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- (71) **Applicant (for all designated States except US):** GEORGIA TECH RESEARCH CORPORATION [US/US]; 505 Tenth Street, NW, Atlanta, GA 30332-0415 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** ZHOU, Zhengzhi [CN/US]; c/o Georgia Tech Research Corporation, 505 Tenth Street, NW, Atlanta, GA 30332-0415 (US). NAIR, Sankar [IN/US]; c/o Georgia Tech Research Corporation, 505 Tenth Street, NW, Atlanta, GA 30332-0415 (US).
- (74) **Agents:** VALOIR, Tamsen et al.; Boulware & Valoir, 3 Riverway, Suite 950, Houston, TX 77056 (US).
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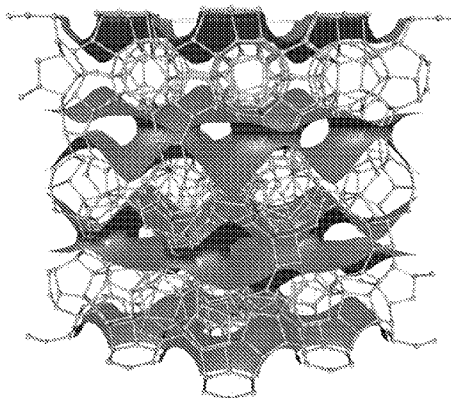
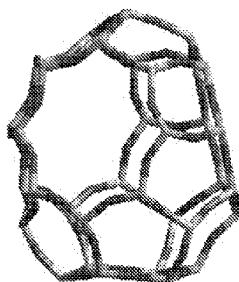
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(54) **Title:** ZEOLITE DDR NANOCRYSTALS

FIGURE 1

DDR building block

DDR pore structure



(57) **Abstract:** DDR nanocrystals were synthesized using hydrothermal secondary growth. The morphology of the nanoparticles can be manipulated by changing the ratio of silica to water, the synthesis temperature, and the mineralizing agents. Specifically, nanocrystals with morphology of hexagonal plates, octahedral, and diamond-like plates are disclosed. These nanoparticles can be used as seed coatings for DDR membrane growth on substrates, and for the fabrication of mixed matrix membranes, and for any other use where uniform, small DDR zeolite crystals are beneficial.

ZEOLITE DDR NANOCRYSTALS

PRIOR RELATED APPLICATIONS

[0001] This application claims priority to US Provisional Application, serial no. 61/471238, filed April 4, 2011, and expressly incorporated by reference herein in its entirety.

FEDERALLY SPONSORED RESEARCH STATEMENT

[0002] Not applicable.

FIELD OF THE INVENTION

[0003] New methods for synthesizing DDR zeolite nanocrystals (200-2000 nanometers in size) are disclosed using hydrothermal secondary growth (seeded growth). By changing the ratio of silica to water, the synthesis temperature, and the mineralizing agents, the morphology and size of the crystals can be manipulated. Specifically, crystals with morphology of hexagonal plates, octahedral, and diamond-like plates are disclosed. These crystals can be used as seed coatings for DDR membrane growth on substrates, and for the fabrication of mixed matrix membranes, among other uses.

BACKGROUND OF THE INVENTION

[0004] The term "zeolite" was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had previously been adsorbed into the material. Based on this, he called the material zeolite, from the Greek zeo, meaning "boil" and lithos, meaning "stone".

[0005] We now know that zeolites are microporous, aluminosilicate or silicate minerals. As of November 2010, 194 unique zeolite frameworks have been

identified (DDR being one of them), and over 40 naturally occurring zeolite frameworks are known.

[0006] Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and many others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite.

[0007] The regular pore structure and the ability to vary pore size, shape and chemical nature makes zeolites very useful as molecular sieves. Depending on their structure and composition, zeolites can separate molecules based on adsorption and/or diffusion of certain molecules preferentially inside the pores or exclusion of certain molecules based on their size. The pore size is typically less than 2 nm and comparable to that of small molecules, allowing the use of zeolites to separate lightweight gases such as CO₂ and CH₄.

[0008] The maximum size of a species that can enter the pores of a zeolite is controlled by the dimensions of the channels in the zeolite. These are conventionally defined by the ring size of the aperture, where, for example, the term "8-ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminum) atoms and 8 oxygen atoms. The rings are not always symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical. The DDR zeolite of this invention has an 8-ring structure (see FIG. 1).

[0009] Thus, zeolites are widely used in industry for water purification, as catalysts, and in nuclear reprocessing. Their biggest use is in the production of laundry detergents, and they are also used in medicine and in agriculture.

[0010] In particular, zeolites have been used in two types of molecular sieving membranes: mixed matrix membranes and pure zeolite membranes. To fabricate a mixed matrix membranes, zeolite crystals are first dispersed in a polymer solution. The dispersion is then cast into a film or spun into a tubular hollow fiber. Since the membrane

thickness is desired to be less than 1 micron, it is necessary to have submicron zeolite particles.

