" is the mole fraction of E and has a value from 0 to 1.0, "y" is the mole ratio of Si to (Al + E) and varies from greater than 9 to 25 and "z" is the mole ratio of O to (Al + E) and has a value determined by the equation:

$$z = (n + k \bullet m + 3 + 4 \bullet y)/2$$

where M is only one metal, then the weighted average valence is the valence of that one metal, i.e. +1 or +2. However, when more than one M metal is present, the total amount of:

$$M_m^{k+} = M_{m1}^{(k1)+} + M_{m2}^{(k2)+} + M_{m3}^{(k3)+} + M_{m4}^{(k4)+} + \ldots$$

and the weighted average valence "k" is given by the equation:

$$\mathbf{k} = \frac{m1 \bullet k1 + m2 \bullet k2 + m3 \bullet k3 \ldots}{m1 + m2 + m3 \ldots}$$

[0025] The microporous crystalline zeolite, UZM-39, may be synthesized by a hydrothermal crystallization of a reaction mixture prepared by combining reactive sources of sodium, organic structure directing agent or agents T, aluminum, silicon, seeds of a layered material L, and optionally E, M, or both. The 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 sodium include but are not limited to sodium hydroxide, sodium aluminate, sodium bromide, and sodium silicate.

[0026] T is the organic structure directing agent or agents derived from reactants R and Q where R is an A,Ω-dihalogen substituted alkane having between 3 and 6 carbon atoms and Q comprises at least one neutral monoamine having 6 or fewer carbon atoms. R may be an A,Ω-dihalogen substituted alkane having between 3 and 6 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

and combinations thereof. Q comprises at least one neutral monoamine having 6 or fewer carbon atoms such as 1-ethylpyrrolidine, 1-methylpyrrolidine, 1-ethylazetidine, 1-methylazetidine, triethylamine, diethylmethylamine, dimethylethylamine, trimethylamine, dimethylbutylamine, dimethylpropylamine, dimethylisopropylamine, methylethylpropylamine, methylethylisopropylamine, dipropylamine, diisopropylamine, cyclopentylamine, methylcyclopentylamine, hexamethyleneimine. Q may comprise combinations of multiple neutral monoamines having 6 or fewer carbon atoms.

[0027] L comprises at least one seed of a layered zeolite. Suitable seed zeolites are layered materials that are microporous zeolites with crystal thickness in at least one dimension of less than 30 to 50 nm. The microporous materials have pore diameters of less than 2 nm. The seed layered zeolite is of a different zeotype than the UZM-39 coherently grown composite being synthesized. Examples of suitable layered materials include but are not limited to UZM-4M (US6776975), UZM-5 (US6613302), UZM-8 (US6756030), UZM-8HS (US7713513), UZM-26 (US-2010-0152023-A1), UZM-27 (US7575737), BPH, FAU/EMT materials, *BEA or zeolite Beta, members of the MWW family such as MCM-22P and MCM-22, MCM-36, MCM-49, MCM-56, ITQ-1, ITQ-2, ITQ-30, ERB-1, EMM-10P and EMM-10, SSZ-25, and SSZ-70 as well as smaller microporous materials such as PREFER (pre ferrierite), NU-6 and the like.

[0028] 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, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, zinc, yttrium, lanthanum, gadolinium, and mixtures thereof. Reactive sources of M include, but are not limited to, the group consisting of halide, nitrate, sulfate, hydroxide, or acetate salts. E is an element selected from the group consisting of gallium, iron, boron and combinations thereof, and suitable reactive sources include, but are not limited to, boric acid, gallium oxyhydroxide, gallium sulfate, gallium nitrate, ferric sulfate, ferric nitrate, ferric chloride and mixtures thereof.

[0029] The reaction mixture containing reactive sources of the desired components can be described in terms of molar ratios of the oxides by the formula:

$$a\text{-}b\ Na_2O : bM_{n/2}O : cRO : dQ : 1\text{-}eAl_2O_3 : eE_2O_3 : fSiO_2 : gH_2O$$

where "a" has a value of 10 to 30, "b" has a value of 0 to 30, "c" has a value of 1 to 10, "d" has a value of 2 to 30, "e" has a value of 0 to 1.0, "f" has a value of 30 to 100, "g" has a value of 100 to 4000. Additionally in the reaction mixture is from 1 to 10 wt.-% of seed zeolite L based on the amount of SiO_2 in the reaction, 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. The examples demonstrate a number of specific orders of addition for the reaction mixture which lead to UZM-39. However, as there are at least 6 starting materials, many orders of addition are possible. For example, the seed crystals L can be added as the last ingredient to the reaction mixture, to the reactive Si source, or at other suitable points. Also, if alkoxides are used, it is preferred to include a distillation or evaporative step to remove the alcohol hydrolysis products. While the organic structure directing agents R and Q can be added separately or together to the reaction mixture at a number of points in the process, it is preferred to mix R and Q together at room temperature and add the combined mixture to a cooled mixture of reactive Si, Al and Na sources maintained at 0-10°C. Alternatively, the mixture of R and Q, after mixing at room temperature, could be cooled and the reactive sources of Si, Al and Na added to the organic structure directing agent mixture while maintaining a temperature of 0-10°C. In an alternative embodiment, the reagents R and Q could be added, separately or together, to the reaction mixture at room temperature.

[0030] The reaction mixture is then reacted at a temperature of 150°C to 200°C, 155°C to 190°C, or 160°C to 180°C, for a period of 1 day to 3 weeks and preferably for a time of 3 days to 12 days in a stirred, sealed reaction vessel under autogenous pressure. After crystallization is complete, the solid product is isolated from the heterogeneous mixture by means such as filtration or centrifugation, and then washed with deionized water and dried in air at ambient temperature up to 100°C.

[0031] The as-synthesized coherently grown composite of TUN and IMF zeotypes, UZM- 39, is characterized by the x-ray diffraction pattern, having at least the d-spacings and relative intensities set forth in Tables A1-A3 below. Diffraction patterns herein were obtained using a typical laboratory powder diffractometer, utilizing the K_α line of copper; Cu K alpha. From the position of the diffraction peaks represented by the angle 2theta, the characteristic interplanar distances d_{hkl} of the sample can be calculated using the Bragg equation. The intensity is calculated on the basis of a relative intensity scale attributing a value of 100 to the line representing the strongest peak on the X-ray diffraction pattern, and then: very weak (vw) means less than 5; weak (w) means less than 15; medium (m) means in the range 15 to

50; strong (s) means in the range 50 to 80; very strong (vs) means more than 80. Intensities may also be shown as inclusive ranges of the above. The X-ray diffraction patterns from which the data (d spacing and intensity) are obtained are characterized by a large number of reflections some of which are broad peaks or peaks which form shoulders on peaks of higher intensity. Some or all of the shoulders may not be resolved. This may be the case for samples of low crystallinity, of particular coherently grown composite structures or for samples with crystals which are small enough to cause significant broadening of the X-rays. This can also be the case when the equipment or operating conditions used to produce the diffraction pattern differ significantly from those used in the present case.

[0032] The X-ray diffraction pattern for UZM-39 contains many peaks. Examples of the x-ray diffraction patterns for various as-synthesized UZM-39 products are shown in FIG.s 1, 3, and 5. Those peaks characteristic of UZM-39 are shown in Tables A1-A3 for various coherently grown composite structures. Additional peaks, particularly those of very weak intensity, may also be present. All peaks of medium or higher intensity present in the UZM-39 family of coherently grown composite structures are represented in at least Table A3.

[0033] Table A1 contains selected d-spacings and relative intensities of the UZM-39 X-ray diffraction pattern. The relative intensities are shown as a range covering UZM-39 materials with varying relative amounts of TUN and IMF zeotypes.

TABLE A1

2θ	d (Å)	I/Io %
7.17-7.21	12.25-12.31	vw-m
7.5-8.1*	11.78-10.91	w-m
8.88	9.95	M
9.17	9.63	w-m
12.47-12.62	7.09-7.00	w-m
17.7	5.01	vw-m
22.8-23.2	3.90-3.83	Vs
23.39-23.49	3.80-3.78	m-s
25.01-25.31	3.56-3.52	M
28.74-29.25	3.10-3.05	w-m
45.08-45.29	2.01-2.00	W

*composite peak consisting of multiple overlapping reflections

[0034] The zeolite may be further characterized by the x-ray diffraction pattern having at least the d-spacings and intensities set forth in Table A2 where the d-spacings and intensities are

provided at different relative concentrations of the components of the coherently grown composite structure.

TABLE A2

I			II			III		
high TUN, low IMF			med TUN, med IMF			low TUN, high IMF		
2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%
7.21	12.25	w-m	7.17	12.31	w-m	7.21	12.25	vw
7.5-8.1*	11.78-10.91	w-m	7.5-8.1*	11.78-10.91	w-m	7.5-8.1*	11.78-10.91	w-m
8.88	9.95	m	8.88	9.95	s	8.88	9.95	m
9.17	9.63	m	9.16	9.65	m	9.17**	9.63	w-m
9.34**	9.46	vw-w	9.30	9.50	m	9.33	9.47	m
12.62	7.00	w	12.50	7.08	w-m	12.47	7.09	w-m
17.70	5.01	vw-w	17.72	5.00	w-m	17.70	5.01	vw-w
19.20	4.62	w-m	22.8-23.2*	3.90-3.83	vs	18.71	4.74	w-m
22.89	3.88	vs	23.43	3.79	s	22.55	3.94	m
23.49	3.78	m	25.12	3.54	m	23.03	3.86	vs
25.31	3.52	m	28.74-29.25*	3.10-3.05	w-m	23.39	3.80	s
29.10	3.07	w	45.29	2.00	w	25.01	3.56	m
45.08	2.01	w				28.76	3.10	w-m
						45.08	2.01	w
* composite peak consisting of multiple overlapping reflections								
** typically a shoulder								

[0035] The zeolite may be yet further characterized by the x-ray diffraction pattern having at least the d-spacings and intensities set forth in Table A3 where the d-spacings and intensities are provided at different relative concentrations of the components of the coherently grown composite structure.

TABLE A3

I			II			III		
high TUN, low IMF			med TUN, med IMF			low TUN, high IMF		
2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%
7.21	12.25	w-m	7.17	12.31	w-m	7.21	12.22	vw
7.5-8.1*	11.78-10.91	w-m	7.5-8.1*	11.78-10.91	w-m	7.5-8.1*	11.78-10.91	w-m
8.88	9.95	m	8.88	9.95	m-s	8.88	9.95	m
9.17	9.63	m	9.16	9.65	m	9.17**	9.63	w-m
9.34**	9.46	vw-w	9.30	9.50	m	9.33	9.47	m
9.98	8.85	vw	12.50	7.08	w-m	12.47	7.09	w-m
11.68	7.57	vw	15.27	5.80	vw-w	12.85	6.88	vw
12.62	7.00	w	15.58	5.68	w	14.62	6.05	vw-w
13.69	6.46	vw-w	17.70	5.01	vw-w	15.27	5.80	w
15.33	5.77	vw-w	18.72	4.74	vw-m	15.57	5.68	w
16.48	5.37	vw-w	19.28	4.60	w	16.60	5.34	w
17.01	5.20	vw	22.61**	3.93	w-m	17.70	5.01	vw-w
17.70	5.01	vw-w	22.8-23.2*	3.90-3.83	vs	18.71	4.74	w-m
19.20	4.62	w-m	23.43	3.79	s	19.30	4.59	w
21.59	4.11	vw-w	24.20	3.68	m	22.55	3.94	m
22.61**	3.93	w-m	25.12	3.54	m	22.86**	3.89	m-s
22.89	3.88	vs	26.34	3.38	w-m	23.03	3.86	vs
23.49	3.78	m	26.75	3.33	w-m	23.39	3.80	s
23.93	3.72	vw-w	28.74-29.25*	3.10-3.05	w-m	24.17	3.68	m
24.13	3.68	m	35.72	2.51	vw-w	25.01	3.56	m
24.64	3.61	w	45.29	2.00	w	26.19	3.40	vw-w
24.93	3.57	w	45.62-47.19*	1.99-1.92	vw-w	26.68	3.34	w-m
25.31	3.52	m				28.76	3.10	w-m
26.62	3.35	w				35.72	2.51	vw-w
29.10	3.07	w				45.08	2.01	w
35.72	2.51	vw-w				45.62-47.19*	1.99-1.92	vw-w

45.08	2.01	w						
45.62-47.19*	1.99-1.92	vw-w						
* composite peak consisting of multiple overlapping reflections								
** Typically a shoulder								

[0036] In Tables A2 and A3, the term "high" refers to 60 to 95 mass-% of the specified component, the term "med" refers to 25 to 70 mass-% of the specified component, and the term "low" refers to 5 to 40 mass-% of the specified component. Some peaks may be shoulders on more intense peaks, and some peaks may be a composite peak consisting of multiple overlapping reflections.

[0037] The UZM-39 material is thermally stable up to a temperature of at least 600°C and in another embodiment, up to at least 800°C. The UZM-39 material may have a micropore volume as a percentage of total pore volume of greater than 60%.

[0038] Characterization of the UZM-39 product by high-resolution scanning electron microscopy shows that the UZM-39 forms in lathes which assemble into rectangular rod particles, often with a starburst cluster arrangement. The starburst cluster rods of UZM-39 can be seen in the scanning electron microscopy results for two particular UZM-39 products in FIG. 7 and in FIG.8.

[0039] UZM-39 is a coherently grown composite structure of TUN and IMF zeotypes. By coherently grown composite structure is meant that both structures are present in a major portion of the crystals in a given sample. This coherently grown composite structure is possible when the two zeotypic structures have nearly identical spacial arrangements of atoms along at least a planar projection of their crystal structure and possess similar pore topologies. FIG. 9 shows a wireframe representation of the TUN framework in the AC plane (left). Each vertex is a tetrahedral site (or T-site) and in the middle of each stick is a corner-shared oxygen atom. A wireframe representation of the IMF framework in the AB plane is shown on the right of FIG. 9. Along these projections, both the TUN and IMF zeotypes contain nearly identical projections of chains of 5-rings connected by 6-rings and 10-rings which form channels running perpendicular to the plane.

[0040] As both the TUN and IMF zeotypes are 3-dimensional 10-ring zeolites and have nearly identical projections in one plane, the two structures can thereby coherently grow off

crystals of the other structure with interfaces at the compatible planes to form a coherently grown composite structure.

[0041] A coherently grown composite structure is not a physical mixture of the two molecular sieves. Electron diffraction, transmission electron microscopy and x-ray diffraction analysis are employed to show that a material is a coherently grown composite structure instead of a physical mixture. Usually the combination of electron diffraction and TEM imaging is most definitive in determining whether one has produced a coherently grown composite structure because it provides direct evidence of the existence of both structures within one crystal.

[0042] Since the coherently grown composite structure zeolites of this invention can have varying amounts of the two structure types, it is to be understood that the relative intensity and line width of some of the diffraction lines will vary depending on the amount of each structure present in the coherently grown composite structure. Although the degree of variation in the x-ray powder diffraction patterns is theoretically predictable for specific structures, the more likely mode of a coherently grown composite structure is random in nature and therefore difficult to predict without the use of large hypothetical models as bases for calculation.

[0043] Unlike a physical mixture of TNU-9 and IM-5, transmission electron microscopy (TEM) analysis using high resolution imaging and computed optical diffractograms shows that UZM-39 is comprised of a coherently grown composite structure of TUN and IMF zeotypes.

