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(54) Title: DIRECT SYNTHESIS OF METAL-CONTAINING CHA ZEOLITES

(57) Abstract: A metal-containing chabazite zeolite, which has an FTIR peak area ratio between the peak at 900-1300 cm⁻¹ (Si-O-Si asymmetric stretch) and the peak at 765-845 cm⁻¹ (~805 cm⁻¹ is Si-O-Si symmetric stretch) of at least 55. A method for preparing metal-containing CHA zeolites with high SCR activity at low reaction temperatures from alkali cation-free reaction mixtures that contain the three OSDA structures: metal-polyamine, N,N,N-trimethyl-1-adamantyl ammonium (TMAda⁺) and TMAOH. The metal-containing CHA zeolites produced by the disclosed method can be identified by XRD, FTIR spectroscopy, FT-VIS spectroscopy, and scanning electron microscopy. A method of selective catalytic reduction of NO_x in exhaust gas using the material described herein is also disclosed.



DIRECT SYNTHESIS OF METAL-CONTAINING CHA ZEOLITES**DESCRIPTION**

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/782,556, filed December 20, 2018, which is hereby incorporated by reference in its entirety.

5 Technical Field

[0002] The present disclosure relates generally to a direct synthesis method of producing metal-containing chabazite (CHA) zeolites, metal-containing chabazite (CHA) zeolites made using the disclosed methods, and methods of selective catalytic reduction using the disclosed zeolites.

Background

10 [0003] Metal-containing aluminosilicate CHA-type zeolites, such as Cu containing CHA zeolites, are important catalysts used in commercial selective catalytic reduction (SCR) systems for NO_x abatement in automotive applications. Due to the stringent emission regulations, commercial Cu containing CHA zeolites are required to display high SCR activity especially at low exhaust temperatures.

15 [0004] Commercial Cu containing CHA catalysts are typically produced from the following steps. First, CHA-type zeolites are produced from reaction mixtures that contain alkali cations. Second, the alkali containing zeolites are ion-exchanged (e.g. ammonium exchange) to remove the alkali cations from the zeolite. Third, the ammonium containing zeolites are exchanged with Cu ions to obtain the Cu containing zeolites. However, the additional ammonium and Cu exchange steps to achieve Cu containing CHA caused increased synthesis cost and lowered efficiency. As a result, there is a need for direct
20 synthesis methods for synthesizing highly active Cu containing CHA zeolites that do not require ammonium exchange and Cu exchange.

25 [0005] Prior to this invention, other reported direct synthesis methods for Cu containing CHA zeolites produce catalysts with a variety of problems. For example, the catalysts typically did not exhibit high SCR activity characteristics that are required for commercial applications or had limitations to the processing techniques. For example, such synthesis methods often require large amounts of expensive organic structure-directing agents (OSDAs) that increase costs or require the use of alkali in the synthesis which need extra ion exchange steps to remove.

30 [0006] The direct synthesis method of making a Cu containing microporous crystalline material is directed to overcoming one or more of the problems set forth above and/or other problems of the prior art.

SUMMARY

[0007] In one aspect, the present disclosure is directed to a metal-containing chabazite zeolite, which has an FTIR peak area ratio between the peak at 900-1300 cm⁻¹ and the peak at 765-845 cm⁻¹ of at least 55.

35 [0008] In another aspect, the present disclosure is directed to a method of selective catalytic reduction (SCR) of NO_x in exhaust gas. The method comprises contacting exhaust gas, such as in the presence of ammonia or urea, with a zeolitic material comprising a copper containing CHA-type zeolite,

which has an FTIR peak area ratio between the peak at 900-1300 cm^{-1} and the peak at 765-845 cm^{-1} of at least 55.

[0009] Another aspect disclosed herein is a direct synthesis method of making a Cu containing microporous crystalline material from reaction mixtures that (1) are essentially void of alkali metal cations and (2) contain Cu-polyamine complex (e.g. Cu-TEPA) as the first OSDA and Copper source and (3) contain N,N,N-trimethyl-1-adamantyl ammonium (TMAda+) or trimethylbenzylammonium (TMBA+) or N,N,N-dimethylethylcyclohexyl ammonium (DMECHA+) organic as the second OSDA and (4) contain tetramethyl ammonium (TMA+) or tetraethyl ammonium (TEA+) organic as the third OSDA.

[0010] In an embodiment, there is described a method of making a microporous crystalline material from reaction mixtures that are essentially void of alkali metal cations, and that comprise organic structure directing agents (OSDA) selected from (1) metal-polyamine as the first OSDA, (2) N,N,N-trimethyl-1-adamantyl ammonium (TMAda+), or trimethylbenzylammonium (TMBA+) or N,N,N-dimethylethylcyclohexylammonium (DMECHA+) organic or mixtures thereof as the second OSDA, and (3) TMA+ or TEA+ or mixtures thereof as the third OSDA. In this embodiment, the method comprises: a) mixing sources of alumina, silica, water, a first OSDA, a second OSDA and optionally a third OSDA and optionally a seed material to form a gel; b) heating the gel in a vessel at a temperature ranging from 80°C to 250°C to form a crystalline chabazite product; and c) calcining the product to produce an aluminosilicate zeolite having a CHA structure, and a silica-to-alumina ratio (SAR) ranging from 5 to 60.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The accompanying figures are incorporated in and constitute a part of this specification.

[0012] FIG. 1A is an x-ray diffraction pattern and FIG. 1B is a deconvolution of peaks between 30-32° for a sample made in accordance to Example 1.

[0013] FIG. 2A is an x-ray diffraction pattern and FIG. 2B is a deconvolution of peaks between 30-32° for a sample made in accordance to Example 2.

[0014] FIG. 3A is an x-ray diffraction pattern and FIG. 3B is a deconvolution of peaks between 30-32° for a sample made in accordance to Example 3.

[0015] FIG. 3C is an x-ray diffraction pattern and FIG. 3D is a deconvolution of peaks between 30-32° for a sample made in accordance to Example 4

[0016] FIG. 4A is an x-ray diffraction pattern and FIG. 4B is a deconvolution of peaks between 30-32° for a sample made in accordance to Comparative Example 1.

[0017] FIG. 5A is an x-ray diffraction pattern and FIG. 5B is a deconvolution of peaks between 30-32° for a sample made in accordance to Comparative Example 2.

[0018] FIG. 6A is an x-ray diffraction pattern and FIG. 6B is a deconvolution of peaks between 30-32° for a sample made in accordance to Comparative Example 3.

[0019] FIG. 7A and FIG. 7B are scanning electron microscope (SEM) images at various magnifications of Example 1.

[0020] **FIG. 8A** and **FIG. 8B** are scanning electron microscope (SEM) images at various magnifications of Example 2.

[0021] **FIG. 9A** and **FIG. 9B** are scanning electron microscope (SEM) images at various magnifications of Example 3.