[0011] In pure zeolite membrane fabrication, zeolite crystals are first deposited as a “seed” coating on a porous substrate and then grown into a thin continuous layer known as a zeolite membrane. The porous substrate provides mechanical stability for the membrane. In this approach crystals with submicron size are also preferred because the seed coatings will then be tightly packed and of high quality. Further, membrane thickness is ideally about 0.5-5 microns.

[0012] Among the various zeolite materials, DDR is a pure silica (SiO_2) zeolite. The dimensions of the molecular sieving pores of the DDR zeolite are 3.6×4.4 angstrom. Due to its relatively small pore size, DDR can be used to separate light gases, such as CO_2 (kinetic diameter = 3.3 angstroms) from CH_4 (diameter = 3.8 angstroms). Other advantages of DDR zeolites include high thermal stability and chemical resistance due to the pure silica composition.

[0013] DDR zeolite crystals were first synthesized in 1986¹ and the synthesis was further developed by several researchers²⁻⁴. These synthesis methods either take long time (9-25 days) or produce very large crystals (20 to 50 micrometers). DDR zeolite membranes were first reported in 2004⁵ and the results showed that CO_2/CH_4 selectivity was 220 at 301°K with feed pressure of 0.5 MPa.

[0014] However, there is no prior art on the synthesis of micron or nanometer sized DDR crystals, which are critical in fabricating high-quality membranes. In this disclosure, methods for synthesizing nanometer to micron size DDR zeolite crystals are described. Not only can the size and shape of the DDR crystal be controlled, but the synthesis time is significantly shortened. Thus, the methods and compositions described herein are a significant improvement on the prior art.

SUMMARY OF THE INVENTION

[0015] The present invention describes a technique to synthesize DDR zeolite crystals with size in the range of 200 nanometers up to 2 microns and with control

over the morphology and size of the crystals. The synthesis was carried out using seed growth under hydrothermal conditions with mixing. The raw materials solution contains organic template 1-Adamantanamine (ADA), a silica source such as Ludox AS-30 colloidal silica (SiO₂), Deionized water (DI), and Potassium Fluoride (KF) and optionally other cations, such as K⁺, Na⁺, Ca²⁺, Mg²⁺ and others, can be added to fine tune the zeolites. The range of molar ratios of these chemicals and other parameters are as follows:

ADA/SiO ₂ : 0.06 to 0.5
KF/SiO ₂ : 0.5 to 1.0
DI/SiO ₂ : 2000 to 14000
KOH : 0-2
Heating time 4-72 hrs, preferably 6-12 hours for nanocrystals, and about 36-60 hrs for micron sized crystals
Shorter heat treatment (6-12 hrs) results in smaller crystals (2-500 nm)
Longer heat treatment (about 36-60, preferably 48 hrs) results in larger crystals (2 μm)
Temperature 100-200°C, preferably 130-150°C or anything in-between or greater than or equal to 160°C.
Temperature ≤150°C results in nanometer octahedrons
Temperatures ≤150°C plus KOH (1-2 molar ratio) results in hexagonal plates
Temperatures ≥160°C results in diamond-like structures

[0016] Generally speaking, a method of making DDR zeolite crystals is provided, wherein the method comprises combining 1-adamantanamine (“ADA”), deionized water, a silica source, potassium fluoride (“KF”), and optionally a source of cations. This is mixed for a period of time and then seed crystals are added to said mixture. While continuing to mix, the mixture is heated at 100-200°C for 4-72 hours to make DDR zeolite crystals of 200-2000 nm. If needed for the application, the crystals can be washed and further calcined to remove the ADA.

[0017] In preferred embodiments, the mixture comprises xADA: 100 SiO₂: yKF: zH₂O: mKOH, wherein x is between 6 and 50, y is between 50 and 100, z is between 2000 and 14000, and m is between 0 to 2. Further preferred embodiments include, initial mixing between 30 minutes and 6 hours; temperature of 130-160°C; heating time between 6 hour and 12 hours.

[0018] The invention also includes the various DDR zeolite crystals made according to the above methods, including crystals having the following characteristics: a)

size in the range of 200 to 2000 nm, b) a morphology selected from the groups consisting of diamond-like, octahedron, or hexagonal plate, c) a BET surface area in the range of 340 m²/g to 380 m²/g and d) a pore volume from 0.123 to 0.132 ml/g. Also invented are crystals being octahedral of 1000-4000 nm, diamond plate of 200-500 nm, octahedral of 200-500 nm and hexagonal plates, preferably of 200-500 nm. The sizes provided herein are average sizes, and preferably are $\pm 20\%$ and more preferably $\pm 10\%$ or 5% .