[0044] In FIG. 10, TEM analysis of a cross sectioned rod particle from the product of Example 17 shows that areas with TUN and IMF structure occur as coherent sub-regions within an effectively single-crystalline zeolite particle. On the left side of FIG. 11, electron diffraction analysis of the left side of the particle shown in Fig 10 shows an electron diffraction pattern which can be indexed to the 002 plane of TUN. On the right side of FIG. 11, the electron diffraction pattern from the right side of the particle shown in FIG 10 is shown. This pattern can be indexed to the 060 plane of IMF. The TUN regions and IMF regions are coherently aligned such that the $[010]_{TUN}$ zone axis and the $[001]_{IMF}$ zone axis are parallel to each other and there is continuity of crystal planes of type $(002)_{TUN}$ and $(060)_{IMF}$, where the indexing is referred to monoclinic $C_{2/m}$ and orthorhombic C_{mcm} unit cells for TUN and IMF respectively (details of structures found on IZA website). In spite of the presence of

the two zeotypes in different portions of the particle, the image does not show any distinct boundary delineating separate crystals of TUN and IMF, indicating that the particle is a coherently grown composite.

[0045] Additionally, UZM-39 zeolite can be characterized by Rietveld analysis of the XRD pattern. Rietveld analysis is a least-squares approach developed by Rietveld (*Journal of Applied Crystallography* 1969, 2: 65–71) to refine a theoretical line XRD profile until it matches the measured XRD pattern as closely as possible and is the preferred method of deriving structural information from samples such as UZM-39 which contain strongly overlapping reflections. It is often used to quantify the amounts of two different phases in a XRD diffractogram. The accuracy of the Rietveld method is determined by parameters such as crystallite size (peak broadening), peak shape function, lattice unit cell constants and background fits. For the samples shown in the examples, applicants have determined the error in the reported value to be ±5% under the conditions used. Applicants have also determined that the Rietveld model used was unable to quantify the amounts of minority composite structure phase components at values less than 10%, but visually, amounts of the minority components can be seen at levels greater than 5% by comparing against the model patterns. Table 1 shows Rietveld refinement results on various UZM-39 samples from the examples and shows that UZM-39 contains greater than 0 and less than 100 wt.% IMF zeotype and less than 100wt.% and greater than 0 wt.% TUN zeotype. In another embodiment, UZM-39 contains greater than 5 and less than 95 wt.% IMF zeotype and less than 95wt.% and greater than 5 wt.% TUN zeotype, and in yet another embodiment, UZM-39 contains greater than 10 and less than 90 wt.% IMF zeotype and less than 90wt.% and greater than 10 wt.% TUN zeotype. As can be seen in Table 1 and examples, a wide range of coherently grown composite structures are possible by modifying the synthesis conditions.

[0046] As synthesized, the UZM-39 material will contain some exchangeable or charge balancing cations in its pores. These exchangeable cations can be exchanged for other cations, or in the case of organic cations, they can be removed by heating under controlled conditions. It is also possible to remove some organic cations from the UZM-39 zeolite directly by ion exchange. The UZM-39 zeolite may be modified in many ways to tailor it for use in a particular application. Modifications include calcination, ion-exchange, steaming, various acid extractions, ammonium hexafluorosilicate treatment, or any combination thereof, as outlined for the case of UZM-4M in US 6,776,975 B1 which is incorporated by reference

in its entirety. Conditions may be more severe than shown in US 6,776,975. Properties that are modified include porosity, adsorption, Si/Al ratio, acidity, thermal stability, and the like.

[0047] After calcination, ion-exchange and calcination and on an anhydrous basis, the microporous crystalline zeolite UZM-39 has a three-dimensional framework of at least AlO_2 and SiO_2 tetrahedral units and an empirical composition in the hydrogen form expressed by an empirical formula of

$$\mathbf{M1_a^{N+}Al_{(1-x)}E_xSi_{y'}O_{z''}}$$

where M1 is at least one exchangeable cation selected from the group consisting of alkali, alkaline earth metals, rare earth metals, ammonium ion, hydrogen ion and combinations thereof, "a" is the mole ratio of M1 to (Al + E) and varies from 0.05 to 50, "N" is the weighted average valence of M1 and has a value of +1 to +3, E is an element selected from the group consisting of gallium, iron, boron, and combinations thereof, x is the mole fraction of E and varies from 0 to 1.0, y' is the mole ratio of Si to (Al + E) and varies from greater than 9 to virtually pure silica and z" is the mole ratio of O to (Al + E) and has a value determined by the equation:

$$\mathbf{z'' = (a \bullet N + 3 + 4 \bullet y')/2}$$

[0048] In the hydrogen form, after calcination, ion-exchange and calcination to remove NH_3, UZM-39 displays the XRD pattern shown in Table B1-B3. Those peaks characteristic of UZM-39 are shown in Tables B1- B3 for various coherently grown composite structures. Additional peaks, particularly those of very weak intensity, may also be present. All peaks of medium or higher intensity present in the UZM-39 family of coherently grown composite structures are represented in at least Tables B3.

[0049] Table B1 contains selected d-spacings and relative intensities of the hydrogen form of UZM-39 X-ray diffraction pattern. The relative intensities are shown as a range covering UZM-39 materials with varying relative amounts of TUN and IMF zeotypes.

TABLE B1

2θ	d (Å)	I/Io %
7.11-7.16	12.42-12.25	vw-m
7.5-8.1*	11.78-10.91	m-s
8.84	10.00	m-s
9.06-9.08	9.75-9.73	w-m
9.24	9.56	vw-m
12.46-12.53	7.10-7.06	w-m
22.56	3.94	vw-m

22.75-23.2	3.90-3.83	vs
23.40	3.80	m-s
24.12-24.23	3.69-3.67	w-m
24.92-25.37	3.57-3.51	m
28.71-29.27	3.11-3.05	w-m
45.32-45.36	2.00	w

*composite peak consisting of multiple overlapping reflections

[0050] The zeolite may be further characterized by the x-ray diffraction pattern having at least the d-spacings and intensities set forth in Table B2 where the d-spacings and intensities are provided at different relative concentrations of the components of the coherently grown composite structure.

TABLE B2

A			B			C		
high TUN, low IMF			med TUN, med IMF			low TUN, high IMF		
2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%
7.12	12.40	w-m	7.11	12.42	w-m	7.16	12.25	vw-w
7.5-8.1*	11.78-10.91	m	7.5-8.1*	11.78-10.91	m-s	7.5-8.1*	11.78-10.91	m-s
8.84	10.00	m-s	8.84	10.00	m-s	8.84	10.00	m-s
9.06	9.75	m	9.08	9.73	m	9.06**	9.75	w
9.24**	9.56	vw-w	9.24	9.56	m	9.24	9.56	m
12.53	7.06	w	12.48	7.09	m	12.46	7.10	m
22.89	3.88	vs	22.56**	3.94	w-m	22.56	3.94	w-m
23.40	3.80	m	22.75-23.2*	3.90-3.83	vs	23.06	3.85	vs
24.23	3.67	w-m	23.40	3.80	s	23.40	3.80	s
25.22	3.53	m	24.17	3.68	m	24.12	3.69	m
29.08	3.07	w-m	24.92-25.37*	3.57-3.51	m	25.06	3.55	m
45.36	2.00	w	28.71-29.27*	3.11-3.05	w-m	28.82	3.10	w-m
			45.34	2.00	w	45.32	2.00	w
* composite peak consisting of multiple overlapping reflections								
** Typically a shoulder								

[0051] The zeolite may be yet further characterized by the x-ray diffraction pattern having at least the d-spacings and intensities set forth in Table B3 where the d-spacings and intensities are provided at different relative concentrations of the components of the coherently grown composite structure.

TABLE B3

I			II			III		
high TUN, low IMF			med TUN, med IMF			low TUN, high IMF		
2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%	2-Theta	d(Å)	I/Io%
7.12	12.40	w-m	7.11	12.42	w-m	7.16	12.25	vw-w
7.5-8.1*	11.78-10.91	m	7.5-8.1*	11.78-10.91	m-s	7.5-8.1*	11.78-10.91	m-s
8.84	10.00	m-s	8.84	10.00	m-s	8.84	10.00	m-s
9.06	9.75	m	9.08	9.73	m	9.06**	9.75	w
9.24**	9.56	vw-w	9.24	9.56	m	9.24	9.56	m
12.53	7.06	w	11.76	7.52	vw-w	11.76	7.52	vw-w
14.38	6.15	w	12.48	7.09	m	12.46	7.10	m
14.64	6.05	vw	14.38	6.15	vw-w	14.38	6.15	vw
15.26	5.80	vw-w	14.64	6.05	vw-w	14.64	6.05	w
15.52	5.70	vw	15.26	5.80	w	15.26	5.80	w
16.46	5.38	vw	15.52	5.70	w-m	15.52	5.70	w-m
17.72	5.00	w	16.50	5.37	vw-w	16.58	5.34	w
22.56**	3.94	vw-w	17.72	5.00	w-m	17.72	5.00	w-m
22.89	3.88	vs	18.64	4.76	vw-w	18.64	4.76	w
23.06**	3.85	w-m	22.56**	3.94	w-m	22.56	3.94	w-m
23.40	3.80	m	22.75-23.2*	3.90-3.83	vs	23.06	3.85	vs
23.82	3.73	w-m	23.40	3.80	s	23.40	3.80	s
24.23	3.67	w-m	24.17	3.68	m	24.12	3.69	m
24.70	3.60	w-m	24.70	3.60	w-m	25.06	3.55	m
25.22	3.53	m	24.92-25.37*	3.57-3.51	m	26.16	3.40	vw-w
26.51	3.36	w-m	26.32	3.38	w	26.74	3.33	w-m
29.08	3.07	w-m	26.76	3.33	w-m	28.82	3.10	w-m
35.86	2.50	vw-w	28.71-29.27*	3.11-3.05	w-m	30.12	2.96	w
45.36	2.00	w	30.13	2.96	vw-w	35.86	2.50	vw-w
45.66-47.37*	1.98-1.91	vw-w	35.86	2.50	vw-w	45.32	2.00	w

			45.34	2.00	w	45.66-47.37*	1.98-1.91	vw-w
			45.66-47.37*	1.98-1.91	vw-w			
* composite peak consisting of multiple overlapping reflections								
** Typically a shoulder								

[0052] In Tables B2 and B3, the term "high" refers to 60 to 95 mass-% of the specified component, the term "med" refers to 25 to 70 mass-% of the specified component, and the term "low" refers to 5 to 40 mass-% of the specified component. Some peaks may be shoulders on more intense peaks, and some peaks may be a composite peak consisting of multiple overlapping reflections.

[0053] After acid treating, such as exposure to HNO_3 or H_2SiF_6, and on an anhydrous basis, the microporous crystalline zeolite UZM-39 has a three-dimensional framework of at least AlO_2 and SiO_2 tetrahedral units and an empirical composition in the acid treated form expressed by an empirical formula of

$$\mathbf{M1_a^{N+}Al_{(1-x)}E_xSi_{y'}O_{z''}}$$

where M1 is at least one exchangeable cation selected from the group consisting of alkali, alkaline earth metals, rare earth metals, ammonium ion, hydrogen ion and combinations thereof, "a" is the mole ratio of M1 to (Al + E) and varies from 0.05 to 50, "N" is the weighted average valence of M1 and has a value of +1 to +3, E is an element selected from the group consisting of gallium, iron, boron, and combinations thereof, x is the mole fraction of E and varies from 0 to 1.0, y' is the mole ratio of Si to (Al + E) and varies from greater than 9 to virtually pure silica and z" is the mole ratio of O to (Al + E) and has a value determined by the equation:

$$\mathbf{z'' = (a \bullet N + 3 + 4 \bullet y')/2}$$

[0054] Similar to the as-synthesized material, the modified UZM-39 materials are thermally stable up to a temperature of at least 600°C and in another embodiment, up to at least 800°C and may have a micropore volume as a percentage of total pore volume of greater than 60%.

[0055] By virtually pure silica is meant that virtually all the aluminum and/or the E metals have been removed from the framework. It is well known that it is virtually impossible to remove all the aluminum and/or E metal. Numerically, a zeolite is virtually pure silica

when y' has a value of at least 3,000, preferably 10,000 and most preferably 20,000. Thus, ranges for y' are from 9 to 3,000; from greater than 20 to 3,000; from 9 to 10,000; from greater than 20 to 10,000; from 9 to 20,000; and from greater than 20 to 20,000.

[0056] In specifying the proportions of the zeolite starting material or adsorption properties of the zeolite product and the like herein, the "anhydrous state" of the zeolite will be intended unless otherwise stated. The term "anhydrous state" is employed herein to refer to a zeolite substantially devoid of both physically adsorbed and chemically adsorbed water.

[0057] The UZM-39 zeolite is employed as at least a portion of a catalyst in a dehydrocyclodimerization process for preparing an aromatic stream from a light aliphatic hydrocarbon stream. The process uses a dehydrocyclodimerization catalyst which comprises the UZM-39 zeolite component, optionally a binder component, and optionally a metal component. The metal component may be a metal such as gallium to promote the dehydrogenation function. The gallium component may be incorporated into the catalytic composite in any suitable manner known to the art which results in a uniform dispersion of the gallium such as by ion-exchange, cogelation, or impregnation either after, before, or during the compositing of the catalyst formulation. Usually the gallium is deposited onto the catalyst by impregnating the catalyst with a salt of the gallium metal. The particles are impregnated with using gallium metal or gallium containing compounds such as gallium oxyhydroxide, gallium nitrate, gallium chloride, gallium bromide, gallium sulfate, gallium acetate, and gallium oxide. The amount of gallium which is deposited onto the catalyst varies from 0.1 to 5 weight percent of the finished catalyst expressed as the metal. The gallium compound may be impregnated onto the support particles by any technique well known in the art such as dipping the catalyst into a solution of the metal compound or spraying the solution onto the support. One method of preparation involves the use of a steam jacketed rotary dryer. The support particles are immersed in the impregnating solution contained in the dryer and the support particles are tumbled therein by the rotating motion of the dryer. Evaporation of the solution in contact with the tumbling support is expedited by applying steam to the dryer jacket. Following drying, the gallium impregnated catalyst may then be calcined to convert the gallium to the oxide phase. An exemplary method for performing the gallium incorporation step is disclosed in US6657096, hereby incorporated by reference.

[0058] The zeolite as outlined above, or a modification thereof, may be in a composite with commonly known binders. The UZM-39 is used as a catalyst or catalyst support in

various reactions. The UZM-39 preferably is mixed with a binder for convenient formation of catalyst particles in a proportion of 5 to 100 mass % UZM-39 zeolite and 0 to 95 mass-% binder, with the UZM-39 zeolite preferably comprising from 10 to 90 mass-% of the composite. The binder should preferably be porous, have a surface area of 5 to 800 m^2 /g, and be relatively refractory to the conditions utilized in the hydrocarbon conversion process. Non-limiting examples of binders are alumina, titania, zirconia, zinc oxide, magnesia, boria, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, aluminophosphates, silica-zirconia, silica, silica gel, and clays. Preferred binders are aluminophosphates, amorphous silica and alumina, including gamma-, eta-, and theta-alumina, with aluminophosphates being especially preferred.

[0059] The zeolite with or without a binder can be formed into various shapes such as pills, pellets, extrudates, spheres, etc. Preferred shapes are extrudates and spheres. Extrudates are prepared by conventional means which involves mixing of the composition either before or after adding metallic components, with the binder and a suitable peptizing agent to form a homogeneous dough or thick paste having the correct moisture content to allow for the formation of extrudates with acceptable integrity to withstand direct calcination. The dough then is extruded through a die to give the shaped extrudate. A multitude of different extrudate shapes are possible, including, but not limited to, cylinders, cloverleaf, dumbbell and symmetrical and asymmetrical polylobates. It is also within the scope of this invention that the extrudates may be further shaped to any desired form, such as spheres, by any means known to the art.

[0060] Spheres can be prepared by the well known oil-drop method which is described in U.S. Pat. No 2,620,314 which is incorporated by reference. The method involves dropping a mixture of zeolite, and for example, alumina sol, and gelling agent into an oil bath maintained at elevated temperatures. The droplets of the mixture remain in the oil bath until they set and form hydrogel spheres. The spheres are then continuously withdrawn from the oil bath and typically subjected to specific aging treatments in oil and an ammoniacal solution to further improve their physical characteristics. The resulting aged and gelled particles are then washed and dried at a relatively low temperature of 50°C to 200°C and subjected to a calcination procedure at a temperature of 450°C to 700°C for a period of 1 to 20 hours. This treatment effects conversion of the hydrogel to the corresponding oxide or phosphate matrix.