5 [0022] **FIG. 9C** and **FIG. 9D** are scanning electron microscope (SEM) images at various magnifications of Example 4.

[0023] **FIG. 10A** and **FIG. 10B** are scanning electron microscope (SEM) images at various magnifications of Comparative Example 1.

10 [0024] **FIG. 11A** and **FIG. 11B** are scanning electron microscope (SEM) images at various magnifications of Comparative Example 2.

[0025] **FIG. 12A** and **FIG. 12B** are scanning electron microscope (SEM) images at various magnifications of Comparative Example 3.

[0026] **FIG. 13A** shows Fourier-transform infrared spectroscopy (FTIR) / Attenuated Total Reflection (ATR) spectra of calcined Examples 1-4 and Comparative Examples 1-3.

15 [0027] **FIG. 13B** shows the same spectra normalized based on Si-O-Si symmetric stretch from 765 to 845 cm^{-1} .

[0028] **FIG. 14** shows Fourier-transform visible spectrum (FT-VIS) of calcined Examples 1-4 and Comparative Examples 1-3 normalized based on 1 wt.% CuO content with a $\text{Cu}(\text{OH})_2$ powder as a reference.

20 [0029] Aside from the subject matter discussed above, the present disclosure includes a number of other features such as those explained hereinafter. Both the foregoing description and the following description are exemplary only.

DETAILED DESCRIPTION OF THE INVENTION

25 [0030] As used herein “essentially void of alkali metal cations,” means having trace amounts of alkali metal cations. In an embodiment, “essentially void” or “trace amounts” means 0.3 wt% alkali oxides, such as Na_2O or K_2O , or less.

[0031] As indicated, the disclosed zeolite comprises a metal-containing chabazite zeolite, such as a copper or iron containing zeolite, which has an FTIR peak area ratio between the peak at 900-1300 cm^{-1} and the peak at 765-845 cm^{-1} of at least 55. In an embodiment, the chabazite zeolite has a silica-to-alumina ratio (SAR) ranging from 5 to 60, such as from 10 to 50, or even from 10 to 30.

30 [0032] When the described zeolite comprises copper, it is present in an amount of at least 0.5 weight percent of the total weight of the material, such as an amount ranging from 0.5 to 10 weight percent of the total weight of the material.

[0033] When the described zeolite comprises iron, it is present in an amount of at least 0.5 weight percent of the total weight of the material, such as an amount ranging from 0.5 to 10 weight percent of the total weight of the material.

35 [0034] In an embodiment, the total alkali oxide amount is present in an amount less than 0.3 weight percent, such as less than 0.1 weight percent.

[0035] In an embodiment, the disclosed zeolite has a peak area ratio between the FT-VIS peak ranging from 500-1100 nm and the FT-VIS peak of $\text{Cu}(\text{OH})_2$ between 500-1100 nm of lower than 2.5.

[0036] The disclosed method of making a microporous crystalline material and the resulting Cu containing zeolite material having a CHA-type framework structure are directed to overcoming one or more of the problems set forth above and/or other problems of the prior art. Unlike the prior art, for example, there is described a method for preparing Cu containing CHA zeolites with high selective catalytic reduction ("SCR") activity at low reaction temperatures from alkali cation-free reaction mixtures that contain the following OSDA structures: Cu-polyamine complex (e.g. Cu-TEPA) as the first OSDA and Cu source; N,N,N-trimethyl-1-adamantyl ammonium (TMAda⁺) or trimethylbenzylammonium (TMBA⁺) or N,N,N-dimethylethylcyclohexylammonium (DMECHA⁺) organic as the second OSDA; 10 tetramethyl ammonium hydroxide (TMAOH) or tetraethyl ammonium hydroxide (TEAOH) as an optional third OSDA.

[0037] Cu-polyamine complex serves as both the OSDA and Cu source. In one embodiment, polyamine may be selected from Diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 15 pentaethylenhexamine, N-(2-hydroxyethyl) ethylenediamine, N,N-bis(2-aminoethyl)-1,3-propanediamine, 1,2-bis(3-aminopropylamino), 1,4,8,11-tetraazacyclotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, and combinations thereof, amongst others. In an embodiment, the polyamine is tetraethylenepentamine.

[0038] In an embodiment, the method of making a microporous crystalline material from reaction mixtures that (1) are essentially void of alkali metal cations and (2) contain Cu-TEPA as the first OSDA and (3) N,N,N-trimethyl-1-adamantyl ammonium (TMAda⁺) as the second OSDA and (4) TMA⁺ or TEA⁺ as the third OSDA. 20

[0039] In an embodiment, the method comprises:

a) mixing sources of alumina, silica, water, Cu-TEPA, TMAdaOH, TMAOH (or TEAOH) and 25 optionally a seed material to form a gel;

b) heating the gel in a vessel at a temperature ranging from 80°C to 250°C to form a crystalline chabazite product; and

c) calcining the product to produce an aluminosilicate zeolite having a CHA structure, and a silica-to-alumina ratio (SAR) ranging from 5 to 60, such as from 10 to 50, or even from 10 to 30.

[0040] In an embodiment, the gel may have a water to silica ($\text{H}_2\text{O}/\text{SiO}_2$) molar ratio of 1-50. The gel may also have a TMAdaOH to silica (TMAdaOH/ SiO_2) molar ratio ranging from 0.01-0.5. In one embodiment, the as synthesized material following step b) exhibits an XRD peak area ratio between the [3,1,0] peak and the peak doublet (sum of [3,-1,-1] peak and [3,1,0] peak) of at least 0.15. 30

[0041] In one embodiment, the reaction mixtures with (A) molar composition $1 \text{ SiO}_2 : m \text{ Al}_2\text{O}_3 : n \text{ Cu-TEPA} : x \text{ TMAdaOH} : y \text{ TMAOH} : z \text{ H}_2\text{O}$, where $m = 0.016-0.2$, $n = 0.01-0.12$, $x = 0.01-0.50$, $y = 0.01-0.50$, $z = 1-50$ and (B) trace concentrations of alkali cations. 35

[0042] In one embodiment, the disclosed method may further comprise adding to the microporous crystalline material at least one metal chosen from copper, iron or combinations thereof, to form a metal containing chabazite.

[0043] When the metal added to the microporous crystalline material comprises copper, the copper comprises at least 0.5 weight percent of the total weight of the material, such as an amount ranging from 0.5 to 10 weight percent of the total weight of the material.

[0044] When the metal added to the microporous crystalline material comprises iron, the iron comprises at least 0.5 weight percent of the total weight of the material, such as an amount ranging from 0.5 to 10 weight percent of the total weight of the material.

[0045] Non-limiting examples of sources of alumina that may be used in the present disclosure include aluminum hydroxide, such as aluminum trihydroxide, alumina, alumina hydrates, aluminum alkoxides, aluminum nitrate, aluminum sulfate and aluminum acetate.