[0019] The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims or the specification means one or more than one, unless the context dictates otherwise.

10 **[0020]** The term “about” means the stated value plus or minus the margin of error of measurement or plus or minus 10% if no method of measurement is indicated.

[0021] The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or if the alternatives are mutually exclusive.

15 **[0022]** The terms “comprise”, “have”, “include” and “contain” (and their variants) are open-ended linking verbs and allow the addition of other elements when used in a claim.

[0023] The phrase “consisting of” is a closed linking verb, and does not allow the inclusion of other elements.

20 **[0024]** The phrase “consisting essentially of” occupies a middle ground, and does not allow the inclusion of other material elements, but allows the inclusion of non-material elements that do not materially change the invention, such as different buffers, salts, drying steps, rinsing steps, re-precipitation steps, post-synthesis steps, and the like.

[0025] The following abbreviations are used herein:

ADA	1-Adamantanamine
BET surface area	BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for the measurement of the specific surface area of a material. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory in a journal for the first time; “BET” consists of the first initials of their family names. Methods of calculating same are provided in the

	literature (e.g., en.wikipedia.org/wiki/BET_theory)
DDR	Refers to a type of silica zeolite with an 8 ring structure, as shown in Figure 1.
DI	Deionized water
DLS	Dynamic light scattering
HR	Hour(s)
KF	Potassium Fluoride
KOH	Potassium hydroxide
PDI	Polydispersity index—a measure of the distribution of molecular mass in a given polymeric sample. The PDI calculated is the weight average molecular weight divided by the number average molecular weight. It indicates the distribution of individual molecular masses in a batch of polymers. The PDI has a value equal to or greater than 1, but as the polymer chains approach uniform chain length, the PDI approaches unity. PDI was measured herein by DLS, which gives the size distribution, from which we get the average size and PDI.
SEM	Scanning electron micrograph
SiO ₂	Silica, source Ludox AS-30 colloidal silica

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] FIG. 1 DDR zeolite structure.

[0027] FIG. 2 is an SEM micrograph of DDR zeolite crystals with size of
5 about 2 micrometers.

[0028] FIG. 3 is an SEM micrograph of diamond-like DDR zeolite nanocrystals with about 500 x 250 nanometer size.

[0029] FIG. 4 is an SEM micrograph of octahedral DDR zeolite nanocrystals with about 300 nanometer size.

10 [0030] FIG. 5 is an SEM micrograph of hexagonal plate DDR zeolite nanocrystals with about 500 nanometer size.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0031] In a typical synthesis by the inventive method described herein, ADA was first dissolved in DI water. Then silica was added to the solution and the solution was
15 mixed. After mixing the solution for 5 to 10 minutes, KF was added to the solution. The solution was mixed for another two hours. A small amount of crystal seeds synthesized

using methods reported in literature⁴ was added to the solution. The solution was then put inside an autoclave with a Teflon liner and heated up to 160°C. The autoclaves were rotated (end-over-end) with a speed of 60 rpm in order to ensure adequate mixing and dispersal of regents during the seed growth. This mixing also appears to help with obtaining smaller crystals, and is important for nanometer sized crystal production. The reaction time was about 48 hours. The particles were then collected after the autoclaves were cooled to room temperature, washed with DI water and centrifuged until the pH of the wash water was close to 7.0. The particles were then dried and calcined at 700°C for 8 hours. The ramping rate of calcination was 0.5°C per minute.

10 **[0032]** The particles were first characterized with X-ray powder diffraction (XRD). The XRD pattern (not shown) of the crystals agrees well with the reference XRD pattern, confirming that the desired DDR zeolite was synthesized. The crystals were also observed with scanning electron microscopy (SEM) (Figure 2), which showed that these first crystals had an octahedral morphology and size of about 2 microns.

15 **[0033]** The particle size of these crystals was further reduced in subsequent experiments. The as-synthesized 2-micron crystals were ball-milled, and dispersed in water to form a suspension of 0.2 ~1 g/l. These were used as the seed crystals for the subsequent reactions.

20 **[0034]** A mixture of ADA, silica, DI water, and KF was prepared as described above. When the mixture was put into the autoclave, 5 to 10 grams of the suspension with ball-milled particles were also added into the autoclaves. Depending on the desirable morphology, 0.1 to 0.3 grams KOH can be added to the solution. The autoclaves were heated to 150-160°C while rotating the chambers, as above.

25 **[0035]** The rotation speed was maintained at 60 rpm for these smaller crystals. The reaction time varied from 6-12 hours, shorter times resulting in smaller crystals. The synthesis temperature can also have effect on both size and morphology. Lower temperatures result in smaller crystals and if $\leq 150^{\circ}\text{C}$ (130, 140 and 150°C were all tested) leads to nanometer sized octahedrons or hexagonal plates if KOH is also added, while higher temperatures ($\geq 160^{\circ}\text{C}$) surprisingly lead to diamond plate like crystals.