[0061] The dehydrocyclodimerization conditions which are employed vary depending on such factors as feedstock composition and desired conversion. A desired range of conditions for the dehydrocyclodimerization of C_2-C_6 aliphatic hydrocarbons to aromatics include a temperature from 350°C to 650°C (662°F to 1202°F), a pressure from 0 to 300 psi(g) (0 to 2068 kPa(g)), and a liquid hourly space velocity from 0.2 to 5 hr^{-1}. One embodiment of the invention employs process conditions including a temperature in the range from 400°C to 600°C (752°F to 1112°F), a pressure in the range from 0 to 150 psi(g) (0 to 1034 kPa(g)), and a liquid hourly space velocity of between 0.5 to 3.0 hr^{-1}. It is understood that, as the average carbon number of the feed increases, a temperature in the lower end of the temperature range is required for optimum performance and conversely, as the average carbon number of the feed decreases, the higher the required temperature.

[0062] The feed stream to the dehydrocyclodimerization process is defined herein as all streams introduced into the dehydrocyclodimerization reaction zone. Included in the feed stream is the at least one aliphatic hydrocarbon having from 2 to 6 carbon atoms. The feed stream is referred to as comprising C_2-C_6 aliphatic hydrocarbons. By C_2-C_6 aliphatic hydrocarbons is meant one or more open, straight or branched chain isomers having from two to six carbon atoms per molecule. Furthermore, the hydrocarbons in the feedstock may be saturated or unsaturated. Preferably, the hydrocarbons are C_3's and/or C_4's selected from isobutane, normal butane, isobutene, normal butene, propane and propylene. Examples of potential feed streams include C_3 and/or C_4 derived streams from FCC cracked products, light gasses from a delayed coking process, and liquefied petroleum gas streams (LPG). Diluents may also be included in the feed stream. Examples of such diluents include water, nitrogen, helium, argon, neon. Aromatic products generated by the dehydrocyclodimerization process may include benzene, toluene, xylenes, aromatics with 9 or 10 carbon atoms, and mixtures thereof. In one embodiment, the aromatic products include benzene, toluene, and xylenes. The aromatic products may be used as reactants in later refining or petrochemical processes.

[0063] Molecular hydrogen is produced in a dehydrocyclodimerization reaction as well as aromatic hydrocarbons. For example, reacting a C_4 paraffin will yield 5 moles of hydrogen for every one mole of aromatic produced. Because the equilibrium concentration of aromatics is inversely proportional to the fifth power of the hydrogen concentration, it is desired to carry out the reaction in the absence of added hydrogen. Adherence to this practice, however, promotes catalyst deactivation and, as a result, short catalyst life before regeneration. The

rapid deactivation is believed to be caused by excessive carbon formation (coking) on the catalyst surface. This coking tendency makes it necessary to relatively frequently perform catalyst regeneration. Reducing the deactivation occurring during successive regenerations requires a hydrothermally stable zeolite, that is, a zeolite for which surface area, micropore volume and/or tetrahedral Al content are stable after exposure to high temperatures and steam quantities. The catalyst used in this dehydrocyclodimerization has the advantage of hydrothermal stability which may lead to longer catalyst life.

[0064] The catalyst may be in a fixed bed system, a moving bed system, a fluidized bed system, or in a batch type operation; however, in view of the danger of attrition losses of the valuable catalyst and of the well-known operational advantages, it is preferred to use either a fixed bed system or a dense-phase moving bed system.

[0065] In a fixed bed system or a dense-phase moving bed system, the feed stream is preheated by any suitable heating means to the desired reaction temperature and then passed into a dehydrocyclodimerization zone containing a bed of catalyst. It is understood that the dehydrocyclodimerization zone may be one or more separate reactors with suitable means between separate reactors if any to compensate for any endothermicity encountered in each reactor and to assure that the desired temperature is maintained at the entrance to each reactor. It is also important to note that the feed stream may be contacted with the catalyst bed in either upward, downward, or radial flow fashion with the latter being preferred. In addition, the feed stream is in the vapor phase when its' components contact the catalyst bed. Each reactor may contain one or more fixed or dense-phase moving beds of catalyst.

[0066] The dehydrocyclodimerization system may comprise a dehydrocyclodimerization zone containing one or more reactors and/or beds of catalyst. In a multiple bed system, it is, of course, within the scope of the present invention to use one catalyst in less than all of the beds with another dehydrocyclodimerization or similarly behaving catalyst being used in the remainder of the beds. Specific to the dense-phase moving bed system, it is common practice to remove catalyst from the bottom of a reactor in the dehydrocyclodimerization zone, regenerate it by conventional means known to the art, and then return it to the top of that reactor or another reactor in the dehydrocyclodimerization zone. The reactor or reactors utilized in the process may be linked to a product recovery system in various manners described in the prior art to achieve specific desired results. U.S. Pat. No. 4,642,402 for example discloses a method of combining a reaction zone and product recovery zone to optimize the xylene produced in

a dehydrocyclodimerization process. The product recovery section may recover streams such as hydrogen, light hydrocarbons, and benzene. In an embodiment, at least a portion of a light hydrocarbon stream comprising C_2-C_6 hydrocarbons is recycled to the dehydrocyclodimerization zone as a portion of the feedstream. In another an embodiment, at least a portion of the benzene stream is recycled to the dehydrocyclodimerization zone as a portion of the feedstream

[0067] After some time on stream (several days to a year), the catalyst described above will have lost enough activity due to coking and hydrogen exposure so that it must be reactivated. It is believed that the exact amount of time which a catalyst can operate without necessitating regeneration or reactivation will depend on a number of factors. One factor, as is demonstrated herein is whether water is added to the feed stream.

[0068] When the catalyst requires regeneration, typically oxidation or burning of catalyst deactivating carbonaceous deposits with oxygen or an oxygen-containing gas is used. Catalyst regeneration techniques are well known and not discussed in detail here. Examples include US 4,795,845 (hereby incorporated by reference) which discloses burning the coke accumulated upon the deactivated catalyst at catalyst regeneration conditions in the presence of an oxygen-containing gas, and US 4,724,271 (hereby incorporated by reference) which additionally discloses water removal steps in the catalyst regeneration procedure. The regeneration may proceed in one or multiple burns. For example, there may be a main burn followed by a clean-up burn. The main burn constitutes the principal portion of the regeneration process with the clean-up burn gradually increasing the amount of molecular oxygen in the gas introduced to the regeneration catalyst until the end of the clean-up burn which is indicated by a gradual decline in the temperature at the edit of the catalyst bed until the inlet and outlet temperatures of the catalyst bed merges.

[0069] In addition to deactivation by coking requiring regeneration, dehydrocyclodimerization catalysts can be deactivated by exposure to hydrogen at high temperatures and then require reactivation. Similarly, when the catalyst requires reactivation, it is removed from the operating reactor and contacted with fluid water. Suitable reactivation processes are known and not discussed in detail here. One example is US 6,395,664. Using procedures in the art, the catalyst can be reactivated multiple times. Thus, the catalyst can be hydrogen deactivated, then reactivated, then hydrogen deactivated again, then reactivated again and so forth. No limit on the number of times that a particular catalyst can be deactivated and

subsequently reactivated is known. The application and use of additional required items are well within the purview of a person of ordinary skill in the art. US 3,652,231; US 3,647,680; and US 3,692,496; which are incorporated by reference into this document, may be consulted for additional detailed information.

[0070] The following examples are presented in illustration of this invention and are not intended as undue limitations on the generally broad scope of the invention as set out in the appended claims.

[0071] The structure of the UZM-39 zeolite of this invention was determined by x-ray analysis. The x-ray patterns presented in the following examples were obtained using standard x-ray powder diffraction techniques. The radiation source was a high-intensity, x-ray tube operated at 45 kV and 35 ma. The diffraction pattern from the copper K-alpha radiation was obtained by appropriate computer based techniques. Flat compressed powder samples were continuously scanned at 2° to 56° (2θ). Interplanar spacings (d) in Angstrom units were obtained from the position of the diffraction peaks expressed as θ where θ is the Bragg angle as observed from digitized data. Intensities were determined from the integrated area of diffraction peaks after subtracting background, "I_o" being the intensity of the strongest line or peak, and "I" being the intensity of each of the other peaks.

[0072] As will be understood by those skilled in the art the determination of the parameter 2θ is subject to both human and mechanical error, which in combination can impose an uncertainty of ±0.4° on each reported value of 2θ. This uncertainty is, of course, also manifested in the reported values of the d-spacings, which are calculated from the 2θ values. This imprecision is general throughout the art and is not sufficient to preclude the differentiation of the present crystalline materials from each other and from the compositions of the prior art. In some of the x-ray patterns reported, the relative intensities of the d-spacings are indicated by the notations vs, s, m, and w which represent very strong, strong, medium, and weak, respectively. In terms of 100 x I/I_o, the above designations are defined as:

vw= <5; w = 6-15; m = 16-50: s = 51-80; and vs = 80-100

[0073] In certain instances the purity of a synthesized product may be assessed with reference to its x-ray powder diffraction pattern. Thus, for example, if a sample is stated to be pure, it is intended only that the x-ray pattern of the sample is free of lines attributable to crystalline impurities, not that there are no amorphous materials present.

[0074] 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 an undue limitation on the broad scope of the invention as set forth in the appended claims.

EXAMPLE 1

[0075] A sample of UZM-39 was prepared as follows. 6.02 g of NaOH, (97%) was dissolved in 125.49 g water. 0.62 g $Al(OH)_3$, (29.32 wt.-% Al) was added to the NaOH solution to form a first solution. Separately, 0.24 g of the layered material UZM-8 was stirred into 30.0 g Ludox AS-40 to form a second solution. The second solution was added to the first solution. The mixture was cooled to 0°C-4°C. Separately, 6.54 g 1,4-dibromobutane, (99 wt.-%) was mixed with 7.65 g 1-methylpyrrolidine, (97 wt.-%) to form a third solution. The third solution was added to the cooled mixture of the first and second solutions to form the final reaction mixture. The final reaction mixture was transferred to a 300 cc stirred autoclave and digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD as shown in FIG. 1. Analytical results show this material has the following molar rations: Si/Al of 12.64, Na/Al of 0.116, N/Al of 0.92, C/N of 7.23.

[0076] Scanning Electron Microscopy (SEM) revealed crystals of intergrown, square rod morphology in starbursts, 250 to 700 nm along a face of the square with an aspect ratio of from 2:1 to 5:1. The micrograph is shown in FIG. 7. The product was calcined at 550°C for 3 hrs under air. The XRD pattern of the calcined material is shown in FIG. 2.

COMPARATIVE EXAMPLE 2

[0077] The preparation of Example 1 was followed, except that the layered material UZM-8 was not added to the second solution. After 144 hours of stirring at 100 rpm at 160°C, the product was isolated by filtration. The product was identified as analcime by XRD.

COMPARATIVE EXAMPLE 3

[0078] 6.68 g of NaOH, (97%) was dissolved in 145.44 g water. 2.86 g $Al(NO_3)_3 \bullet 9H_2O$ (97%) was added to the sodium hydroxide solution. 13.33 g Aerosil 200 was stirred into the mixture. 13.1 g H_2O was added. 7.26 g 1,4-dibromobutane, (99%) and 5.84 g 1-methylpyrrolidine, (97%) were added and the mixture was stirred vigorously for a day. The mixture was divided equally and loaded into eight 45cc Parr vessels and placed into a rotisserie

oven at 160°. The mixture in one of the Parr vessels produced a material at 256 hours identified by XRD as having the TUN structure. Analytical results showed this material to have the following molar ratios, Si/Al of 15.51, Na/Al of 0.12, N/Al of 1.29, and C/N of 6.89. SEM analysis revealed a squat rod cluster morphology, 300-800nm in length and with an aspect ratio of 1.

[0079] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500° under air for 2 hours to convert NH_4^+ into H^+.

Analysis for the calcined, ion-exchanged sample showed 39.2 wt.% Si, 2.34 wt.% Al, <0.005 wt.% Na with a BET surface area of 378 m^2/g, pore volume of 0.220 cm^3/g, and micropore volume of 0.190 cm^3/g.

[0080] Analysis of the H+-form of this material by Rietveld XRD refinement showed that the material consisted entirely of TUN structure type. TEM analysis confirmed that no coherent growth of IMF crystals occurred.

EXAMPLE 4

[0081] 6.40 g of NaOH, (97%) was dissolved in 111.88 g water. 1.16 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution to create a first solution. Separately, 0.30 g of the layered material (UZM-8) was stirred into 37.5 g Ludox AS-40 to form a second solution. The second solution was added to the first solution and vigorously stirred for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane, (99 wt.-%) was mixed with 9.56 g 1-methylpyrrolidine, (97 wt.-%) to form a third solution. The third solution was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.07, Na/Al of 0.124, N/Al of 0.90, C/N of 6.85.

EXAMPLE 5

[0082] 7.19 g of NaOH, (99 wt.-%%) was dissolved in 90.1 g water. 1.56 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution to create a first solution. Separately, 0.405 g of the layered material (UZM-8) was stirred into 50.62 g Ludox AS-40 to form a second

solution. The second solution was added to the first solution and vigorously stirred for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 11.04 g 1,4-dibromobutane, (99 wt.-%), was mixed with 12.90 g 1-methylpyrrolidine, (97 wt.-%) to form a third solution. The third solution was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred for 5 minutes and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. 16.5 g of the product was isolated by filtration. The product was identified by XRD to be UZM-39 with a very slight MOR impurity. Analytical results showed this material to have the following molar ratios, Si/Al of 14.14, Na/Al of 0.16, N/Al of 1.02, C/N of 7.33.

EXAMPLE 6

[0083] 37.62 g of NaOH, (97 wt.-%) was dissolved in 600 g water to create a sodium hydroxide solution. 6.96 g $Al(OH)_3$ (29.32 mass% Al) was added to the sodium hydroxide solution to create a first solution. Separately, 1.80 g of the layered material (UZM-8) was stirred into 225 g Ludox AS-40 to form a second solution. The second solution was added to the first solution and vigorously stirred for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 49.08 g 1,4-dibromobutane (99 wt.-%) was mixed with 57.36 g 1-methylpyrrolidine (97 wt.-%) for 1-5 minutes to form a third solution. The third solution was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred for 5 minutes and transferred to a 2 liter stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 250 rpm. The product was isolated by filtration. The product was identified by XRD as UZM-39. Analytical results showed this material to have the following molar ratios, Si/Al of 11.62, Na/Al of 0.12, N/Al of 0.88, C/N of 7.36.

[0084] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 7

[0085] 505.68 g of NaOH, (99 wt.-%) was dissolved in 10542 g water. 52.08 g $Al(OH)_3$, (29.3 wt.-% Al), was added to the sodium hydroxide solution to create a first solution. Separately, 20.16 g of the layered material (UZM-8) was stirred into 2520 g Ludox AS-40 to

form a second solution. The second solution was added to the first solution and vigorously stirred for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 549.36 g 1,4-dibromobutane (99 wt.-%) was mixed with 642.6 g 1-methylpyrrolidine, (97 wt.-%), for 3-5 minutes to form a third solution. The third solution was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred for 5 minutes and pumped into a 5 gallon stirred autoclave. The final reaction mixture was digested at 160°C for 150 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified by XRD as UZM-39. Analytical results showed this material to have the following molar ratios, Si/Al=13.35, Na/Al=0.087, N/Al=0.96, C/N=7.12.