[0046] Non-limiting examples of sources of silica that may be used in the present disclosure include colloidal silica, silica gel, precipitated silica, silica-alumina, fumed silica, silicon alkoxides, and the like.

[0047] Non-limiting examples of sources of copper that may be used in the present disclosure include copper salts such as cupric acetate, cupric nitrate, cupric sulfate, cupric hydroxide, cupric oxide and cupric chloride.

[0048] Non-limiting sources of iron that may be used in the present disclosure include an iron salt such as ferric nitrate, ferric chloride, ferrous chloride, and ferrous sulfate.

[0049] The suitable metals used for forming metal-polyamine complexes are not limited to Cu and Fe, which are usually used for SCR applications. Optionally the transition metal centers can also be Mn, Co, Ni, Pd, Pt and Zn.

[0050] The molar polyamine/metal ratio that may be used in the present disclosure is 0.2-5, such as 1-2.

[0051] In one embodiment, there is disclosed a copper containing chabazite zeolite synthesized according to methods described herein. In one embodiment, the disclosed copper containing chabazite zeolite in the as-synthesized form exhibits an XRD peak area ratio between the higher-degree [3,1,0] shoulder peak of the XRD peak doublet at 30-32° 2 theta and the whole peak doublet ([3,1,0] and main [3,-1,-1] peak) is at least 0.15.

[0052] In an embodiment, the disclosed Cu containing zeolite material has an absorbance of the FTIR peak centered at 1030-1080 cm⁻¹ of at least 0.3 absorbance units. In an embodiment, the disclosed Cu containing zeolite material having a CHA-type framework structure, has an intense peak near 1050-1070 cm⁻¹ FTIR spectrum, which is much weaker in the products from the prior art. In an embodiment, the peak area ratio of the peak at 900-1300 cm⁻¹ to the peak at 765-845 cm⁻¹ (805 cm⁻¹ is Si-O-Si symmetric stretch) is at least 55 for the disclosed zeolite material, such as at least 60.

[0053] In an embodiment, the disclosed Cu containing zeolite material having a CHA-type framework structure, has a peak area in the 500-1100 nm range of the FT-VIS spectrum much lower than

that in the products from the prior art. In an embodiment, the ratio of the peak area of Inventive examples relative to the reference $\text{Cu}(\text{OH})_2$ peak area is below 2.5, such as below 2.2.

[0054] The Cu containing CHA zeolites produced by the disclosed method can be uniquely identified by methods that characterize detailed structure and morphology of zeolites. The inventors have shown that X-ray diffraction (XRD), FTIR spectroscopy, FT-VIS spectroscopy, and scanning electron microscopy (SEM) can be used to easily differentiate the Cu CHA zeolites prepared from these disclosed methods from CHA zeolites produced from prior synthetic methods.

[0055] In an embodiment, there is disclosed a Cu containing zeolite material having a CHA-type framework structure, having a crystal morphology, including crystal size, which is different from the products from prior art. The zeolite crystals prepared using the disclosed methods have a size ranging from 0.1-10 microns. In an embodiment, each crystal contains nanocrystals. The crystal surfaces of the comparative samples 1 and 3 are smooth with some nanoparticles partially deposited on their surfaces. The crystals of comparative sample 2 are very large (about 5 microns) and contain many layers of small crystals.

[0056] In an embodiment, there is disclosed a method of selective catalytic reduction (SCR) of NO_x in exhaust gas using the material described herein. For example, in an embodiment, the method comprises contacting exhaust gas with a zeolitic material comprising a copper containing CHA-type zeolites, which show higher SCR activities at low reaction temperatures (150 °C, 175 °C, 200 °C) than the products from prior art.

[0057] In another embodiment, the method comprises contacting exhaust gas with a zeolitic material comprising a copper containing CHA-type zeolites, which show higher SCR activities at low reaction temperatures (150 °C, 175 °C, 200 °C) than the products from prior art upon the hydrothermal treatment at 750°C with 10% moisture for 16 hrs.

[0058] In an embodiment, the contacting step for the method of selective catalytic reduction (SCR) of NO_x in exhaust gas is performed in the presence of ammonia or urea.

EXAMPLES

[0059] The following non-limiting examples, which are intended to be exemplary, further clarify the present disclosure.

Example 1 – Direct synthesis of Cu-CHA

[0060] Pseudo-boehmite alumina was dissolved into a mixture of Cu-TEPA, TMAdaOH, and TMAOH solution for about 60 minutes followed by slow addition of silica sol (40% SiO_2 , Ludox AS-40). The gel was stirred for 60 minutes and seed material was added (1 wt. % of total mass of silica + alumina) before loading into an autoclave (Parr Instruments). The molar composition of the gel was 1.0 SiO_2 /0.042 Al_2O_3 /0.028 Cu-TEPA/0.062 TMAdaOH/0.062 TMAOH/12.5 H_2O .

[0061] The autoclave was heated to 160°C and maintained at the temperature for 96 hours while stirring at 150 RPM. After cooling, the product was recovered by filtration, washed with deionized water, and dried in a 110°C convection oven. The as-synthesized product was examined by XRD, and it was found a Cu containing zeolite having chabazite framework had been obtained (Figure 1). The product

was calcined in air at 600 °C for 5 hrs to remove the residual organic. The occluded organic in the dried as-synthesized zeolite was removed by calcination in air at 600°C for 5 hours. The product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (SAR) of 22.2 and contained 3.7 wt.% CuO (Table 1).

Example 2 – Direct synthesis of Cu-CHA

5 [0062] Sample 2 was prepared using the same protocol as described in Example 1 except the molar composition of the final mixture was adjusted to prepare a CHA zeolite with a different SAR. The composition of the final reaction mixture was 1.0 SiO_2 /0.049 Al_2O_3 /0.032 Cu-TEPA/0.062 TMAdaOH/0.062 TMAOH/12.3 H_2O .

10 [0063] The autoclave was heated to 140°C and maintained at the temperature for 144 hours while stirring at 150 RPM. After cooling, the product was recovered by filtration, washed with deionized water, and dried in a 110°C convection oven. The as-synthesized product was examined by XRD, and it was found a Cu containing zeolite having chabazite framework had been obtained (Figure 2). The product was calcined in air at 600 °C for 5 hrs to remove the residual organic. The occluded organic in the dried as-synthesized zeolite was removed by calcination in air at 600°C for 5 hours. The product had a
15 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (SAR) of 21.4 and contained 4.3 wt.% CuO (Table 1).

Example 3 – Direct synthesis of Cu-CHA

[0064] Sample 3 was prepared using the same protocol as described in Example 1 except the molar composition of the final mixture was adjusted to prepare a CHA zeolite with a different SAR. The composition of the final reaction mixture was 1.0 SiO_2 /0.061 Al_2O_3 /0.033 Cu-TEPA/0.067
20 TMAdaOH/0.080 TMAOH/12.9 H_2O .