[0036] The washing and calcination steps were the same as described above for the 2-micrometer crystals, i.e., the particles were washed with DI water and centrifuged until the pH of the wash water was close to 7.0. The particles were then dried and calcined at 700°C for 8 hours. The ramping rate of calcination was 0.5°C per minute.

5 [0037] These various DDR zeolite particles were also characterized with XRD, SEM, dynamic light scattering (DLS), and N₂ physisorption. DLS provides statistical information about the particle size and particle size distribution, and generally showed a narrow size range for each of our syntheses. N₂ physisorption provided information regarding surface area and pore volume for porous materials.

10 [0038] The following examples are illustrative only, and are not intended to unduly limit the scope of the invention.

EXAMPLE 1: OCTAHEDRAL DDR

[0039] Larger DDR crystals with octahedron morphology and approximate 2-micron size were synthesized in this first Example.

15 [0040] A mixture of ADA, Silica, KF and DI was made with the molar ratio of 6:100:50:8000. ADA was first dissolved in DI water. Due to the low solubility of ADA in water, the mixture was really only partially solubilized and much remained as a suspension of ADA in water. Silica was then added to the suspension and mixed. After mixing the suspension for 5-10 minutes, KF was added to the suspension. The mixture was
20 further mixed at room temperature for 2 hours.

[0041] Next 30 grams of the mixture was poured into an autoclave with a Teflon liner of 45 ml. Then 5-10 grams of seed crystals were added to the autoclave. The autoclave was then sealed and heated to 160°C inside an oven. The reaction was maintained for 48 hours. The autoclaves were then cooled to room temperature. The crystals were
25 collected and washed with DI water and centrifuged for several times. Some of the crystals were calcined at 700°C for 8 hours to remove the organic template ADA.

[0042] The calcined crystals were then characterized with XRD, SEM, and N₂ physisorption. The XRD pattern (not shown) agreed well with the reference pattern,

confirming the material was a DDR zeolite. The SEM image (Figure 2) revealed that the crystals from this synthesis method had octahedron morphology. The size of the crystals was estimated from SEM micrograph and was in the range of 2-3 micrometers. Due to their larger size, DLS could be not performed for these crystals. However, BET surface area and pore volume of the crystals from N₂ physisorption were 348 m²/g and 0.124 ml/g, respectively. These results were consistent with the reported values for DDR⁶.

EXAMPLE 2: DIAMOND DDR

[0043] In this Example, we show the synthesis of a DDR crystal with diamond-like morphology and approximate 500 x 250 nanometer size. General speaking, decreasing the time of the heat treatment unexpectedly changed the morphology and reduced the size.

[0044] In a typical synthesis, a mixture of ADA, Silica, KF and DI was made with the molar ratio of 6:100:50:10000. ADA was first dissolved in DI water. Due to the low solubility of ADA in water, the mixture was actually a partial suspension of ADA in water. Silica was then added to the suspension and mixed. After mixing the suspension for 5-10 minutes, KF was added to the suspension. The mixture was further mixed at room temperature for 2 hours.

[0045] After the mixture was prepared, 30 grams of the mixture was poured into an autoclave with a Teflon liner of 45 ml. 5 to 10 grams of seed crystals were added to the autoclave. The autoclave was then sealed and heated up to 160°C inside an oven. The reaction was maintained for 8 hours. The autoclaves were then cooled to room temperature. The crystals were collected and washed with DI water and centrifuged for several times. Some of the crystals were calcined at 700°C for 8 hours to remove the organic template ADA.

[0046] The calcined crystals were then characterized with XRD, SEM, DLS, and N₂ physisorption. The XRD pattern (not shown) agrees well with the reference pattern. SEM image (Figure 3) revealed that the crystals from this method had a diamond-like morphology with a long axis of about 500 nm and a short axis of about 250 nm. DLS (not shown) confirmed that the average size of the crystals was 398 nm with a polydispersity

index of 0.075. BET surface area and pore volume of the crystals from N₂ physisorption were 371 m²/g and 0.132 ml/g, respectively.

EXAMPLE 3: SMALLER OCTHEDRAL DDR

[0047] Next DDR crystals with octahedron morphology and approximately 300 nanometer size were synthesized. Generally, lowering the temperature and heating time reduced crystal size.

[0048] In a typical synthesis, a mixture of ADA, Silica, KF and DI was made with the molar ratio of 6:100:50:10000. ADA was first dissolved in DI water. Due to the low solubility of ADA in water, the resulting mixture was a suspension of ADA in water. Silica was then added to the suspension and mixed. After mixing the suspension for 5-10 minutes, KF was added to the suspension. The mixture was further mixed at room temperature for 2 hours.