EXAMPLE 8

[0086] The preparation of Example 4 was followed except that UZM-8 was replaced with 0.30 g UZM-26. The product was identified by XRD as UZM-39. Analytical results showed this material to have the following molar ratios: Si/Al=12.88, Na/Al=0.25, N/Al=0.88, C/N=7.31.

EXAMPLE 9

[0087] 6.27 g of NaOH, (99%), was dissolved in 111.88 g water to create a sodium hydroxide solution. 1.16 g $Al(OH)_3$ (29.32 mass% Al) was added to the sodium hydroxide solution to create a first solution. 37.5 g Ludox AS-40 and then 0.22 g of the layered material UZM-5 were added to the first solution. The first solution was vigorously stirred for 1-2 hours. The first solution was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane (99%) was mixed with 9.56 g 1-methylpyrrolidine (97%) for 1-5 minutes to form a second solution. The second solution was added to the cooled first solution to create the final reaction mixture. The final reaction mixture was vigorously stirred for 5 minutes and transferred to a 300cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified by XRD as UZM-39 with a very small EUO or NES contaminant.

COMPARATIVE EXAMPLE 10

[0088] This example is identical to example 4 except that UZM-8 was replaced with 0.30 g UZM-39. The product was identified as a composition comprising MTW, UZM-39, ANA and MOR.

EXAMPLE 11

[0089] 6.27 g of NaOH, (97 wt.-%) was dissolved in 111.88 g water. 1.16 g $Al(OH)_3$, (29.32 wt. % Al), was added to the sodium hydroxide solution to create a first solution. Separately, 0.30 g of the layered material (UZM-8) was stirred into 37.5 g Ludox AS-40 to form a second solution. The second solution was added to the first solution and vigorously stirred for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 12.27 g 1,4-dibromobutane (99 wt.-%) was mixed with 14.34 g 1-methylpyrrolidine (97 wt.-%) to form a third solution. The third solution was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 with an ESV impurity by XRD. Analytical results showed this material to have the following molar ratios, Si/Al=13.17, Na/Al=0.126, N/Al=1.03, C/N=7.22.

EXAMPLE 12

[0090] The procedure of Example 4 was followed except 9.56 g 1-methylpyrrolidine, (97 wt.-%), was replaced with 8.05 g dimethylethylamine, (97 wt.-%). The product was identified as a composition comprising mordenite and UZM-39.

EXAMPLE 13

[0091] 6.27 g of NaOH (99 wt.-%) was dissolved in 111.88 g water. 1.16 g $Al(OH)_3$ (29.32 wt.-% Al) was added to the sodium hydroxide solution to create a first solution. 0.30 g of the layered material UZM-8 and 37.5 g Ludox AS-40 were added to the first solution. The first solution was vigorously stirred for 1-2 hours. The first solution was cooled to 0°C-4°C. Separately, 4.02 g dimethylethylamine (97 wt.-%) was mixed with 4.78 g 1-methylpyrrolidine (97 wt.-%) for 1-2 minutes to form an amine solution. 8.18g 1,4-dibromobutane (99 wt.-%) was added to the amine solution and then mixed for 1-2 minutes to form a second solution. The second solution was added to the cooled first solution to create the final reaction mixture. The final reaction mixture was vigorously stirred for 5 minutes and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 192 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD.

Analytical results showed this material to have the following molar ratios, Si/Al=12.42, Na/Al=0.175, N/Al=0.91, C/N=6.92.

[0092] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 38.7% Si, 2.97% Al, 0.0089% Na with a BET surface area of 375 m^2/g, pore volume of 0.238 cm^3/g, and micropore volume of 0.184 cm^3/g. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 14

[0093] 6.21 g of NaOH, (99%), was dissolved in 111.88 g water to create a sodium hydroxide solution. 1.16 g $Al(OH)_3$ (29.32 wt.-% Al) was added to the sodium hydroxide solution to create a first solution. 0.30 g of the layered material (UZM-8) and 37.5 g Ludox AS-40 were added to the first solution. The first solution was vigorously stirred for 1-2 hours. The first solution was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane (99 wt.-%) was mixed with 9.56 g 1-methylpyrrolidine (97 wt.-%) for 1-5 minutes to form a second solution. The second solution was added to the cooled first solution to create the final reaction mixture. The final reaction mixture was vigorously stirred for 5 minutes and transferred to a 300cc stirred autoclave. The final reaction mixture was digested at 170°C for 96 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.76, Na/Al of 0.116, N/Al of 0.94, C/N of 6.98.

EXAMPLE 15

[0094] 6.21 g of NaOH, (99%), was dissolved in 111.88 g water to create a sodium hydroxide solution. 1.16 g $Al(OH)_3$ (29.32 wt.-% Al) was added to the sodium hydroxide solution to create a first solution. 0.30 g of the layered material (UZM-8) and 37.5 g Ludox AS-40 were added to the first solution. The first solution was vigorously stirred for 1-2 hours. The first solution was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane (99 wt.-%) was mixed with 9.56 g 1-methylpyrrolidine (97 wt.-%) for 1-5 minutes to form a second solution. The second solution was added to the cooled first solution to create the final reaction mixture.

The final reaction mixture was vigorously stirred for 5 minutes and transferred to a 300cc stirred autoclave. The final reaction mixture was digested at 175°C for 44 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.97, Na/Al of 0.20, N/Al of 0.95, C/N of 6.98.

EXAMPLE 16

[0095] 5.96 g of NaOH, (97%) and 0.25 g KOH, (86%) were dissolved in 111.88 g water. 1.22 g $Al(OH)_3$, (27.9 wt.-% Al), was added to the sodium hydroxide solution. 37.5 g Ludox AS-40 and then 0.30 g of the layered material UZM-8 were added to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane, (99%) was mixed with 9.56 g 1-methylpyrrolidine, (97%) to form a third mixture. The third mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. The x-ray diffraction pattern is shown in FIG. 3. Analytical results showed this material to have the following molar ratios, Si/Al of 11.69, Na/Al of 0.137, K/Al of 0.024, N/Al of 0.848, C/N of 7.16.

[0096] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 39.4% Si, 3.23% Al, 0.011% Na, 0.005% K with a BET surface area of 362 m^2/g, pore volume of 0.231 cm^3/g, and micropore volume of 0.176 cm^3/g. The x-ray diffraction pattern in shown in FIG. 4.

EXAMPLE 17

[0097] 5.96 g of NaOH, (99%) and 0.50 g KOH, (86%) were dissolved in 111.88 g water. 1.16 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution. 37.5 g Ludox AS-40 and then 0.30 g of the layered material UZM-8 were added to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 4.09 g 1,4-dibromobutane, (99%) was mixed with 11.15 g 1-methylpyrrolidine, (97%) to form a third

mixture. The third mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 11.98, Na/Al of 0.114, K/Al of 0.0375 N/Al of 0.84, C/N of 7.50.

[0098] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 37.7% Si, 3.01% Al, 0.012% Na, 0.006% K. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1. TEM analysis showed that UZM-39 is a coherently grown composite structure of TUN and IMF zeotypes, the results of which analysis are shown in Figures 10 and 11.

EXAMPLE 18

[0099] 5.64 g of NaOH, (97%) and 1.00 g KOH, (86%) were dissolved in 111.88 g water. 1.22 g $Al(OH)_3$, (27.9 wt.-% Al), was added to the sodium hydroxide solution. 37.5 g Ludox AS-40 and then 0.30 g of the layered material UZM-8 were added to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane, (99%) was mixed with 9.56 g 1-methylpyrrolidine, (97%) to form a third mixture. The third mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 11.29, Na/Al of 0.078, K/Al of 0.053 N/Al of 0.88, C/N of 6.92. The SEM image of the product is shown in FIG. 8.

[00100] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 42.6% Si, 3.65% Al, 0.0018% Na, 0.02% K with a BET surface area of 351 m^2/g, pore volume of 0.218 cm^3/g, and micropore volume of 0.170

cm^3/g. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 19

[00101] 5.02 g of NaOH, (97%) and 2.00 g KOH, (86%) were dissolved in 111.88 g water. 1.22 g $Al(OH)_3$, (27.9 wt.-% Al), was added to the sodium hydroxide solution. 37.5 g Ludox AS-40 and then 0.30 g of the layered material UZM-8 were added to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane, (99%) was mixed with 9.56 g 1-methylpyrrolidine, (97%) to form a third mixture. The third mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 136 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD with a likely small amount of NES contaminant. Analytical results showed this material to have the following molar ratios, Si/Al of 10.99, Na/Al of 0.088, K/Al of 0.11 N/Al of 0.84, C/N of 7.36.

EXAMPLE 20

[00102] 5.96 g of NaOH, (99%) was dissolved in 111.88 g water. 1.22 g $Al(OH)_3$, (27.9 wt.-% Al), was added to the sodium hydroxide solution. Then 0.24 g $Mg(OH)_2$ (95%), 37.5 g Ludox AS-40, and 0.30 g of the layered material UZM-8 were added in the order listed to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane, (99%) was mixed with 9.56 g 1-methylpyrrolidine, (97%) and added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 144 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.12, Na/Al of 0.148, Mg/Al of 0.38 N/Al of 0.91, C/N of 6.96.

[00103] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 39.6% Si, 2.99% Al, 83ppm Na, 0.14%Mg with a

BET surface area of 351 m^2/g, pore volume of 0.218 cm^3/g, and micropore volume of 0.170 cm^3/g.

EXAMPLE 21

[00104] 5.96 g of NaOH, (99%) and 0.51 g $La(OH)_3$, (99.9%) were dissolved in 111.88 g water. 1.16 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution. 37.5 g Ludox AS-40 and then 0.30 g of the layered material UZM-8 were added to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane, (99%) was mixed with 9.56 g 1-methylpyrrolidine, (97%) and added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 168 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.22, Na/Al of 0.20, La/Al of 0.18, N/Al of 0.89, C/N of 7.13.

[00105] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 39.1% Si, 3.06% Al, 60ppm Na, 0.25% La with a BET surface area of 335 m^2/g, pore volume of 0.226 cm^3/g, and micropore volume of 0.163 cm^3/g.

EXAMPLE 22

[00106] 3.14 g of NaOH, (97%) was dissolved in 106.41 g water. 1.16 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution. 37.5 g Ludox AS-40 and then 0.30 g of the layered material UZM-8 were added to the first solution. Next 26.7 g Na silicate solution (13.2 wt.% Si; 6.76 wt.% Na) is added to the above and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.18 g 1,4-dibromobutane, (99%) was mixed with 9.56 g 1-methylpyrrolidine, (97%) to form a third mixture. The third mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 224 hours with stirring at 100 rpm. The product was isolated by filtration. The product was

identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 11.75, Na/Al of 0.11, N/Al of 0.90, C/N of 6.99.

[00107] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged three times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 38.8% Si, 3.05% Al, 0.011% Na, with a BET surface area of 364 m^2/g, pore volume of 0.273 cm^3/g, and micropore volume of 0.174 cm^3/g. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 23

[00108] 5.33 g of NaOH, (99%) was dissolved in 111.88 g water. 1.16 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution. Separately, 0.30 g of Beta zeolite was stirred into 37.5 g Ludox AS-40 to make a second mixture. This second mixture was added to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 8.89 g 1,5-dibromopentane, (97%) was mixed with 9.56 g 1-methylpyrrolidine, (97%) to form a third mixture. The third mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 256 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 13.24, Na/Al of 0.13, N/Al of 0.91, C/N of 7.21.

[00109] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged three times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

COMPARATIVE EXAMPLE 24

[00110] 10.8g of Aerosil 200 was added, while stirring, to a solution of 12.24g 1,5-bis(N-methylpyrrolidinium)pentane dibromide in 114g H_2O. A very thick gel was formed. Separately, a solution was made from 60g H_2O, 3.69g NaOH (99%), 0.95g sodium aluminate (26.1% Al by analysis), and 1.86g NaBr (99%). This second solution was added to the above mixture which thins out a bit. The final mixture was divided equally between 7 45cc Parr vessels. One vessel,

which was digested for 12 days at 170°C in a rotisserie oven at 15rpm, yielded a product which was determined by XRD as having the IMF structure. The product was isolated by filtration. The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500° under air for 2 hours to convert NH_4^+ into H^+. Analysis of the H+-form of this material by Rietveld XRD refinement showed that the material consisted entirely of IMF structure type. TEM analysis confirmed that no coherent growth of TUN crystals occurred.

EXAMPLE 25

[00111] 31.98 g of NaOH, (99%) was dissolved in 671.3 g water. 6.96 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution. Separately, 1.80 g of the layered material UZM-8 was stirred into 225.0 g Ludox AS-40 to make a second mixture. This second mixture was added to the first solution and stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 53.34 g 1,5-dibromopentane, (97%) was mixed with 57.36 g 1-methylpyrrolidine, (97%) to form a third mixture. The third mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 2 L stirred autoclave. The final reaction mixture was digested at 160°C for 256 hours with stirring at 250 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.30, Na/Al of 0.13, N/Al of 0.92, C/N of 7.51.

[00112] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged three times with 1 M ammonium nitrate solution at 75° followed by a calcination at 500° under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 39.0% Si, 2.93% Al, 0.008% Na. Analysis of the H+-form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 26

[00113] 5.76 g of NaOH, (97%) was dissolved in 111.88 g water. 1.22 g $Al(OH)_3$, (27.9 wt.-% Al), was added to the sodium hydroxide solution. When this became a solution, 37.5 g Ludox AS-40 was added. Next 0.30 g of the layered material UZM-8 was added. The mixture was stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 0.89 g 1,5-dibromopentane, (97%) was mixed with 7.36 g 1,4-dibromobutane, (99%), then 9.56 g 1-

methylpyrrolidine, (97%) was added to form a second mixture. The second mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 176 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.15, Na/Al of 0.15, N/Al of 0.90, C/N of 7.59.

[00114] The product generated by this synthesis was calcined under flowing air at 600°C for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75°C followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 38.6% Si, 2.85% Al, <0.01% Na. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 27

[00115] 5.76 g of NaOH, (97%) was dissolved in 111.88 g water. 1.22 g $Al(OH)_3$, (27.9 wt.-% Al), was added to the sodium hydroxide solution. When this became a solution, 37.5 g Ludox AS-40 was added. Next, 0.30 g of the layered material UZM-8 was added and the mixture was stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 1.78 g 1,5-dibromopentane, (97%) was mixed with 6.54 g 1,4-dibromobutane, (99%), then 9.56 g 1-methylpyrrolidine, (97%) was added to form a second mixture. The second mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 176 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.24, Na/Al of 0.107, N/Al of 0.93, C/N of 6.91.

[00116] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75°C followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 38.7% Si, 2.98% Al, 158ppm Na with a BET surface area of 333 m^2/g, pore volume of 0.201 cm^3/g, and micropore volume of 0.164 cm^3/g. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 28

[00117] 5.76 g of NaOH, (97%) was dissolved in 111.88 g water. 1.22 g $Al(OH)_3$, (27.9 wt.-% Al), was added to the sodium hydroxide solution. When this became a solution, 37.5 g Ludox AS-40 was added. Next, 0.30 g of the layered material UZM-8 was added and the mixture was stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 2.67 g 1,5-dibromopentane, (97%) was mixed with 5.73 g 1,4-dibromobutane, (99%), then 9.56 g 1-methylpyrrolidine, (97%) was added to form a second mixture. The second mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 176 hours with stirring at 100 rpm. The product was isolated by filtration. The product was identified as UZM-39 by XRD. The x-ray diffraction pattern is shown in FIG. 5. Analytical results showed this material to have the following molar ratios, Si/Al of 12.15, Na/Al of 0.108, N/Al of 0.86, C/N of 7.68.