[0065] The autoclave was heated to 160°C and maintained at the temperature for 96 hours while stirring at 150 RPM. The product was examined by XRD, and it was found a Cu containing zeolite having chabazite framework had been obtained. The product showed the X-ray diffraction pattern of chabazite (Figures 3A and B). The product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (SAR) of 16.6 and contained 4.1 wt.%
25 CuO (Table 1).

Example 4 – Direct synthesis of Cu-CHA

[0066] Sample 4 was prepared using the same protocol as described in Example 1. The composition of the final reaction mixture was 1.0 SiO_2 /0.042 Al_2O_3 /0.028 Cu-TEPA/0.062 TMAdaOH/0.062 TMAOH/12.5 H_2O .

30 [0067] The autoclave was heated at 140°C for 48 hours followed by 180°C for 24 hours while stirring at 150 RPM. The product was examined by XRD, and it was found a Cu containing zeolite having chabazite framework had been obtained. The product showed the X-ray diffraction pattern of chabazite (Figures 3C and D). The product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (SAR) of 23.6 and contained 3.6 wt.% CuO (Table 1).

Comparative Example 1

35 [0068] The method disclosed by Trukhan et al. in US 8,715,618 B2 (9,272,272 B2) describes direct synthesis of Cu containing CHA prepared using a mixture of N,N,N-trimethyl-1-adamantyl ammonium (TMAdaOH) with trimethylbenzylammonium hydroxide (TMBA) or tetramethyl ammonium

hydroxide (TMAOH) as the combined OSDAs, and Cu Nitrate or $\text{Cu}(\text{NH}_3)_4\text{CO}_3$ as the Cu source.

Example 10 from US 8,715,618 B2 is an example of the preparation of CHA zeolites from a gel that contains OSDAs TMAdaOH and TMAOH and Cu source $\text{Cu}(\text{NH}_3)_4\text{CO}_3$.

[0069] In this Example, the method was reproduced for comparison to the current disclosed methods. Aluminum triisopropylate, TMAdaOH, TMAOH, $\text{Cu}(\text{NH}_3)_4\text{CO}_3$, Ludox AS-40, deionized water and CHA seeds were mixed to form the reported gel composition of $36 \text{ SiO}_2/2.7\text{Al isoprop.}/2.6\text{TMAdaOH}/3.0\text{TMAOH}/1.02\text{Cu amine}/448\text{H}_2\text{O}$, which was identical to the reported gel composition of $36\text{SiO}_2/2.7\text{Al isoprop.}/2.6\text{TMAdaOH}/3.0\text{TMAOH}/0.96\text{Cu amine}/448\text{H}_2\text{O}$.

[0070] The gel was loaded into an autoclave (Parr Instruments) and heated to 160°C and maintained at the temperature for 48 hours while stirring at 200 RPM. The product was recovered, dried, and calcined in air at 600°C for 5 hrs. The product showed the XRD pattern of chabazite (Figure 4). The CuO content and SAR of the material (3.1 wt.% CuO and 26.0 SAR) were very similar to those reported in Example 10 of US 8,715,618 B2 (3.0 wt.% CuO and 25.1 SAR). The SEM image (Figure 10) also indicates a similar material to that reported in Example 10 of US 8,715,618 B2.

[0071] The zeolites prepared using the method of Comparative Example 1 exhibit lower SCR activity than the current invention.

Comparative Example 2

[0072] The methods disclosed by Moliner Marin et al. in US 2016/0271596 A1 describes the preparation of Cu containing CHA zeolites from a gel that contains Cu-TEPA with either N,N,N-trimethyl-1-adamantyl ammonium (TMAda⁺) cation or benzyl trimethylammonium cation (TMBA⁺) with optionally one or more precursors including alkali cations and fluoride anions. All examples presented were prepared from gels that contains N,N,N-trimethyl-1-adamantyl ammonium (TMAda⁺) cations with the addition of either alkali cations or NH_4F .

[0073] Example 2 is an example of the preparation of Cu-CHA zeolites from a gel that contains Cu-TEPA and N,N,N-trimethyl-1-adamantyl ammonium (TMAdaOH) with the addition of NaOH. The comparative sample was prepared using the same protocol as described in Example 2. Copper (II) sulfate, tetraethylenepentamine (TEPA), N,N,N-trimethyl-1-adamantammonium hydroxide, sodium hydroxide, aluminum hydroxide, and Ludox AS40 were mixed together to form a gel with the following molar composition: The gel composition was SiO_2 : 0.033 Al_2O_3 : 0.049 $\text{Cu}(\text{TEPA})^{2+}$: 0.19 TMA⁺DA: 0.12 NaOH: 18.3 H_2O which was identical to the reported gel composition of SiO_2 : 0.033 Al_2O_3 : 0.049 $\text{Cu}(\text{TEPA})^{2+}$: 0.19 TMA⁺DA: 0.12 NaOH: 18.3 H_2O .

[0074] The final gel was loaded into Teflon-lined stainless steel autoclaves (Parr Instruments) and heated at 150°C for 14 days under static conditions. After filtering, washing, and drying, the product showed the XRD pattern of chabazite (Figure 5).

[0075] The product was calcined in air at 550°C for 6 hrs to remove the residual organic. The SAR of the material (28.9 SAR) was similar to that reported in Example 2 of US 2016/0271596 A1 (27.8 SAR). The 5.7 wt.% CuO content of the material was higher than the reported 4.0 wt.% CuO but is close

to the initial 6.1 wt.% CuO content in the starting gel. The SEM image (Figure 11) also indicates a similar material to that reported in Example 2 of US 2016/0271596 A1.

[0076] The zeolites prepared using the method of Comparative Example 2 exhibit lower SCR activity than the current invention.

5 Comparative Example 3

[0077] The methods disclosed by Rivas-Cardona et al. in US 2015/0151286 A1 and US 2015/0151287 A1 describes the preparation of Cu containing CHA zeolites from a gel that contains Cu-TEPA with a second OSDA TMAda (US 2015/0151286 A1) or DMECHA (US 2015/0151287 A1) with optionally NaOH.

10 [0078] A comparative sample was prepared using the same protocol for the synthesis of JMZ-4 as described in both [0032] and Example 1 presented in 2015/0151286 A1. Since there is no specific gel composition available provided in the patent, we used a gel with molar composition SiO_2 : $0.04\text{Al}_2\text{O}_3$: 0.30 TMAda: 0.03 Cu-TEPA: 18 H_2O falling in the claimed composition range. Aluminum source $\text{Al}(\text{OEt})_3$ was combined with TMAda in water and mixed for 30 minutes. Next, copper sulfate and TEPA
15 were added to the solution and the mixture was stirred for another 30 minutes. Finally, TEOS was added to the solution and mixed for 60 minutes.