[0049] After the mixture was prepared, 30 grams of the mixture was poured into an autoclave with a Teflon liner of 45 ml. 5 to 10 grams of seed crystals were added to the autoclave. The autoclave was then sealed and heated up inside an oven. To synthesize nanometer sized octahedral DDR nanocrystals, the temperature should be controlled less than or equal to 150°C. The reaction was maintained for 6 hours with rotational mixing. The autoclaves were then cooled to room temperature. The crystals were collected and washed with DI water and centrifuged for several times. Some of the crystals were calcined at 700°C for 8 hours to remove the organic template ADA.

[0050] The calcined crystals were then characterized with XRD, SEM, DLS, and N₂ physisorption. The XRD pattern (not shown) agrees well with the reference pattern and that of diamond-like DDR nanocrystals. SEM image (Figure 4) revealed that the crystals from this synthesis method had an octahedral morphology. DLS (not shown) confirmed that the average size of the crystals was 366 nm with a polydispersity index of 0.034. BET surface area and pore volume of the crystals from N₂ physisorption were 346 m²/g and 0.123 ml/g, respectively.

EXAMPLE 4: HEXAGONAL DDR

[0051] In this Example, we synthesized a DDR crystal with hexagonal plate morphology and about 500 nanometer size. Adding KOH surprisingly changed the crystal structure from octahedral to hexagonal plate.

5 [0052] To synthesize hexagonal plate DDR nanocrystals, a mixture of ADA, Silica, KF and DI was made with the molar ratio of 6:100:50:10000. ADA was first dissolved in DI water. Silica was then added to the suspension and mixed. After mixing the suspension for 5-10 minutes, KF was added to the suspension. 0.28 grams KOH were added to the mixture after adding KF. The mixture was mixed at room temperature for 2 hours.

10 [0053] After the mixture was prepared, 30 grams of the mixture were poured into an autoclave with a Teflon liner of 45 ml. 5 to 10 grams of seed crystals were added to the autoclave. The autoclave was then sealed and heated up inside an oven. The temperature was set at 150°C and the chambers rotationally mixed, as above. The reaction was maintained for 6 hours. The autoclaves were then cooled to room temperature. The crystals
15 were collected and washed with DI water and centrifuged for several times. Some of the crystals were calcined at 700°C for 8 hours to remove the organic template ADA.

[0054] The calcined crystals were then characterized with XRD, SEM, DLS, and N₂ physisorption. The XRD pattern (not shown) agreed well with the reference pattern and that of diamond-like DDR nanocrystals. SEM image (Figure 5) revealed that the
20 crystals from this synthesis method had a hexagonal plate morphology, which has previously not been reported in literature. DLS (not shown) confirmed that the average size of the crystals was 484 nm with a polydispersity index of 0.055. BET surface area and pore volume of the crystals from N₂ physisorption were 356 m²/g and 0.126 ml/g, respectively.

[0055] Table 1 summarized the average size, PDI, BET surface area and
25 Pore volume for the crystals of the four examples described herein.

DDR Crystal (example no.)	Average size (nm)	Polydispersity Index (PDI)	BET surface area) (m ² /g)	Pore Volume (ml/g)
Octahedron (1)	2000	Not available	348.0	0.124
Diamond (2)	398	0.075	371.6	0.132
Octahedron (3)	366	0.034	346.2	0.123
Hexagonal plate (4)	484	0.055	356.3	0.126

[0056] The crystals prepared herein can be used for any use that DDR zeolites have traditionally been used for. One particular use is for CO₂ removal e.g., from refinery or chemical plant waste or natural gas usage.

5 [0057] The following references are incorporated by reference in their entirety.

[0058] 1. Marler, B., et al., STUDIES ON CLATHRASILS .8. NONASILS-4158, 88SIO₂.8M₈.8M₉.4M₂₀ - SYNTHESIS, THERMAL-PROPERTIES, AND CRYSTAL-STRUCTURE. Journal of Inclusion Phenomena, 1986. 4(4): p. 339-349.

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[0060] 3. Gascon, J., et al., Accelerated synthesis of all-silica DD3R and its
15 performance in the separation of propylene/propane mixtures. Microporous and Mesoporous Materials, 2008. 115(3): p. 585-593.

[0061] 4. Yang, Q.L., S.L. Zhong, and X. Lin, Synthesis of DDR-Type Zeolite in Fluoride Medium. Chinese Journal of Inorganic Chemistry, 2009. 25(2): p. 191-194.

20 [0062] 5. Tomita, T., K. Nakayama, and H. Sakai, Gas separation characteristics of DDR type zeolite membrane. Microporous and Mesoporous Materials, 2004. 68(1-3): p. 71-75.

[0063] 6. Himeno, S., et al., Characterization and selectivity for methane and carbon dioxide adsorption on the all-silica DD3R zeolite. Microporous and Mesoporous
25 Materials, 2007. 98(1-3): p. 62-69.