[00118] The product generated by this synthesis was calcined under flowing air at 600°C for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75°C followed by a calcination at 500° under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 38.7% Si, 2.98% Al, 79ppm Na. The x-ray diffraction pattern is shown in FIG. 6. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

EXAMPLE 29

[00119] 5.80 g of NaOH, (97%) was dissolved in 111.88 g water. 1.16 g $Al(OH)_3$, (29.32 wt.-% Al), was added to the sodium hydroxide solution. When this became a solution, 37.5 g Ludox AS-40 was added. Next, 0.30 g of the layered material UZM-8 was added and the mixture was stirred vigorously for 1-2 hours. The mixture was cooled to 0°C-4°C. Separately, 4.45 g 1,5-dibromopentane, (97%) was mixed with 4.09 g 1,4-dibromobutane, (99%), then 9.56 g 1-methylpyrrolidine, (97%) was added to form a second mixture. The second mixture was added to the cooled mixture to create the final reaction mixture. The final reaction mixture was vigorously stirred and transferred to a 300 cc stirred autoclave. The final reaction mixture was digested at 160°C for 224 hours with stirring at 100 rpm. The product was isolated by filtration.

The product was identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 11.75, Na/Al of 0.13, N/Al of 0.86, C/N of 7.59.

[00120] The product generated by this synthesis was calcined under flowing air at 600° for 6 hours. It was then ion exchanged four times with 1 M ammonium nitrate solution at 75°C followed by a calcination at 500°C under air for 2 hours to convert NH_4^+ into H^+. Analysis for the calcined, ion-exchanged sample shows 40.1% Si, 3.32% Al, 90ppm Na with a BET surface area of 305 m^2/g, pore volume of 0.224 cm^3/g, and micropore volume of 0.146 cm^3/g. Analysis of the H^+ form of this material by Rietveld XRD refinement gave the results shown in Table 1.

TABLE 1

Example #	% TUN	% IMF
3	100	0
6	95	5
13	83	17
17	46	54
18	36.5	63.5
23	24	76
24	0	100
25	19	81
26	58	42
27	30	70
28	13	87
29	8	92

EXAMPLE 30

[00121] To determine the quantities of TUN or IMF structure able to be detected in a UZM-39 coherently grown composite structure material, a detection limit study was performed. A series of simulated diffraction patterns were electronically created from the observed diffraction patterns of the H^+ forms of Example 3 and Example 24 products using JADE XRD analysis software (available from Materials Data Incorporated). Mixture levels ranged from 1% to 99% TUN and were created by scaling the smaller percentage constituent to the required level, adding the patterns and saving the composite pattern.

[00122] Rietveld analysis was able to quantify the level of IMF in the UZM-39 coherently grown composite structure at the 10% or greater level, however visually, small percentages of IMF can be determined in samples (Figure 12) largely consisting of TUN at the 5% or greater

level from intensity of peak at d-spacing of 9.46A, while at higher levels, other peaks can be followed such as the increase in peak at d-spacing of 11.4A amongst others. In Figure 12, spectrum 1 is 1% IMF, 99% TUN; spectrum 2 is – 3% IMF, 97% TUN; spectrum 3 is – 5% IMF, 95% TUN; and spectrum 4 is – 10% IMF, 90% TUN.

[00123] Rietveld analysis was able to quantify the level of TUN in the UZM-39 coherently grown composite structure at the 10% or greater level, however Figure 13 shows that, visually, small percentages of TUN can be seen in samples largely consisting of IMF at the 5% or greater level from intensity of peak at d-spacing 12.25A, while at higher levels, other peaks can be followed such as the increase in peak at d-spacing of 9.63A amongst others. In Figure 13, spectrum 1 is – 1% TUN, 99% IMF; spectrum 2 is – 3% TUN, 97% IMF; spectrum 3 is – 5% TUN, 95% IMF; and spectrum 4 is – 10% TUN, 90% IMF.

EXAMPLE 31

[00124] 44.9 g of NaOH, (97%) was dissolved in 1122.3 g water. To this solution was added 10.8g liquid sodium aluminate (22.9% Al_2O_3, 20.2% Na_2O) followed by 105.9g Ultrasil VN3 (90% SiO_2, available from Evonik) to form a first mixture. Separately, 53.5g 1,4-dibromobutane, (99%), was combined with 62.6g 1-methylpyrrolidine, (97%) to form a second mixture. The second mixture was added to the first mixture to create the final reaction mixture. Last, 1 g of the layered material UZM-8 was added and the mixture was stirred vigorously for 1-2 hours before transferring to a 2L stirred autoclave. The final reaction mixture was digested at 160°C for 7days while stirring at 200rpm. The product was isolated by filtration and identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 12.40, Na/Al of 0.21, N/Al of 1.10, C/N of 7.06.

EXAMPLE 32

[00125] NaOH, $Al(OH)_3$, Ga(NO3)3•9H_2O, Ludox AS-40, 1,4-dibromobutane, 1-methylpyrrolidine, water and layered material UZM-8 were combined to form a mixture of composition 0.5Al_2O_3 : 0.5 Ga_2O_3 : 65.4 SiO_2 : 24.6 Na_2O : 9.9 C_4Br_2 : 29.4 1-MP : 2636 H_2O and stirred vigorously for 1-2 hours before transferring to a 2L stirred autoclave. The final reaction mixture was digested at 160°C for 150 hours while stirring at 250rpm. The product was isolated by filtration and identified as UZM-39 by XRD. Analytical results showed this material to have the following molar ratios, Si/Al of 21.61, Si/Ga of 31.35, Si/(Al+Ga) of 12.79, Na/(Al+Ga) of 0.10, N/(Al+Ga) of 0.91, C/N of 7.39.

EXAMPLE 33

[00126] A UZM-39 containing a high quantity of TUN and low quantity of IMF in the H+ form was loaded into a vertical steamer. The UZM-39 was exposed to 100% steam at 725°C for 12 hours or 24 hours. The starting UZM-39 had a BET surface area of 385 m^2/g, pore volume of 0.248 cm^3/g, and micropore volume of 0.180 cm^3/g. After 12 hours of steaming, the UZM-39 was still identified as UZM-39 by XRD though the intensity of the first 5 peaks had increased to strong, strong, very strong, strong and medium respectively. All other peaks were at positions and intensities described in Table B. The material had a BET surface area of 331 m^2/g, pore volume of 0.243 cm^3/g, and micropore volume of 0.151 cm^3/g. After 24 hours of steaming, the UZM-39 was still identified as UZM-39 by XRD though the intensity of the first 5 peaks had increased to medium-strong, strong, strong, medium-strong and medium respectively. All other peaks were at positions and intensities described in Table B. The material had a BET surface area of 327 m^2/g, pore volume of 0.241 cm^3/g, and micropore volume of 0.150 cm^3/g.

EXAMPLE 34

[00127] A UZM-39 containing a high quantity of TUN and low quantity of IMF in the H+ form was put into a round bottom flask containing 6N HNO_3 and outfitted with a condenser and stirrer. The mixture containing UZM-39 and HNO_3 was boiled at reflux for 8 or 16h. The resulting material was filtered, washed and dried. XRD analysis showed the material to be UZM-39 consistent with Table B.

EXAMPLE 35

[00128] The product generated by the synthesis described in Example 1 was bound with SiO_2 in a 75:25 weight ratio by combining 6.71 g Ludox AS-40, 8.31 g UZM-39 and 10.79 g water. This mixture was then evaporated while stirring to form the bound UZM-39/SiO_2. The bound material was then calcined using a 2°C/minute ramp to 550°C, holding for 3 hours and then cooling to room temperature. The 20 to 60 mesh fraction was isolated and then used as the catalytic composite in a chemical reaction to form ethylbenzene and xylenes.

[00129] Benzene and propane were fed at a 2:1 mole ratio into a reactor at 410 psig along with a hydrogen stream such that the hydrogen to hydrocarbon mole ratio was 3.5. Multiple conditions where then set starting at 425°C and 1.8 LHSV (Table 2 and Table 3 Column 1) and

continuing to 485°C and 1.8 LSVH (Table 2 and Table 3 Column 2); continuing again to 535°C and 1.8 LHSV (Table 2 and Table 3 Column 3); continuing again to 535°C and 3 LHSV (Table 2 and Table 3 Column 4); and finally continuing to 575°C and 3 LHSV (Table 2 and Table 3 Column 5). Table 2 shows the percent of benzene and propane conversion to other compounds. Table 3 shows the toluene plus C8 aromatic yield calculated by multiplying selectivity to product with benzene conversion.

TABLE 2

Percent Conversion	Column 1	Column 2	Column 3	Column 4	Column 5
Benzene	7.43	16.15	26.19	22.90	26.79
Propane	57.58	61.58	81.35	68.79	86.50

TABLE 3

Yield	Column 1	Column 2	Column 3	Column 4	Column 5
Toluene plus C8 aromatic	1.9	4.9	14.7	12.5	13.4

The experiment was repeated using bound MFI catalyst as a comparative example. The process of the invention showed 2-3 times the selectivity to C8 aromatics as compared to the results when using the bound MFI. Furthermore, the process of the invention resulted in very little formation of cyclohexane which in turn increases the purity of a potential benzene cut.

CLAIMS:

1. A process for dehydrocyclodimerization comprising contacting a feed comprising at least one aliphatic hydrocarbon having from 2 to 6 carbon atoms per molecule with a microporous crystalline zeolitic catalytic composite at dehydrocyclodimerization conditions to produce at least one aromatic hydrocarbon, the catalytic composite comprising at least a coherently grown composite of TUN and IMF zeotypes having a three-dimensional framework of at least AlO_2 and SiO_2 tetrahedral units and an empirical composition in the as synthesized and anhydrous basis expressed by an empirical formula of:

$$Na_nM_m^{k+}T_tAl_{1-x}E_xSi_yO_z$$

where "n" is the mole ratio of Na to (Al + E) and has a value from 0.05 to 0.5, M represents at least one metal selected from the group consisting of zinc, Group 1 (IUPAC 1), Group 2 (IUPAC 2), Group 3 (IUPAC 3), and the lanthanide series of the periodic table, and any combination thereof, "m" is the mole ratio of M to (Al + E) and has a value from 0 to 0.5, "k" is the average charge of the metal or metals M, T is the organic structure directing agent or agents derived from reactants R and Q where R is an A,Ω-dihalogen substituted alkane having from 3 to 6 carbon atoms and Q is at least one neutral monoamine having 6 or fewer carbon atoms, "t" is the mole ratio of N from the organic structure directing agent or agents to (Al + E) and has a value of from 0.5 to 1.5, E is an element selected from the group consisting of gallium, iron, boron and combinations thereof, "x" is the mole fraction of E and has a value from 0 to 1.0, "y" is the mole ratio of Si to (Al + E) and varies from greater than 9 to 25 and "z" is the mole ratio of O to (Al + E) and has a value determined by the equation:

$$z = (n + k \bullet m + 3 + 4 \bullet y)/2$$

and is characterized in that it has the x-ray diffraction pattern having at least the d-spacings and intensities set forth in Table A1:

TABLE A1

2θ	d (Å)	I/Io %
7.17-7.21	12.25-12.31	vw-m
7.5-8.1*	11.78-10.91	w-m
8.88	9.95	m
9.17	9.63	w-m
12.47-12.62	7.09-7.00	w-m

17.7	5.01	vw-m
22.8-23.2	3.90-3.83	vs
23.39-23.49	3.80-3.78	m-s
25.01-25.31	3.56-3.52	m
28.74-29.25	3.10-3.05	w-m
45.08-45.29	2.01-2.00	w

*composite peak consisting of multiple overlapping reflections

2. The process of claim 1 wherein the coherently grown composite of TUN and IMF zeotypes has a micropore volume as a percentage of total pore volume of greater than 60%.

3. The process of Claim 1 wherein the dehydrocyclodimerization conditions include a temperature from 350°C to 650°C (662°F to 1202°F), a pressure from 0 to 300 psi(g) (0 to 2068 kPa(g)), and a liquid hourly space velocity from 0.2 to 5 hr^{-1}.

4. The process of claim 1 wherein the catalytic composite further comprises gallium and a binder.

5. The process of Claim 1 wherein the dehydrocyclodimerization conditions include a temperature in the range from 400°C to 600°C (752°F to 1112°F), a pressure in or the range from 0 to 150 psi(g) (0 to 1034 kPa(g)), and a liquid hourly space velocity of between 0.5 to 3.0 hr^{-1}.

6. The process of claim 1 wherein the at least one aromatic hydrocarbon is benzene, toluene, or a xylene.

7. The process of claim 1 wherein the feed is selected from the group consisting of C_3 and/or C_4 derived streams from FCC cracked products, light gasses from a delayed coking process, and liquefied petroleum gas streams.

8. The process of claim 1 wherein the product stream further comprises light hydrocarbons which are separated from the product stream and recycled to the contacting with a catalytic composite step or wherein the product stream comprises benzene and xylenes the process further comprising separating the benzene and recycling the separated benzene to the contacting with a catalytic composite step.

9. The process of claim 1 wherein the catalytic composite is located in one or more catalyst zones arranged in series or parallel configuration, and wherein the catalytic composite may be in fixed beds or fluidized beds.

10. The process of claim 1 wherein the microporous crystalline zeolitic catalytic composite has a micropore volume as a percentage of total pore volume of less than 60%.

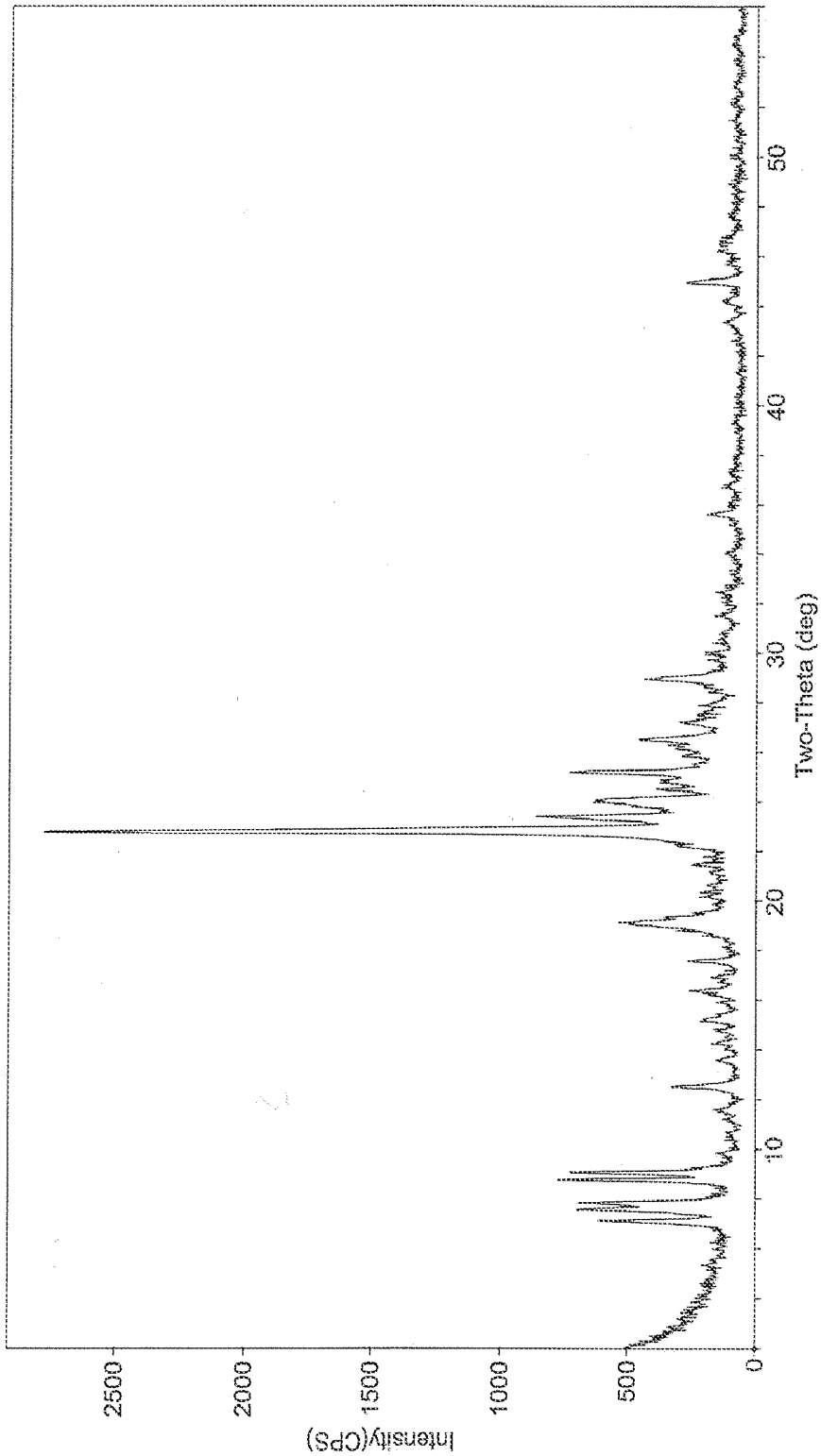

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Two-Theta (deg)