[0079] The gel was loaded into an autoclave (Parr Instruments) and heated to 160°C for 5 days. After filtering, washing, and drying, the product showed pure phase chabazite structure by XRD (Figure 6). The product was calcined in air at 560 °C for 8 hrs to remove the residual organic. The CuO
20 content and SAR of the material (2.9 wt.% CuO and 21.0 SAR) fall in the 10-30 SAR range and 0.1-5 wt.% CuO range recited in US 2015/0151286 A1.

[0080] The zeolites prepared using the method of Comparative Example 3 exhibit lower SCR activity than the current invention.

Experimental Methods

25 [0081] This section summarizes methods used to identify and differentiate Cu-CHA zeolites prepared using the disclosed synthetic method from Cu-CHA zeolites prepared using prior synthetic methods.

[0082] **SCR catalytic tests:** The activities of the hydrothermally aged materials for NO_x conversion, using NH₃ as reductant, were tested with a flow-through type reactor. Powder zeolite samples
30 were pressed and sieved to 35/70 mesh and loaded into a quartz tube reactor. The gas composition for NH₃-SCR was 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, 0.6% H₂O and balance N₂. The space velocity was 50,000 h⁻¹. The reactor temperature was ramped between 150 °C and 550 °C and NO conversion was determined with an MKS MultiGas infrared analyzer at each temperature point.

[0083] One important feature of Cu-CHA zeolites prepared using the disclosed synthetic
35 method is that they exhibited both higher fresh and steamed SCR activity (at low temperature range 150 °C, 175 °C, 200 °C) than Cu-CHA zeolites prepared using prior synthetic methods (as shown in Tables 2 and 3). For example, the SCR activity at 150 °C of the fresh versions of the inventive examples is higher than 45%, such as higher than 50%. It is well known that SCR performance of zeolite materials are

related to structure differences. The Cu containing CHA zeolites produced by the disclosed method can be uniquely identified by methods that measure the detailed structure of the zeolites.

[0084] As shown below, XRD, FTIR spectroscopy, and FT-VIS spectroscopy can be used to differentiate the Cu CHA zeolites prepared from these disclosed methods from CHA zeolites produced from prior synthetic methods.

[0085] **X-ray Diffraction (XRD) patterns:** As shown in Figures 1-3, XRD patterns for the as-synthesized samples prepared using the disclosed method exhibited a pronounced peak splitting between 30-32° (Figures 1-3), which is not present or less apparent in the products prepared from prior art (Figures 4-6). The peak areas of the [3,1,0] peak and the [3,-1,-1] peak were measured and the peak area ratio of [3,1,0] vs. the whole peak doublet ([3,1,0] + [3,-1,-1]) is further compared in Table 4. As an example, the [3,1,0] peak is located at about 31.2 degrees in Figure 1B and the [3,-1,-1] peak is located at about 30.9 degrees in Figure 1B. For the samples prepared using the disclosed method, the peak area ratios are typically high and are measured to be 0.19, 0.18, 0.26, and 0.21 for the samples in Examples 1, 2, 3, and 4, respectively. For the Comparative examples, the ratios are below 0.12 and are all substantially lower than those of the inventive samples. These data indicate that CHA zeolite samples prepared using the disclosed methods are different from the comparative examples.

[0086] **Scanning electron microscope (SEM) images:** SEM provides a direct method to investigate the morphology difference between different zeolite materials. For the CHA zeolite samples prepared using the disclosed methods (Examples 1, 2, 3 and 4), the SEM images show that the samples consist of cubic crystals of a size of 0.1-2 microns. The surfaces of the crystals contain small nanocrystals (Figures 7-9). The SEM images of the comparative examples (Figures 10-12) all indicate crystals different from samples prepared using the disclosed methods.

[0087] **FTIR ATR Spectroscopy measurements:** FTIR spectra were obtained on calcined samples using a single bounce diamond attenuated total reflectance (ATR) accessory on a Nicolet spectrometer from Thermo Scientific. As shown in Figure 13A, FTIR spectra for the samples prepared using the disclosed method exhibited an intense peak between 1030-1080 cm^{-1} , which is much higher than those of the products prepared from prior art (Figure 13A). The peak near 1030-1080 cm^{-1} is a characteristic of the phonon vibration of coupled Si-O-Si oscillators in the crystal lattice, which was from the Si-O-Si asymmetric stretch. The FTIR spectra were also normalized based on the peak near 805 cm^{-1} (Figure 13B), which was from Si-O-Si symmetric stretch. The ratio of the peak area of the peak between 900-1300 cm^{-1} and the peak between 765-845 cm^{-1} was compared in Table 5. As shown in Table 5, the peak area ratios are measured to be 72, 85, 94, and 84 respectively for Examples 1, 2, 3, and 4 prepared using the disclosed method. For the Comparative examples, the ratios are all below 51 and are all substantially lower than those of the inventive samples. These data indicate that CHA zeolite samples prepared using the disclosed methods are different from the comparative examples.

[0088] **FT-VIS Spectroscopy measurements:** FT-VIS spectra were collected on calcined samples on a Bruker Vertex 80 spectrometer under diffuse reflectance conditions utilizing a Harrick praying mantis diffuse reflectance accessory. The background sample PTFE was used as a reference

material for background scans. Figure 14 shows FT-VIS spectra for the samples normalized to 1 wt.% CuO content. Figure 14 also includes a Cu(OH)₂ powder as a reference. As shown in Figure 14, the samples prepared using the disclosed method exhibited much lower peak areas in the 500-1100 nm range than those of the products prepared from prior art. The ratios of peak area of each sample relative to the reference Cu(OH)₂ peak area are compared in Table 6. The ratios are below 1.7 for Examples 1, 2, 3, and 4 prepared using the disclosed method and are higher than 2.8 for the Comparative examples.

[0089] **Surface area measurements:** Surface area was determined in accordance with the BET (Brunauer-Emmett-Teller) nitrogen adsorption method. The general procedure and guidance of ASTM D4365-95 is followed in the application of the BET method to the materials according to the present disclosure. To ensure a consistent state of the sample to be measured, all samples are pretreated. Suitable pretreatment involves heating the sample, such as to a temperature of 400 to 500 °C, for a time sufficient to eliminate free water, such as 3 to 5 hours. In one embodiment, the pretreatment comprises heating each sample to 500 °C for 4 hours.

[0090] **Micropore volume measurements:** The assessment of micropore volume is particularly derived from the BET measurement techniques by an evaluation method called the t-plot method (or sometimes just termed the t-method) as described in the literature (Journal of Catalysis 1964, 3, 32).

Table 1. Analytical data for samples prepared from methods described in this patent application compared to comparative examples.