[0064] What is claimed is:

1. A method for preparing DDR zeolite crystals, said method comprising the steps of:
 - a) combining the following materials to make a mixture: 1-adamantanamine (“ADA”), deionized water (DI), a silica source, potassium fluoride (“KF”), and optionally a source of a cation;
 - 5 b) mixing the mixture of step a) for a period of time;
 - c) adding seed crystals to said mixture;
 - d) continuing to mix said mixture at a temperature of 100-200°C for 4-72 hours to make DDR zeolite crystals of 200-2000 nm.
2. The method of claim 1, further comprising washing said DDR zeolite crystals.
- 10 3. The method of claim 2, further comprising calcining said washed crystals to remove said ADA.
4. The method of claim 1, where the cation is potassium, sodium, calcium, magnesium, manganese, barium, copper, cobalt, or strontium.
5. The method of claim 1, wherein said mixture solution comprises xADA: 100 SiO₂:
15 y KF: z H₂O: mKOH, and wherein x is between 6 and 50, y is between 50 and 100, z is between 2000 and 14000, and m is between 0 to 2.
6. The method of claim 1, wherein period of time in step b) is between 30 minutes and 6 hours.
7. The method of claim 1, wherein the amount of seed crystals is between 0.0002 and
20 0.001 grams per ml of mixture.
8. The method of claim 1, wherein the temperature of step d) is 130-160°C.
9. The method of claim 8, wherein the heating time of step d) is between 6 hour and 12 hours.

10. The method of claim 1, wherein the method is conducted according to the following parameters:

ADA/SiO ₂ : 0.06 to 0.5 molar ratio
KF/SiO ₂ : 0.5 to 1.0 molar ratio
DI/SiO ₂ : 2000 to 14000 molar ratio
KOH : 0-2 molar ratio
i) 6-12 hr heat treatment d) results in smaller crystals (2-500 nm), or ii) about 48 hr heat treatment d) results in larger crystals (2 μm); and
i) Temperature ≤150°C results in nanometer octahedrons or ii) Temperatures ≤150°C plus KOH (1-2 molar ratio) results in hexagonal plates or iii) Temperatures ≥160°C results in diamond-like structures.

11. A composition comprising DDR zeolite crystals, said crystals having the following characteristics: a) size in the range of 200 to 2000 nm, b) a morphology selected from the groups consisting of diamond plate, octahedral, or hexagonal plate, c) a BET surface area in the range of 340 m²/g to 380 m²/g and d) a pore volume from 0.123 to 0.132 ml/g.

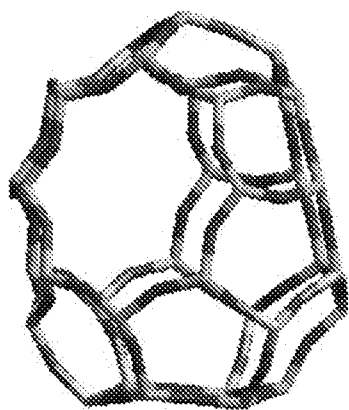
12. The composition of claim 11, wherein said crystals further comprise one of the following:

DDR Crystal shape	Average size (nm)
Octahedron	1000-4000
Diamond	200-500
Octahedron	200-500
Hexagonal plate	200-500

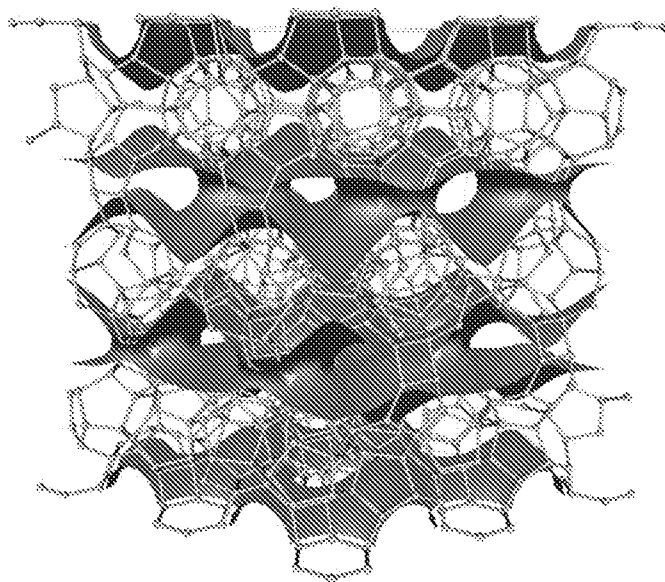
13. The composition of claim 11, wherein said crystals are shaped like hexagonal plates.
14. The composition of claim 11, said crystal shaped like a diamond, having an average size of 500 x 250 nm $\pm$ 20%.
- 5 15. The composition of claim 11, said crystal shaped like a octahedron, having an average size of 300 X 300 nm $\pm$ 20%.
16. The composition of claim 11, said crystal shaped like a hexagonal plate, having an average size of 500 X 500 nm $\pm$ 20%.
17. The composition of claim 11, said crystal shaped like a diamond, having an average
10 size of 500 x 250 nm $\pm$ 10%.
18. The composition of claim 11, said crystal shaped like a octahedron, having an average size of 300 X 300 nm $\pm$ 10%.
19. The composition of claim 11, said crystal shaped like a hexagonal plate, having an average size of 500 X 500 nm $\pm$ 10%.
- 15 20. A separation membrane made with the DDR zeolite crystals of claim 11.