FIG. 1

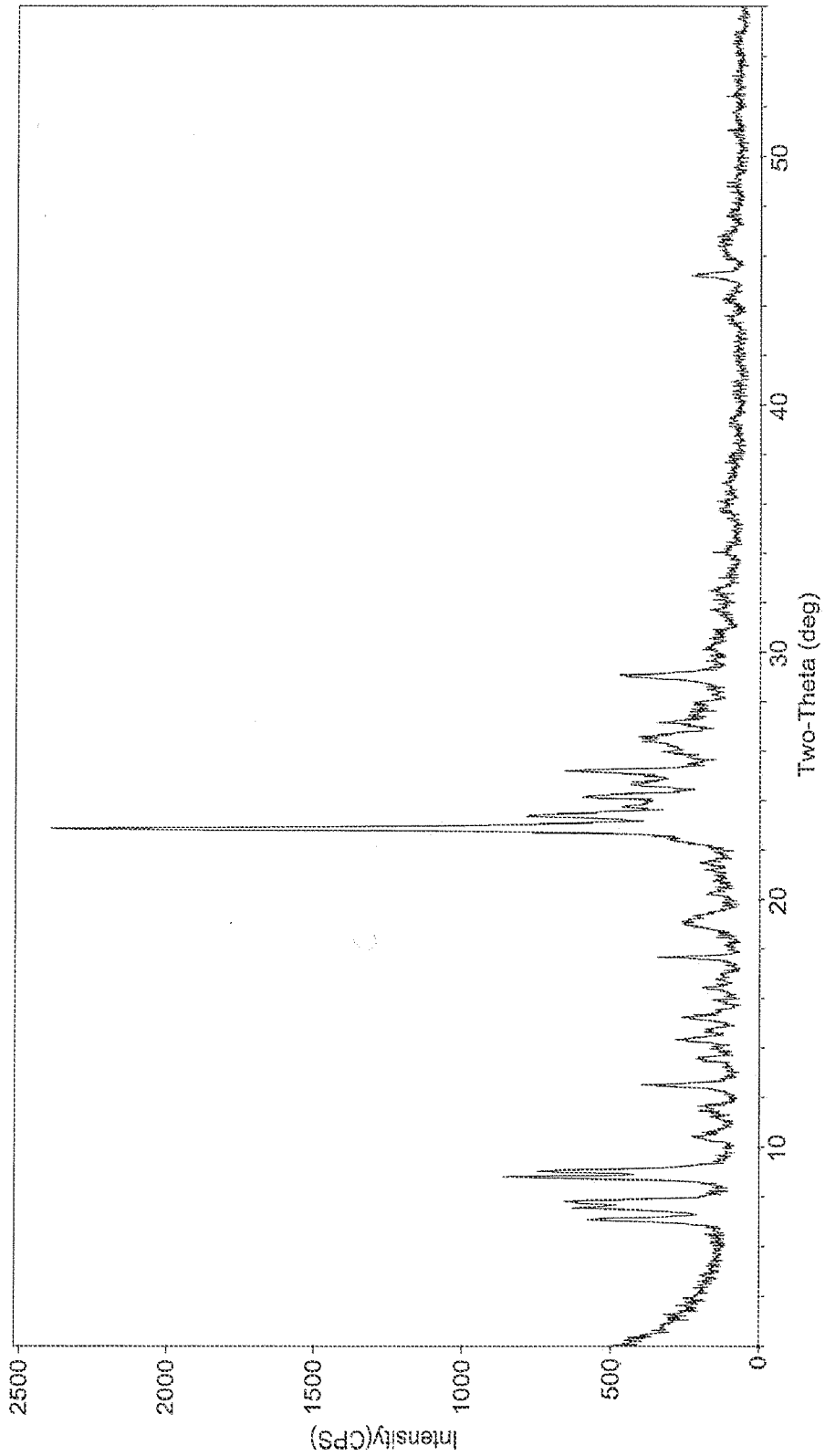

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FIG. 2

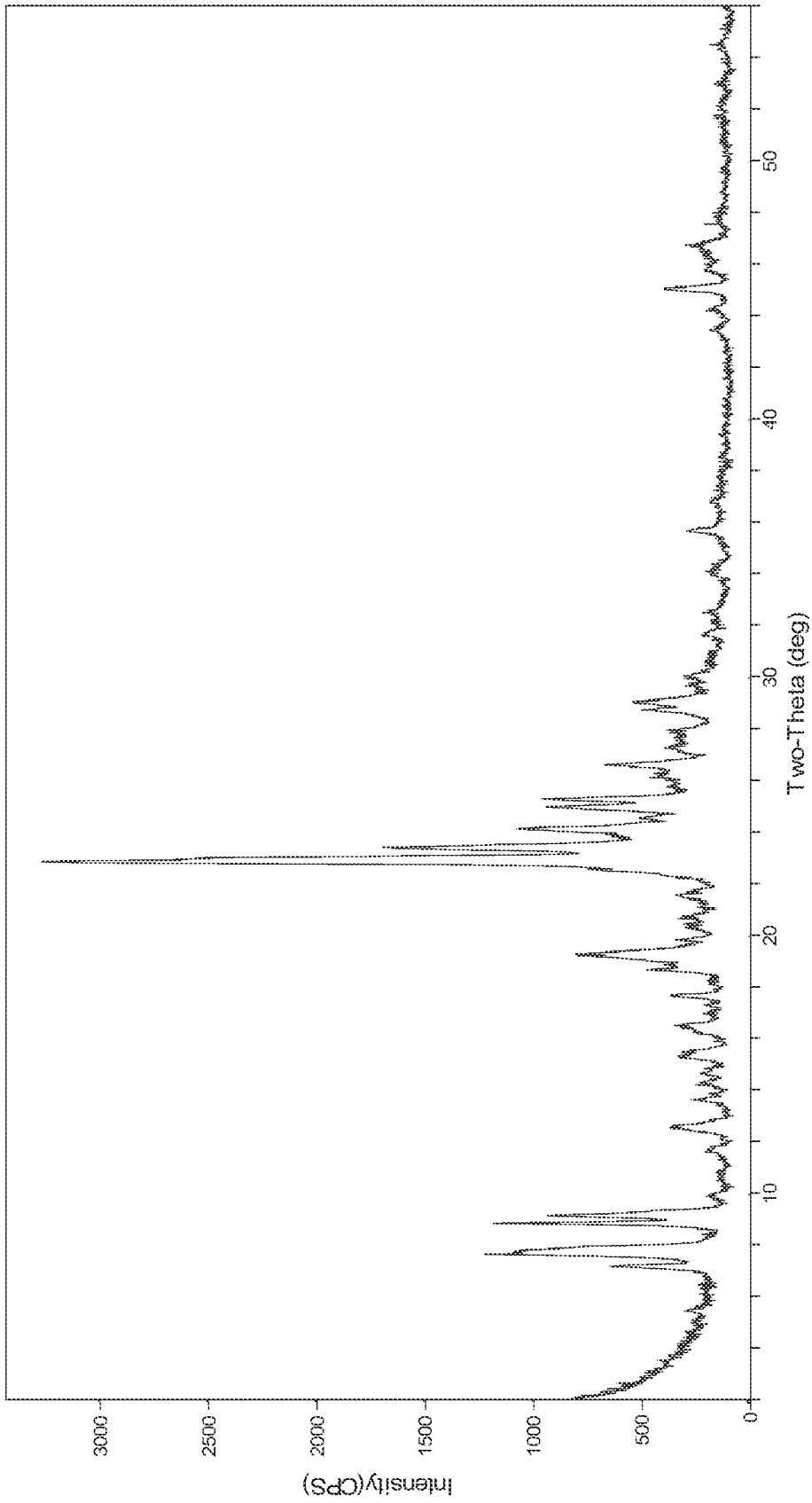

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FIG. 3

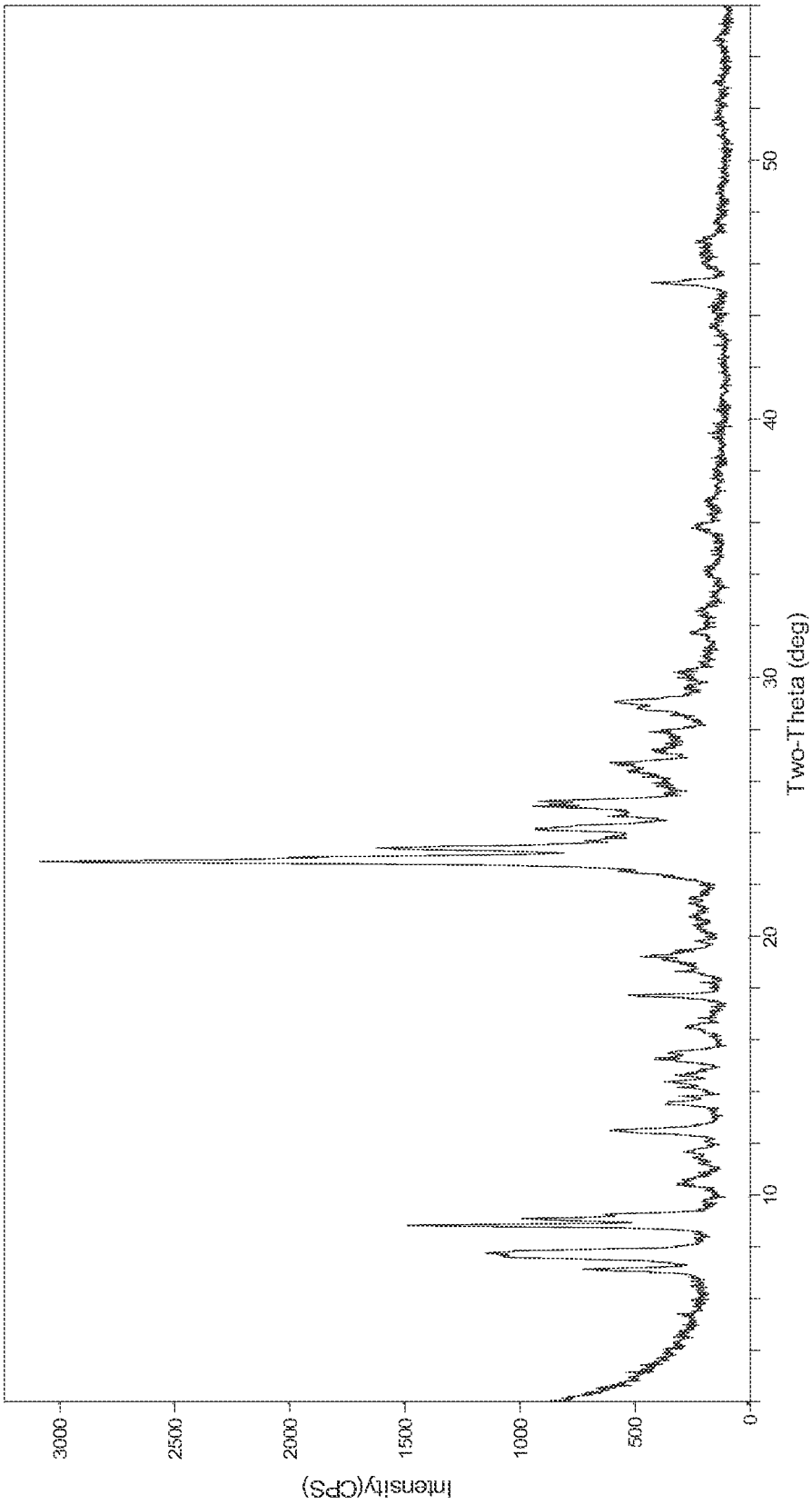

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Two-Theta (deg)

FIG. 4

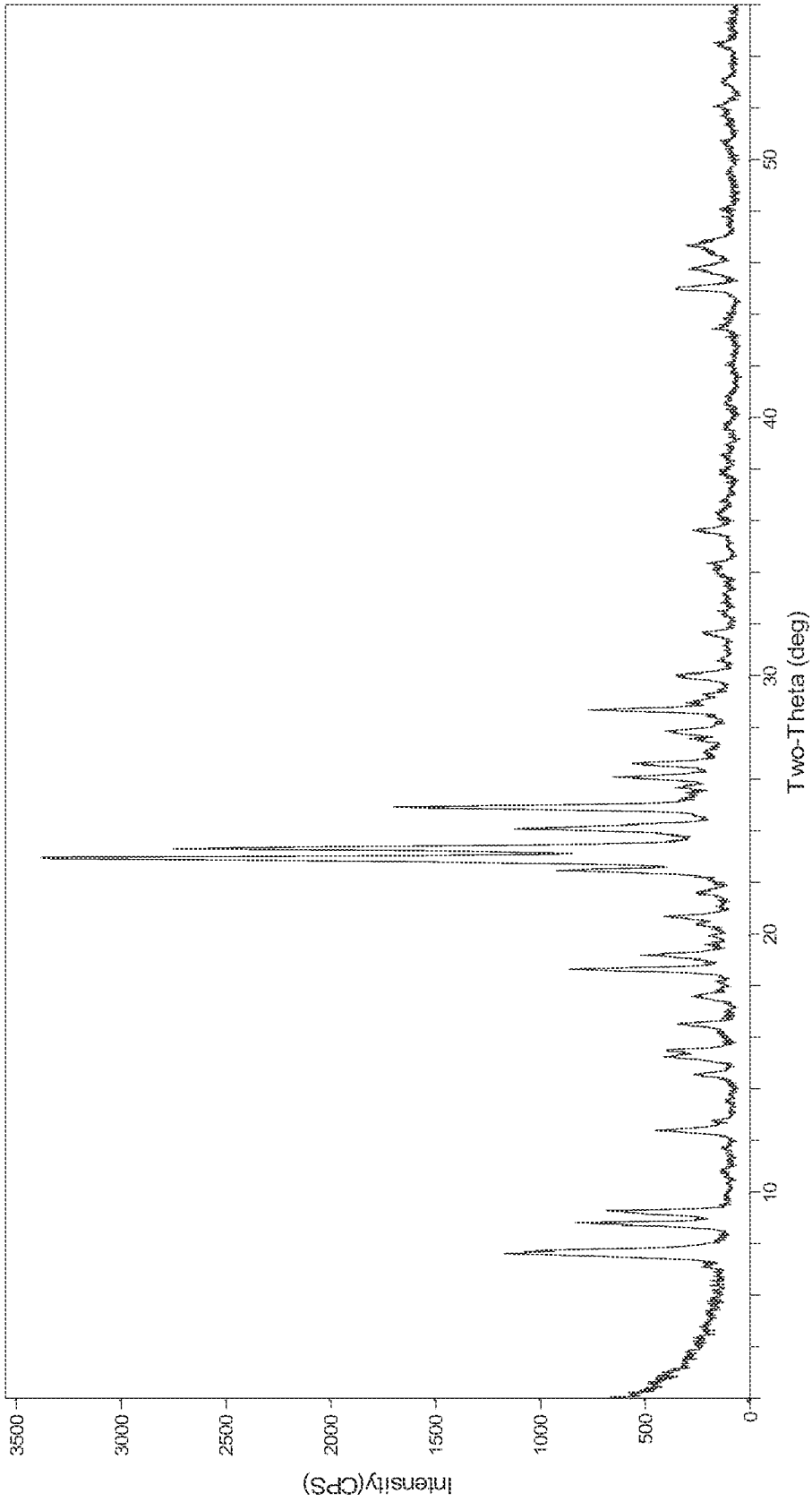

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Two-Theta (deg)