Example	From	SAR	CuO wt. %	Na ₂ O+K ₂ O wt. %	SA m ² /g	MPV cc/g
Inventive 1		22.2	3.7	0.08	707	0.27
Inventive 2		21.4	4.3	0.11	733	0.27
Inventive 3		16.6	4.1	0.20	760	0.28
Inventive 4		23.6	3.6	0.05	750	0.27
Comparative 1	US 8,715,618	26.0	3.1	0.08	681	0.25
Comparative 2	US 2016/0271596	28.9	5.7	0.64	727	0.27
Comparative 3	US 2015/0151286	21.0	2.9	0.04	671	0.22

Table 2. SCR activity (NO conversion at temperatures from 150-550 °C) over **fresh** samples prepared from method described in this patent application compared to samples prepared from prior reported methods.

		Temperature (°C)						
Example	From	150	175	200	250	350	450	550
		NO conversion (%)						
Inventive 1		55.8	87.6	98.8	100	100	90.5	69.9

Inventive 2		78.1	99.3	100	100	100	94.9	74.0
Inventive 3		76.0	96.8	99.7	100	100	94.2	82.5
Inventive 4		68.6	96.9	99.7	100	100	88.4	82.0
Comparative 1	US 8,715,618	39.5	70.3	93.9	99.9	99.4	87.8	75.2
Comparative 2	US 2016/0271596	37.0	63.0	91.6	100	99.9	87.8	67.5
Comparative 3	US 2015/0151286	37.8	64.1	87.2	99.5	99.6	87.9	76.8

Table 3. SCR activity (NO conversion at temperatures from 150-550 °C) over steamed samples prepared from method described in this patent application compared to samples prepared from prior reported methods. Steaming conditions: 750 C, 10% H₂O/air, 16 hours.

		Temperature (°C)						
Example	From	150	175	200	250	350	450	550
		NO conversion (%)						
Inventive 1		38.3	65.7	92.3	99.4	95.3	81.7	62.1
Inventive 2		41.4	71.4	93.7	99.7	96.1	82.8	62.4
Inventive 3		35.3	61.6	89.2	98.6	94.9	85.5	68.7
Inventive 4		40.3	79.1	98.7	100	100	90.9	75.9
Comparative 1	US 8,715,618	28.3	56.2	93.0	99.8	93.3	81.6	59.2
Comparative 2	US 2016/0271596	24.0	42.5	67.2	96.1	90.9	74.8	43.3
Comparative 3	US 2015/0151286	26.5	53.4	87.3	98.3	91.2	79.4	62.4

5 **Table 4.** The ratio of the [3,1,0] peak area and the total peak doublet area ([3,1,0] + [3,-1,-1]).

Examples	area of [3,1,0] peak/ total area ([3,1,0] peak + [3,-1,-1] peak)
Inventive 1	0.19
Inventive 2	0.18
Inventive 3	0.26
Inventive 4	0.21
Comparative 1	0.12
Comparative 2	0.12
Comparative 3	0.09

Table 5. The ratio of the peak area of the peak between 900-1300 cm⁻¹ and the peak between 765-845 cm⁻¹ for Inventive examples and comparative examples.

Examples	Peak area between 900-1300 cm ⁻¹ / peak area between 765-845 cm ⁻¹
Inventive 1	72
Inventive 2	85
Inventive 3	94
Inventive 4	84
Comparative 1	51
Comparative 2	41
Comparative 3	47

Table 6. The ratio of the peak area of Inventive examples and Comparative examples between 500-1100 nm relative to the peak area of the reference $\text{Cu}(\text{OH})_2$

Examples	Peak area/Reference $\text{Cu}(\text{OH})_2$ peak area
Inventive 1	1.1
Inventive 2	1.1
Inventive 3	1.3
Inventive 4	1.7
Comparative 1	3.1
Comparative 2	2.8
Comparative 3	4.5

5

[0091] Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present disclosure.

10

[0092] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope of the invention being indicated by the following claims.

What Is Claimed Is:

1. A metal-containing chabazite zeolite, wherein said material has an FTIR peak area ratio between the peak at 900-1300 cm^{-1} and the peak at 765-845 cm^{-1} ($\sim 805 \text{ cm}^{-1}$ is Si-O-Si symmetric stretch) of at least 55.
- 5 2. The zeolite of claim 1, wherein said material has a silica-to-alumina ratio (SAR) ranging from 5 to 60.
3. The zeolite of claim 1, wherein the metal is copper.
4. The zeolite of claim 3, wherein copper is present in an amount of at least 0.5 weight percent of the total weight of the material.
- 10 5. The zeolite of claim 4, wherein copper comprises an amount ranging from 0.5 to 10 weight percent of the total weight of the material.
6. The zeolite of claim 1, wherein the metal is iron.
7. The zeolite of claim 6, wherein iron is present in an amount of at least 0.5 weight percent of the total weight of the material.
- 15 8. The zeolite of claim 7, wherein iron comprises an amount ranging from 0.5 to 10 weight percent of the total weight of the material.
9. The zeolite of claim 1, wherein the total alkali oxide amount is less than 0.3 weight percent.
10. The zeolite of claim 1, wherein the peak area ratio between the FT-VIS peak between 20 500-1100 nm and the FT-VIS peak area of $\text{Cu}(\text{OH})_2$ between 500-1100 nm is lower than 2.5.
11. A method of selective catalytic reduction (SCR) of NO_x in exhaust gas, said method comprising contacting exhaust gas with a zeolitic material comprising a copper containing CHA-type zeolite, wherein said material has an FTIR peak area ratio between the peak at 900-1300 cm^{-1} and the peak at 765-845 cm^{-1} ($\sim 805 \text{ cm}^{-1}$ is Si-O-Si symmetric stretch) of at least 55.
- 25 12. The method of claim 11, wherein said contacting step is performed in the presence of ammonia or urea.
13. A method of making a microporous crystalline material from reaction mixtures that are essentially void of alkali metal cations and comprise organic structure directing agents (OSDA) selected from (1) metal-polyamine as the first OSDA, (2) N,N,N-trimethyl-1-adamantyl ammonium (TMAda⁺), or 30 trimethylbenzylammonium (TMBA⁺) or N,N,N-dimethylethylcyclohexylammonium (DMECHA⁺) organic or mixtures thereof as the second OSDA, and (3) TMA⁺ or TEA⁺ or mixtures thereof as the third OSDA, the method comprising:
 - a) mixing sources of alumina, silica, water, a first OSDA, a second OSDA and optionally a third OSDA and optionally a seed material to form a gel;
 - 35 b) heating the gel in a vessel at a temperature ranging from 80°C to 250°C to form a crystalline chabazite product; and
 - c) calcining the product to produce an aluminosilicate zeolite having a CHA structure, and a silica-to-alumina ratio (SAR) ranging from 5 to 60.