FIGURE 1

DDR building block



DDR pore structure



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FIGURE 2

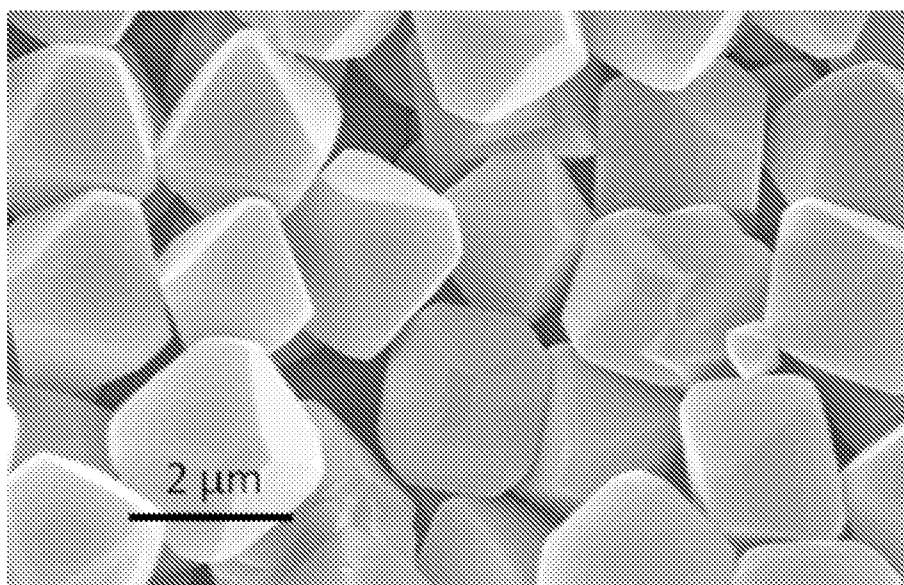
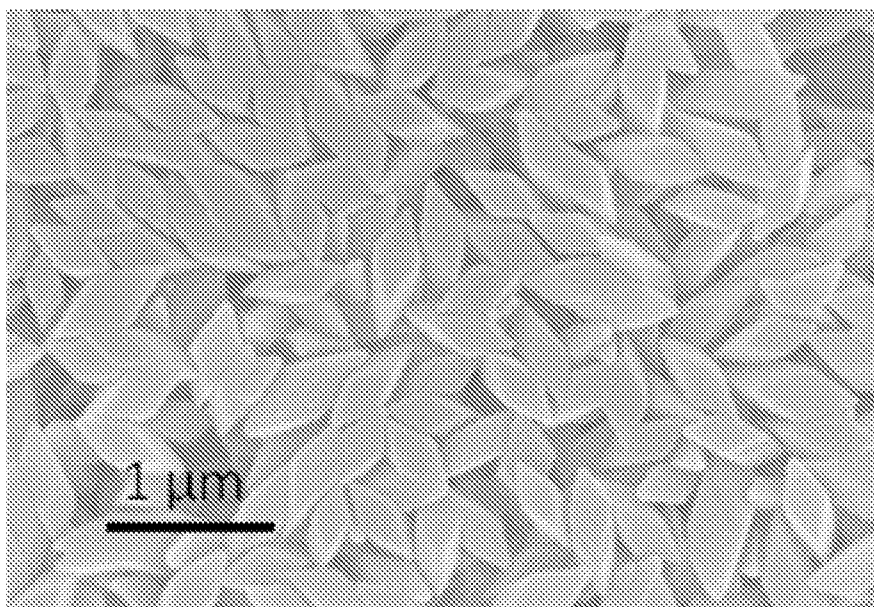