FIG. 5

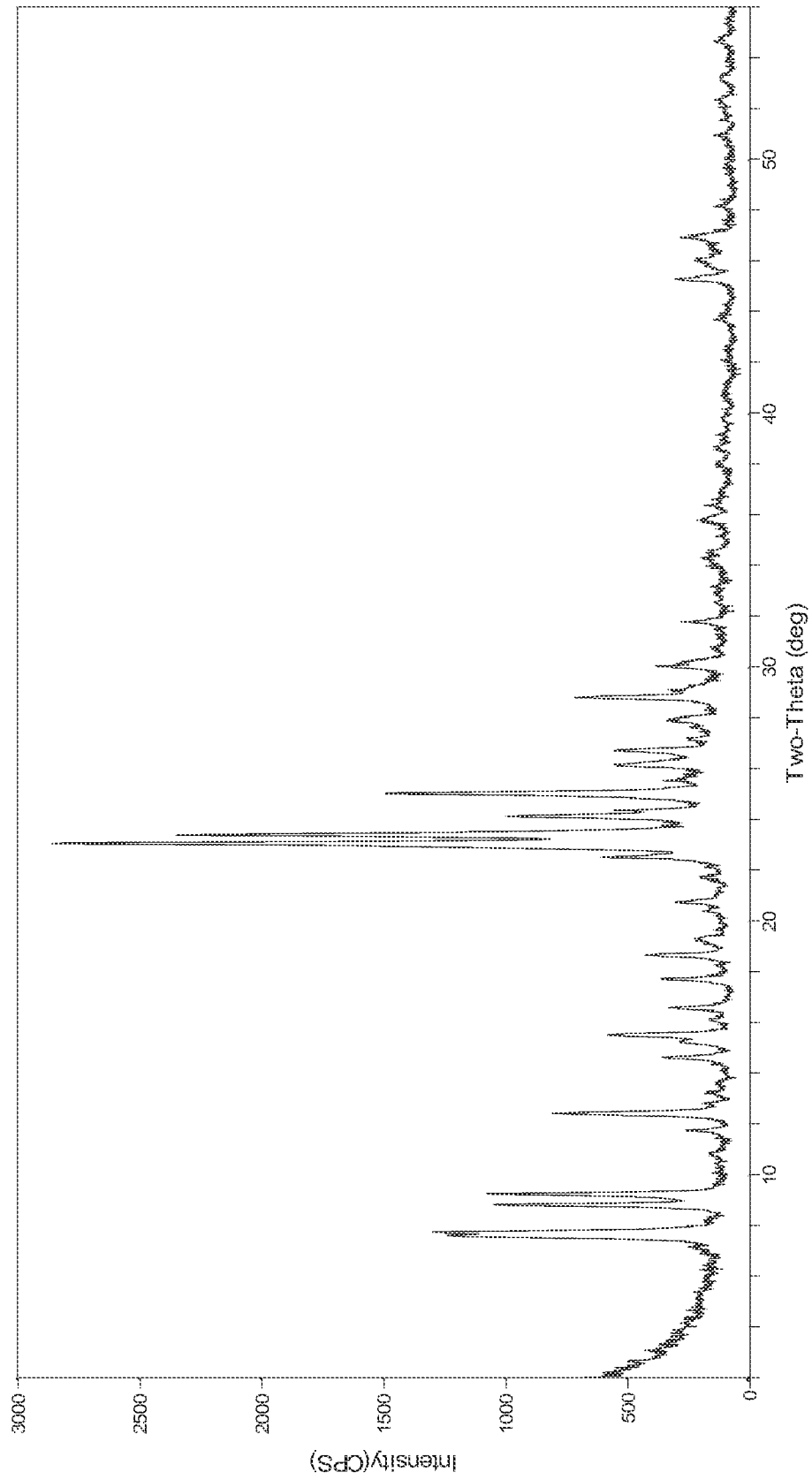

Intensity(CPS)
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Two-Theta (deg)

FIG. 6

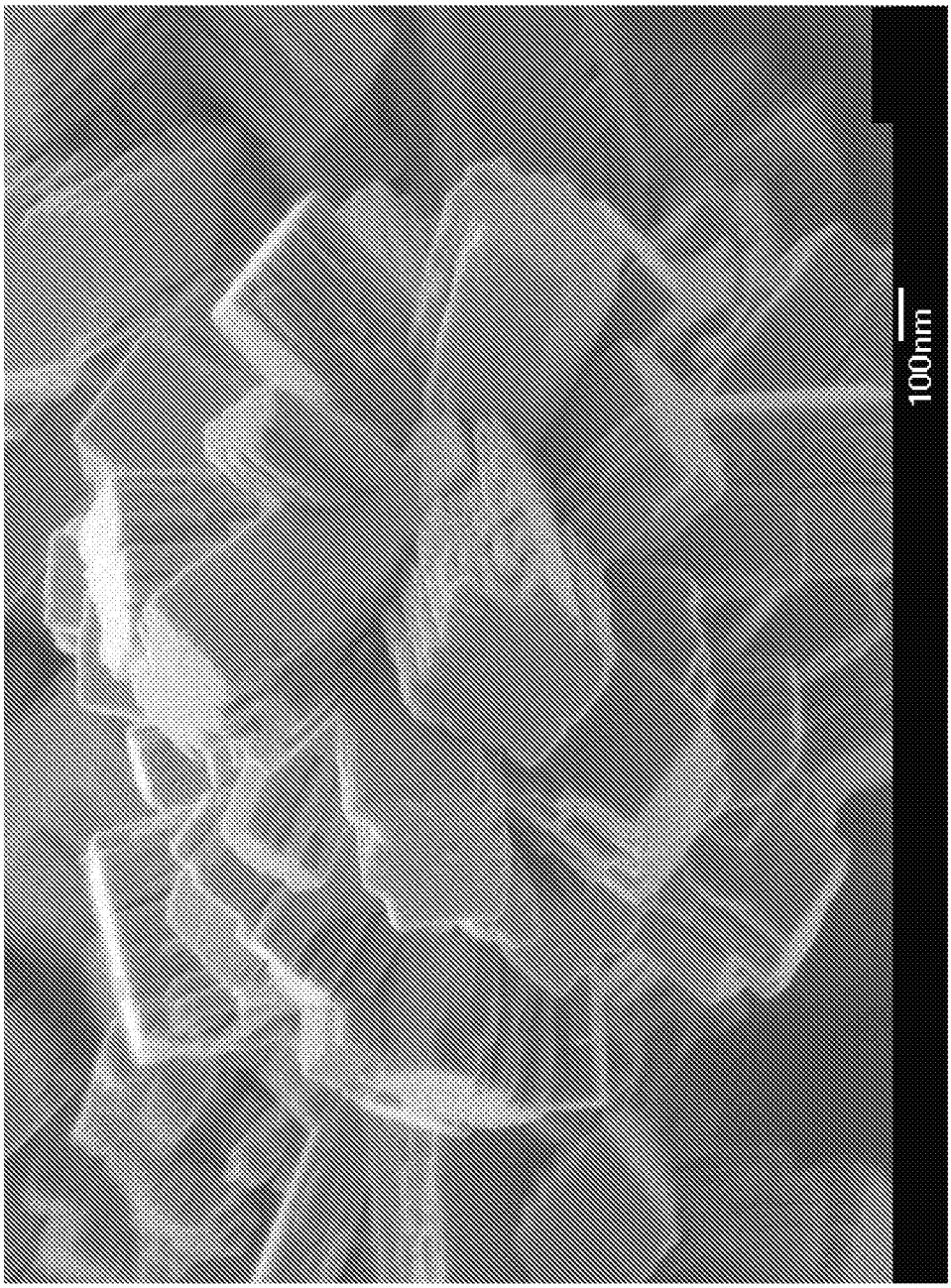


FIG. 7

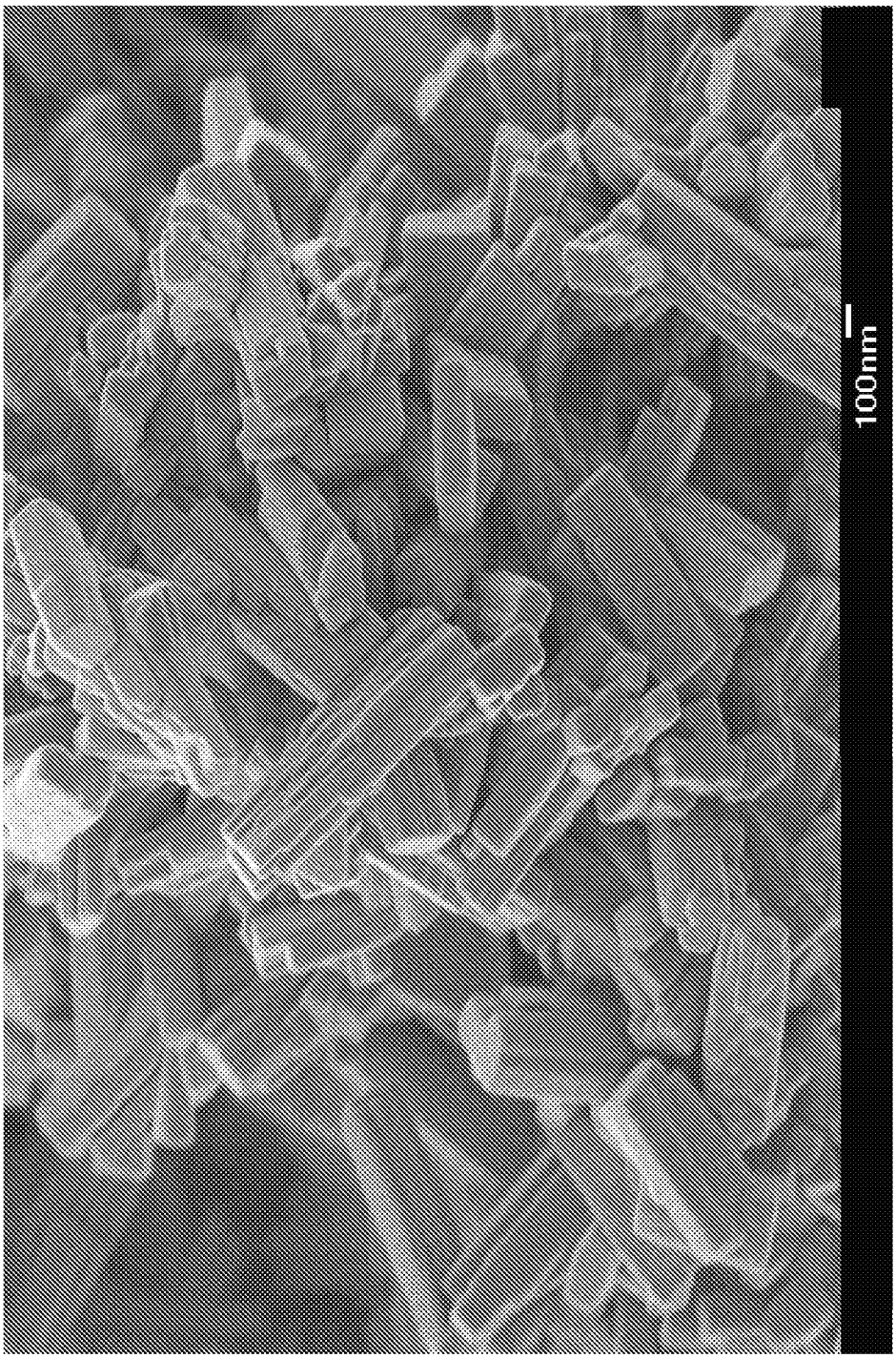
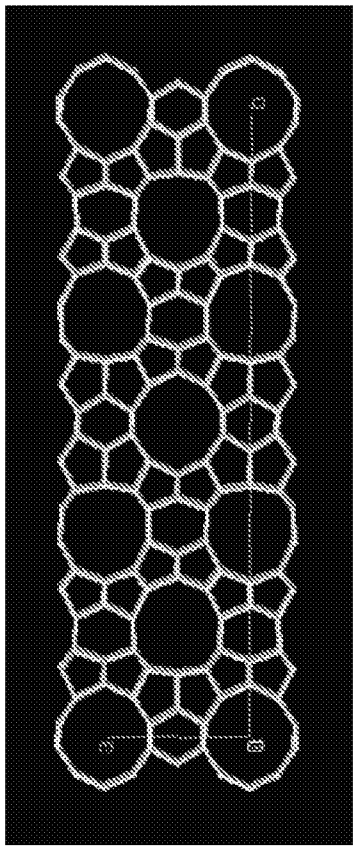