14. The method of claim 13, wherein the reaction mixture has a molar composition of 1 SiO_2 : m Al_2O_3 : n metal-polyamine: x TMAOH : y TMAOH : z H_2O , where $m = 0.016-0.2$, $n = 0.01-0.12$, $x = 0.01-0.50$, $y = 0.01-0.50$, $z = 1-50$.

15. The method of claim 13, wherein the metals used for forming metal-polyamine of the first OSDA are selected from Cu, Fe, Mn, Co, Ni, Pd, Pt and Zn.

16. The method of claim 13, wherein the polyamine of the first OSDA is selected from diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, N, N-(2-hydroxyethyl) ethylenediamine, N,N -bis(2-aminoethyl)-1,3-propanediamine, 1,2-bis(3-aminopropylamino), 1,4,8,11 -tetraazacyclotetradecane, 1,4,8,11 - tetramethyl-1,4,8,11 - tetraazacyclotetradecane, and combinations thereof, amongst others.

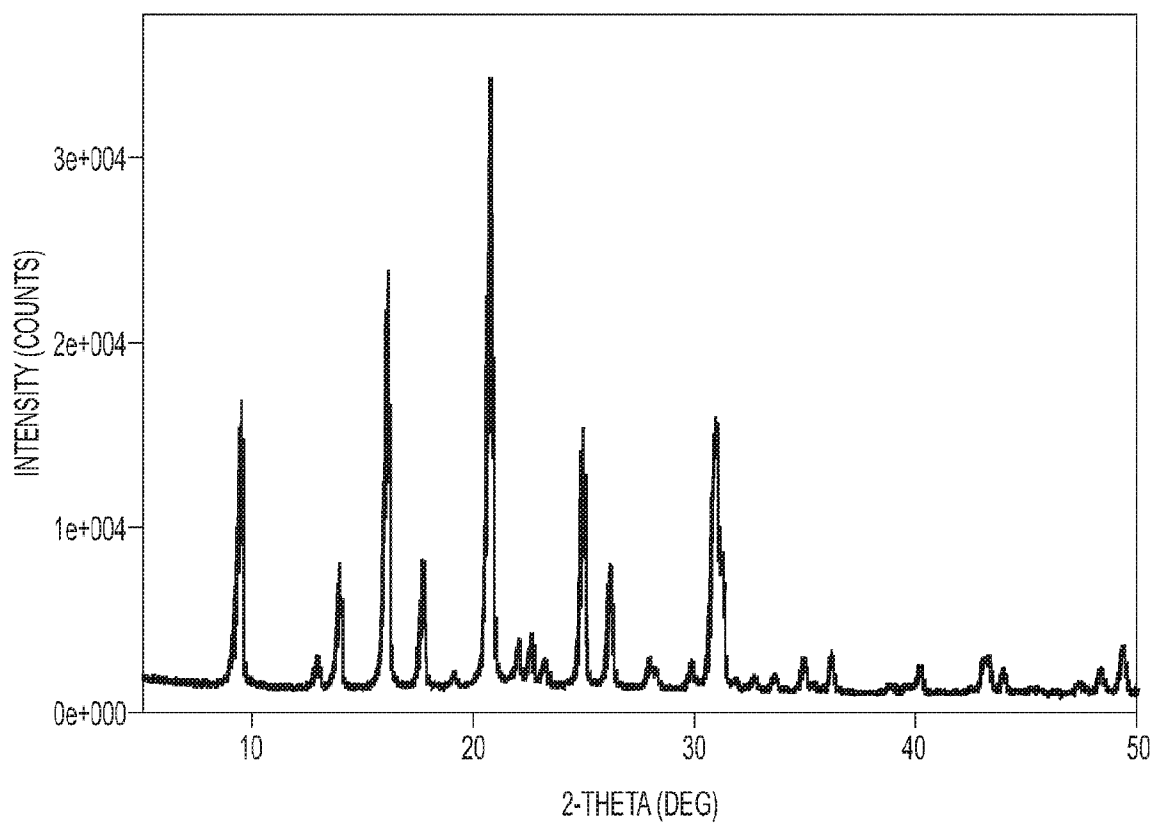
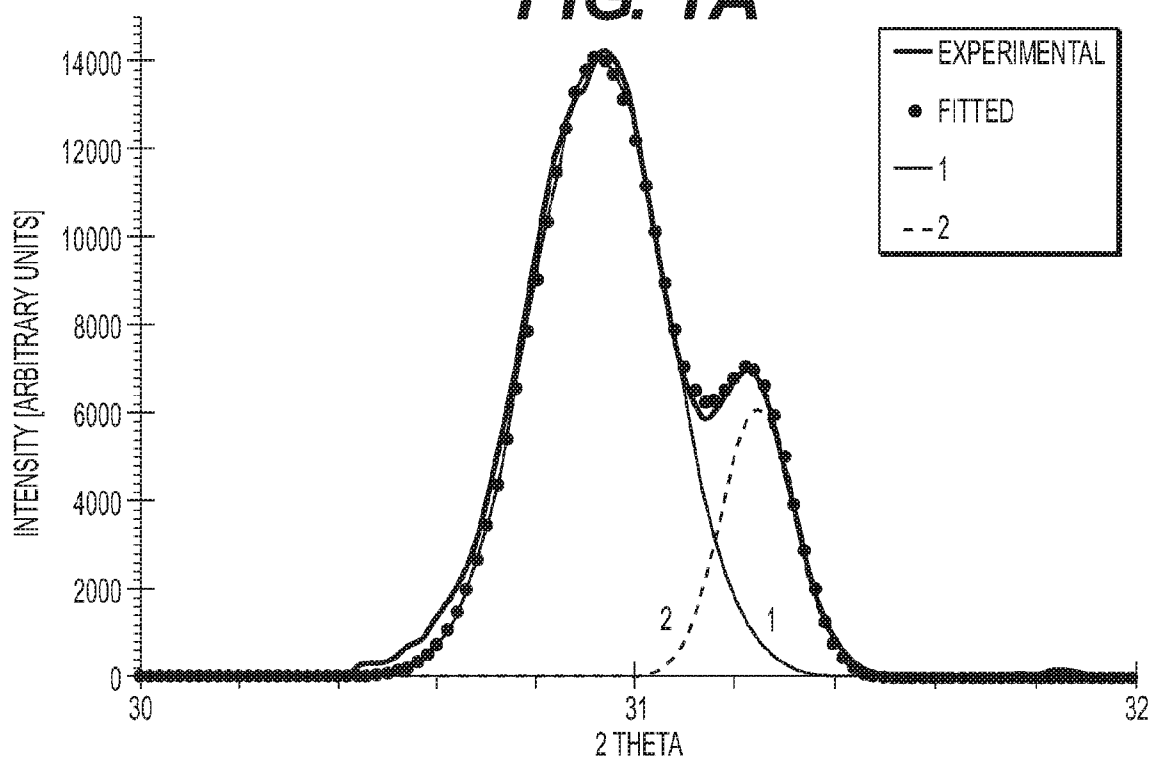
17. The method of claim 16, wherein the polyamine is tetraethylenepentamine (TEPA).