FIGURE 3



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FIGURE 4

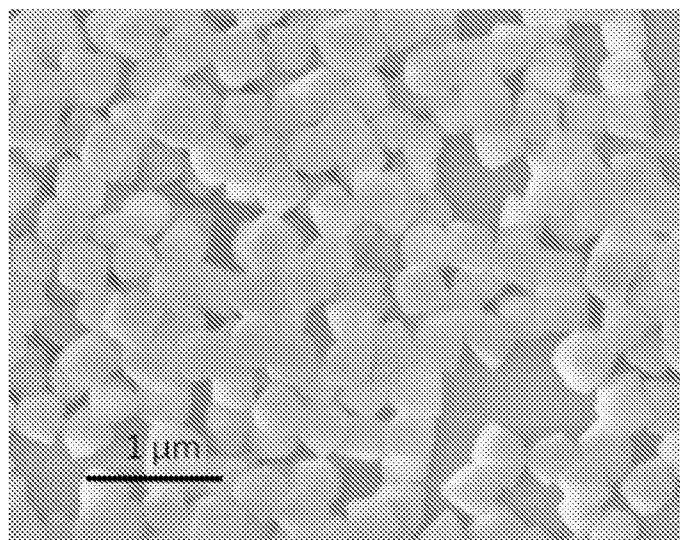
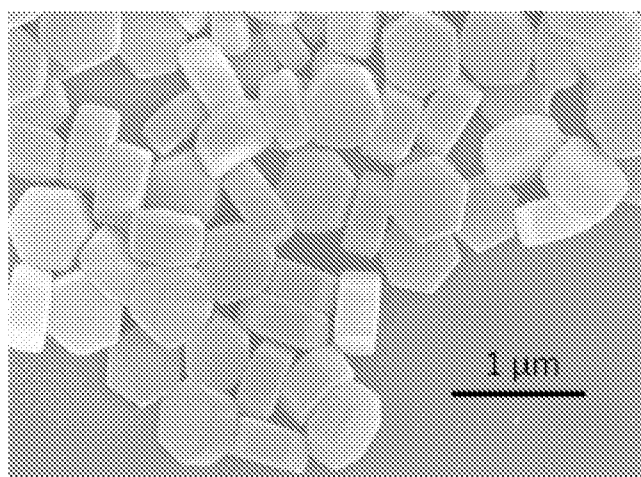


FIGURE 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/25064

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01B 39/00 (2012.01)

USPC - 423/706

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)

USPC -- 423/706

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC -- 423/702, 704, 705

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWEST (USPT, PGPB, JPAB, EPAB); Google

Search Terms: DDR zeolite catalyst ADA I-adamantanamine deionized water silica seed crystal calcined potassium fluoride ratio temperature time heating hour minute

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,953,493 B2 (Nakayama et al.) 11 Oct 2005 (11.10.2005), entire document especially Abstract, col 10, ln 10-30, col 28, ln 13-15, col 10, ln 45-50, col 21, ln 10-20 and Table 2	1-10
Y	US 2009/0111959 A1 (Cao et al.) 30 Apr 2009 (30.04.2009), entire document especially Abstract, para [0039], [0036], [0014]-[0016] and [0044]-[0045]	1-10
Y	US 2008/0047432 A1 (Nonaka et al.) 28 Feb 2008 (28.02.2008), entire document	1-10
Y	US 2009/0011926 A1 (Yajima et al.) 08 Jan 2009 (08.01.2009), entire document	1-10
Y	US 7,014,680 B2 (Nakayama et al.) 21 Mar 2006 (21.03.2006), entire document	1-10

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

* 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 application or patent 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

16 Jul 2012 (16.07.2012)

Date of mailing of the international search report

27 JUL 2012

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/25064

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I: claims 1-10.

Group II: claims 11-20.

See extra sheet for more information.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-10

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Box No. III Observations where unity of invention is lacking (continued)

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: claims 1-10: directed to a method for preparing DDR zeolite crystals, said method comprising the steps of:

- a) combining the following materials to make a mixture: 1. adamantanamine ("ADA"), deionized water (DI), a silica source, potassium fluoride ("KF"), and optionally a source of a cation;
- b) mixing the mixture of step a) for a period of time;
- c) adding seed crystals to said mixture;
- d) continuing to mix said mixture at a temperature of 100-200 degC for 4-72 hours to make DDR zeolite crystals of 200-2000 nm.

Group II: claims 11-20: directed to a composition comprising DDR zeolite crystals, said crystals having the following characteristics:

- a) size in the range of 200 to 2000 nm,
- b) a morphology selected from the groups consisting of diamond plate, octahedral, or hexagonal plate, c) a BET surface area in the range of 340 m²/g to 380 m²/g and
- d) a pore volume from 0.123 to 0.132 ml/g.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not include the inventive concept of DDR zeolite crystals with the claimed morphologies, BET surface area, and pore volume.

Group II does not include the inventive concept of combining, then mixing ADA, DI, a silica source, and KF; and adding seed crystals.

Groups I and II share the technical feature of DDR zeolite crystals of 200-2000 nm. However, this shared technical feature does not represent a contribution over the prior art of US 2009/0111959 A1 to Cao et al. (Abstract: Note that 2 microns = 2000 nm). As the above DDR zeolite crystals were known at the time, as evidenced by the teaching of Cao, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.