FIG. 8



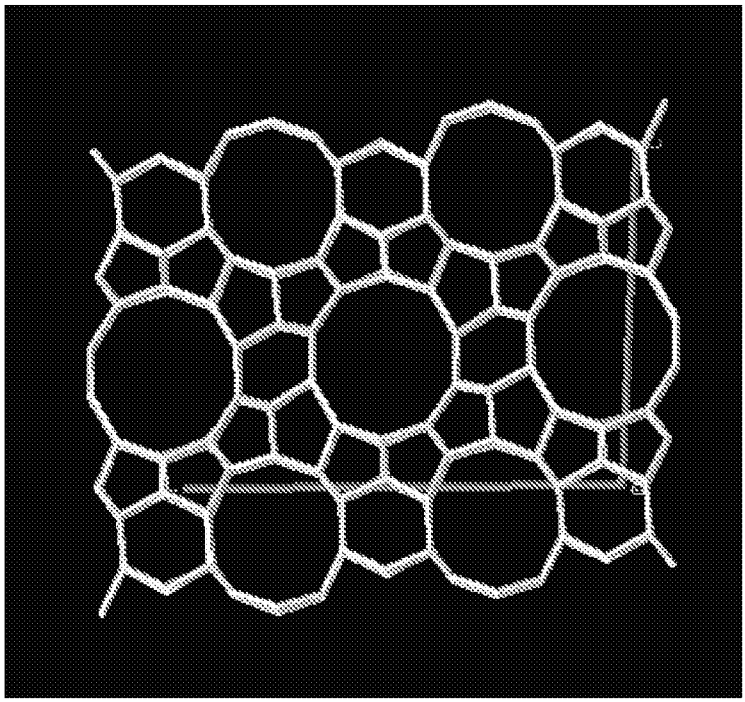


FIG. 9

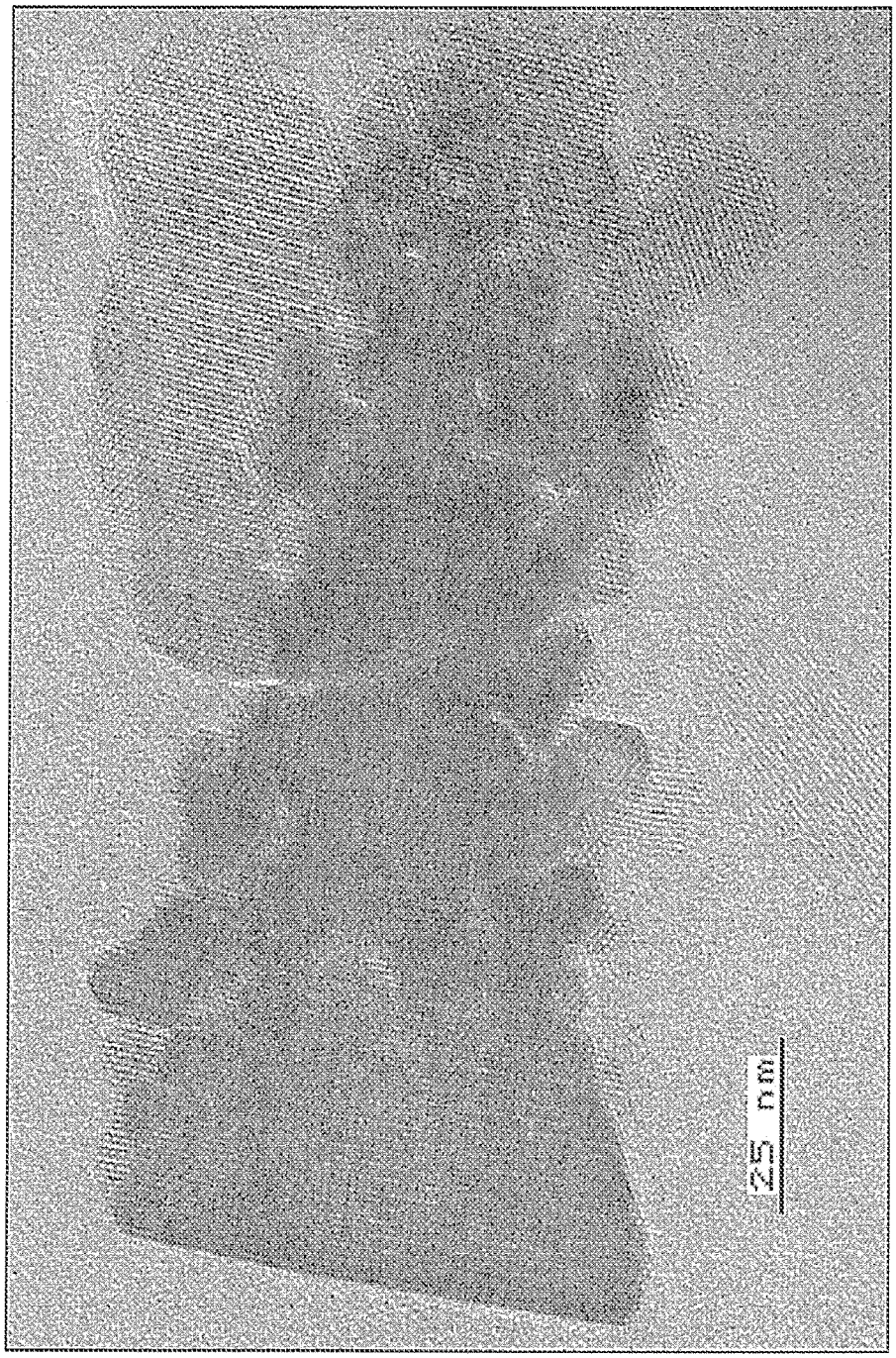


FIG. 10

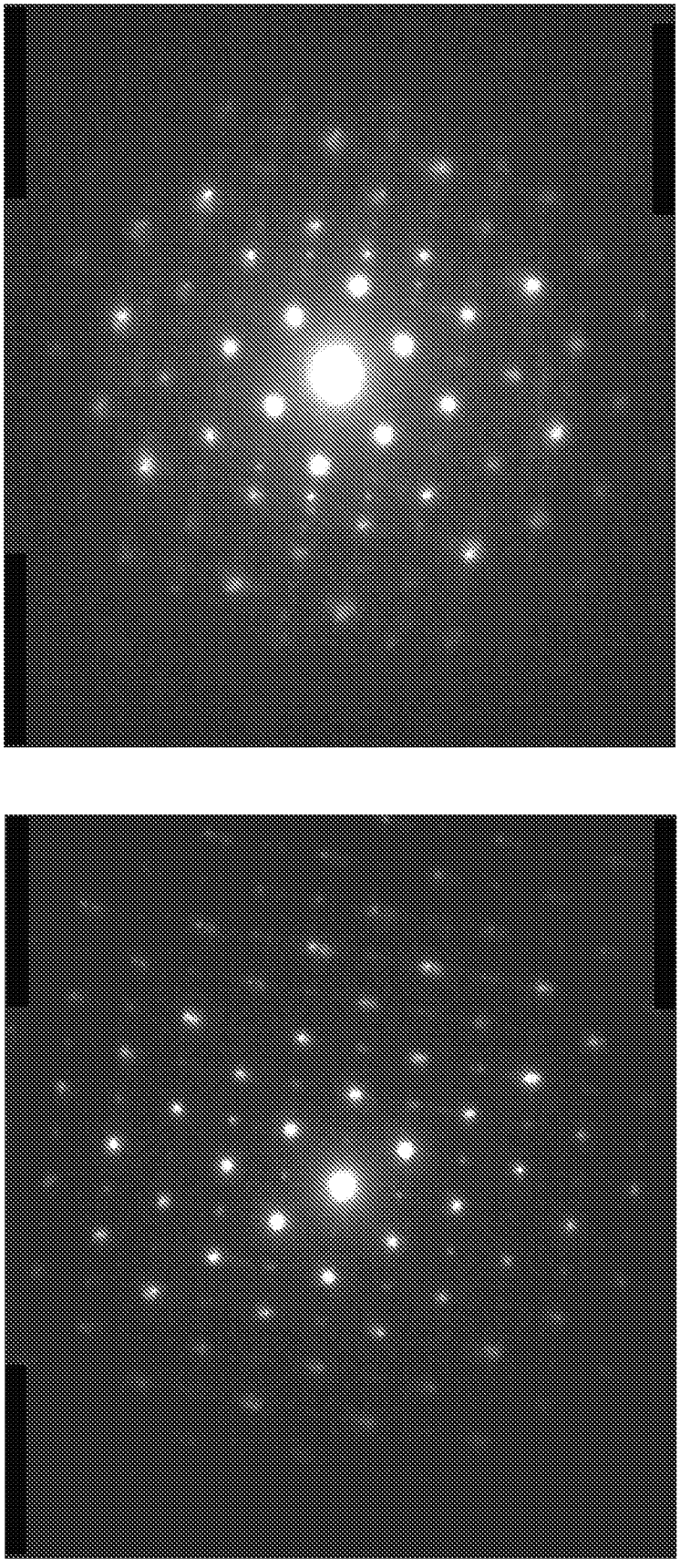


FIG. 11

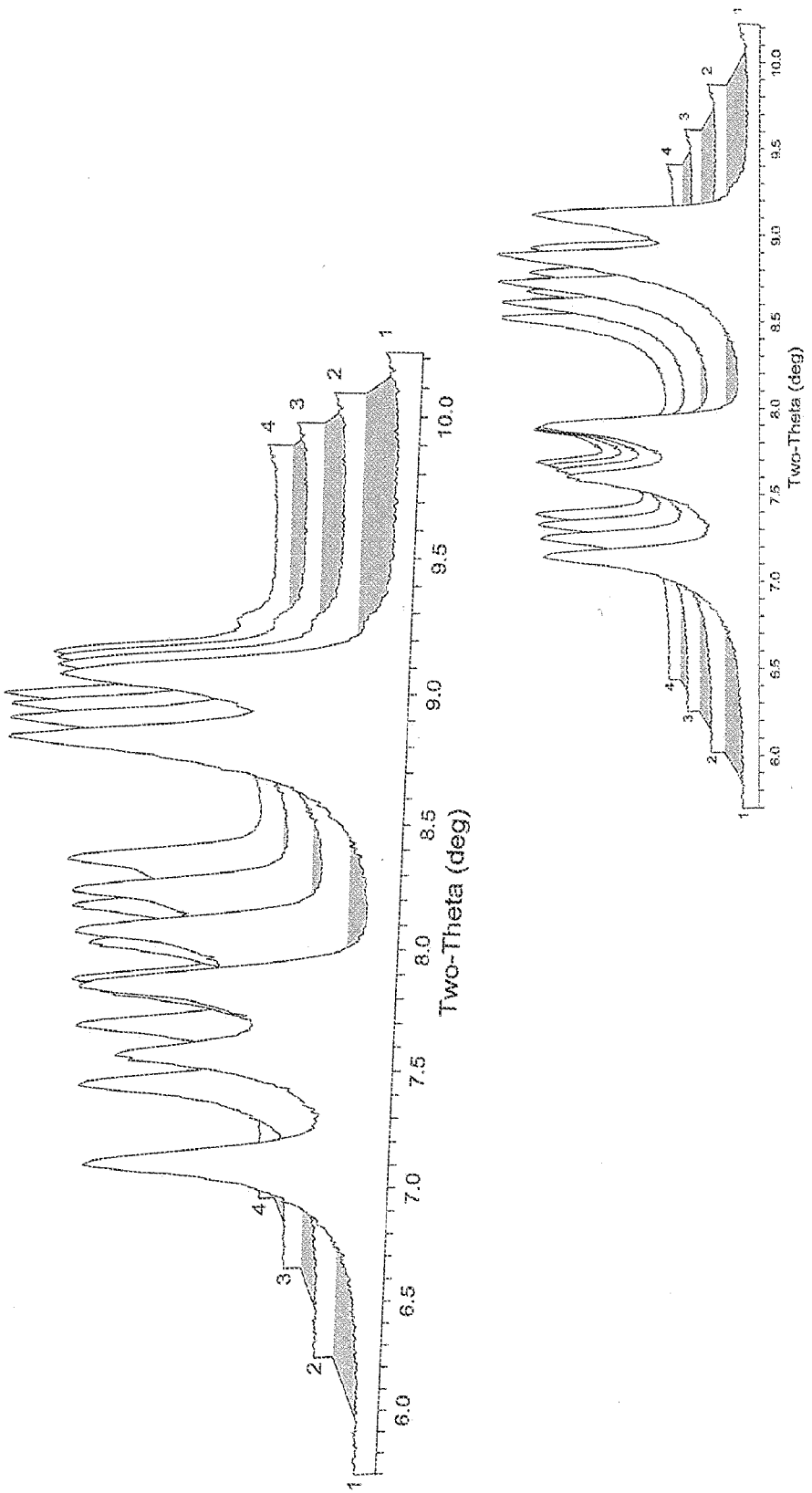

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1
2
3
4
Two-Theta (deg)
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6.5
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7.5
8.0
8.5
9.0
9.5
10.0
1
2
3
4

FIG. 12

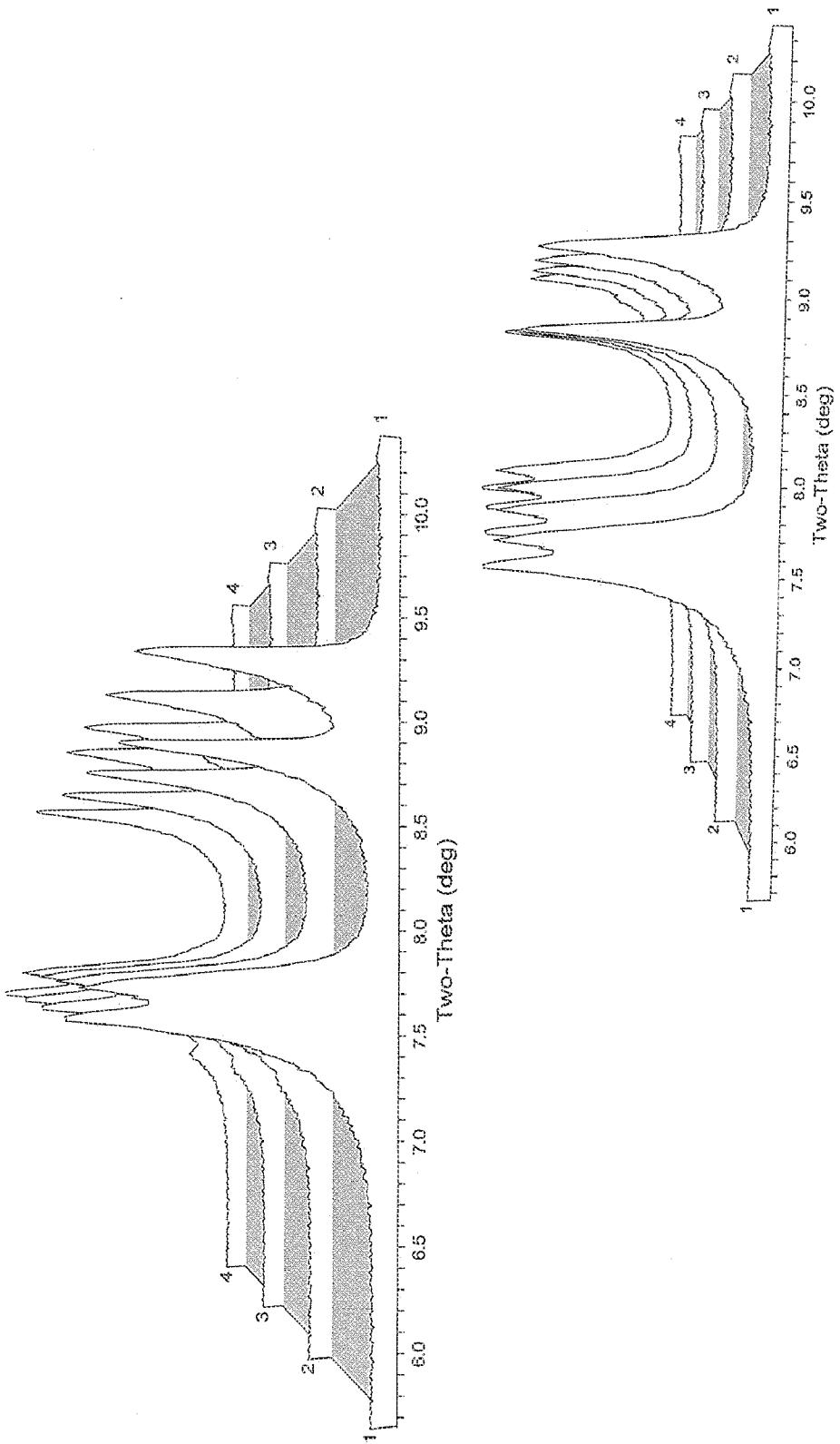

Two-Theta (deg)
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6.5
7.0
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9.0
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10.0
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2
3
4
Two-Theta (deg)
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6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
1
2
3
4

FIG. 13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2013/074241

A. CLASSIFICATION OF SUBJECT MATTER

C07C 2/76 *(2006.01)*
C07C 15/00 *(2006.01)*
C01B 39/48 *(2006.01)*
B01J 29/70 *(2006.01)*
B01J 29/86 *(2006.01)*
B01J 29/87 *(2006.01)*
B01J 29/88 *(2006.01)*

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)

C07C 2/76, 15/00, C01B 39/48, B01J 29/70, 29/86, 29/87, 29/88

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)

RUPAT, EAPATIS, Espacenet, PAJ, USPTO, CIPO, DEPATIS, Patentscope, DWPI, Information Retrieval System of FIPS (http://www1.fips.ru/wps/portal/Registers/)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0226422 A1 (UOP INC.) 24.06.1987, abstract, p. 2, lines 4-30, claims	1-10
A	US 2002/0151757 A1 (KERRY O. BOEHNER et al.) 17.10.2002, abstract, claims	1-10
A	RU 2139844 C1 (FALKEVICH GENRIKH SEMENOVICH et al.) 20.10.1999, abstract, p. 5, lines 39-53, p. 6, lines 1-5	1-10

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 March 2014 (04.03.2014)	20 March 2014 (20.03.2014)
Name and mailing address of the ISA/ FIPS Russia, 123995, Moscow, G-59, GSP-5, Berezhkovskaya nab., 30-1 Facsimile No. +7 (499) 243-33-37	Authorized officer A. Lyskova Telephone No. (495)531-64-81

Form PCT/ISA/210 (second sheet) (July 2009)