18. The method of claim 13, wherein the source of alumina is chosen from aluminum trihydroxide, alumina, pseudoboehmite alumina, silica-alumina and Al isopropoxide.

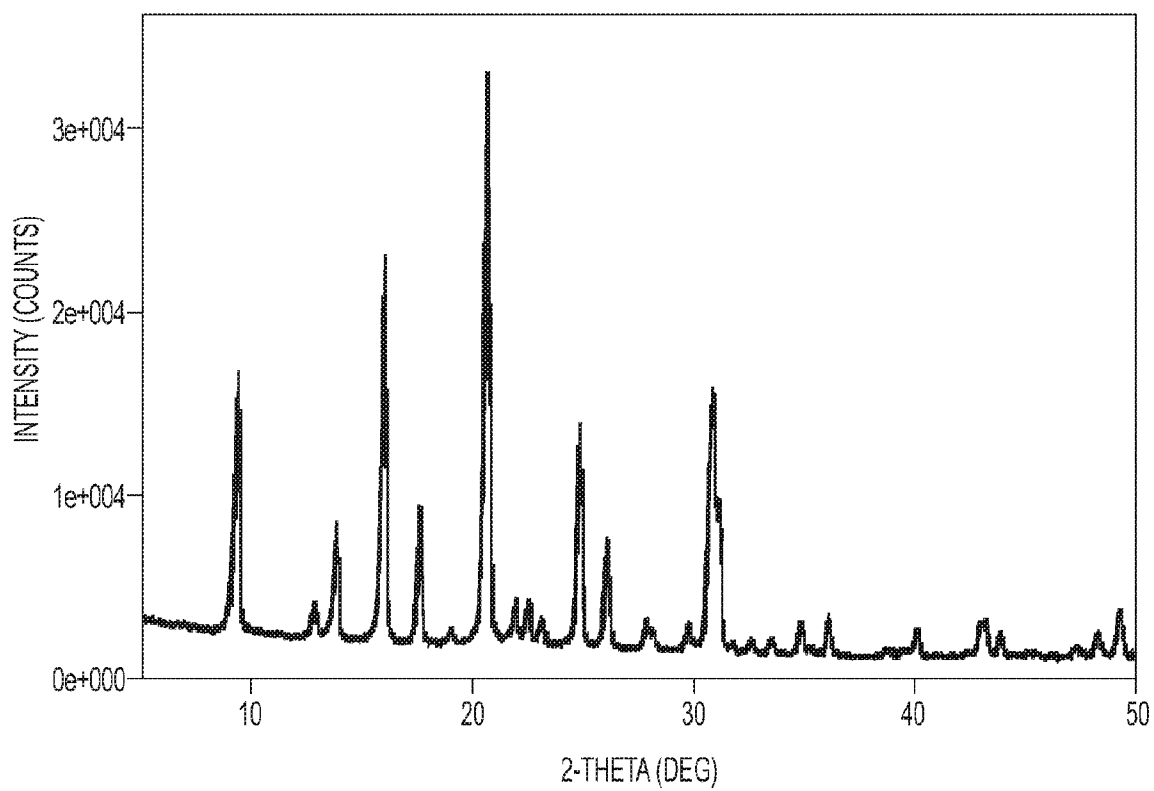
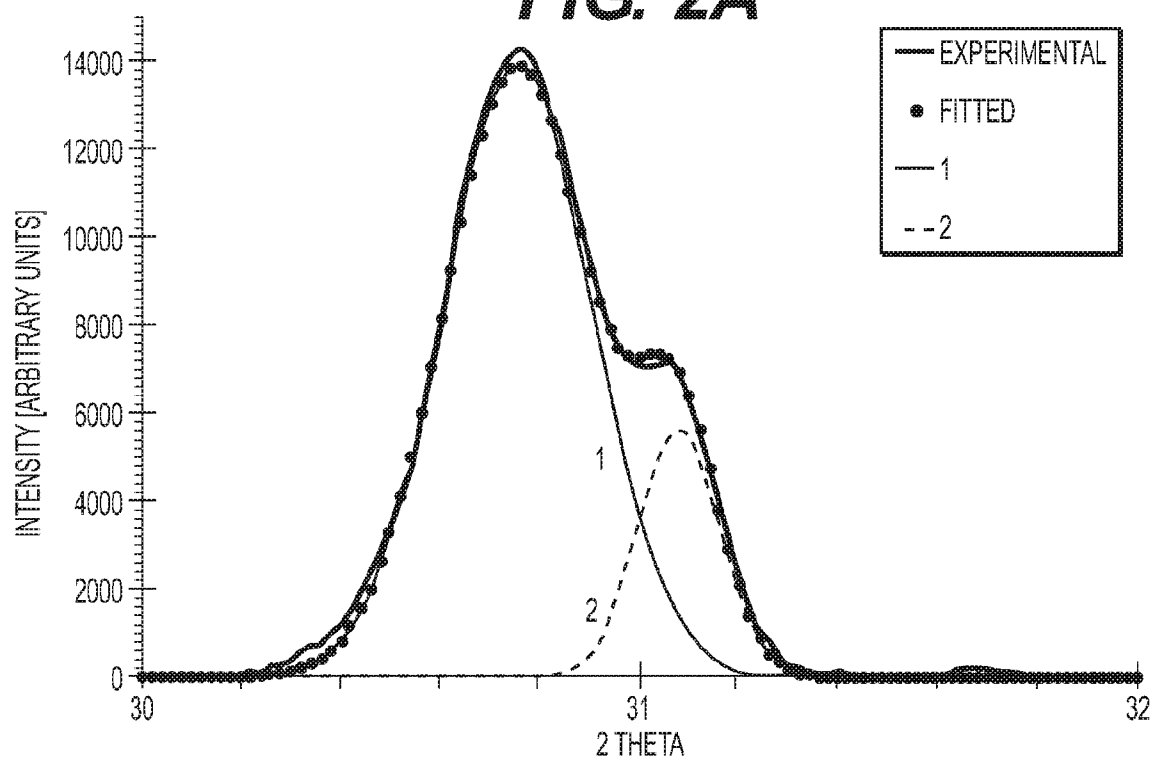
19. The method of claim 13, wherein the source of silica is chosen from silica sol, silica gel, precipitated silica, silica-alumina and fumed silica.

20. The method of claim 13, wherein the as synthesized material following step b) exhibits an XRD peak area ratio between the [3,1,0] peak and the peak doublet (sum of [3,-1,-1] peak and [3,1,0] peak) of at least 0.15.

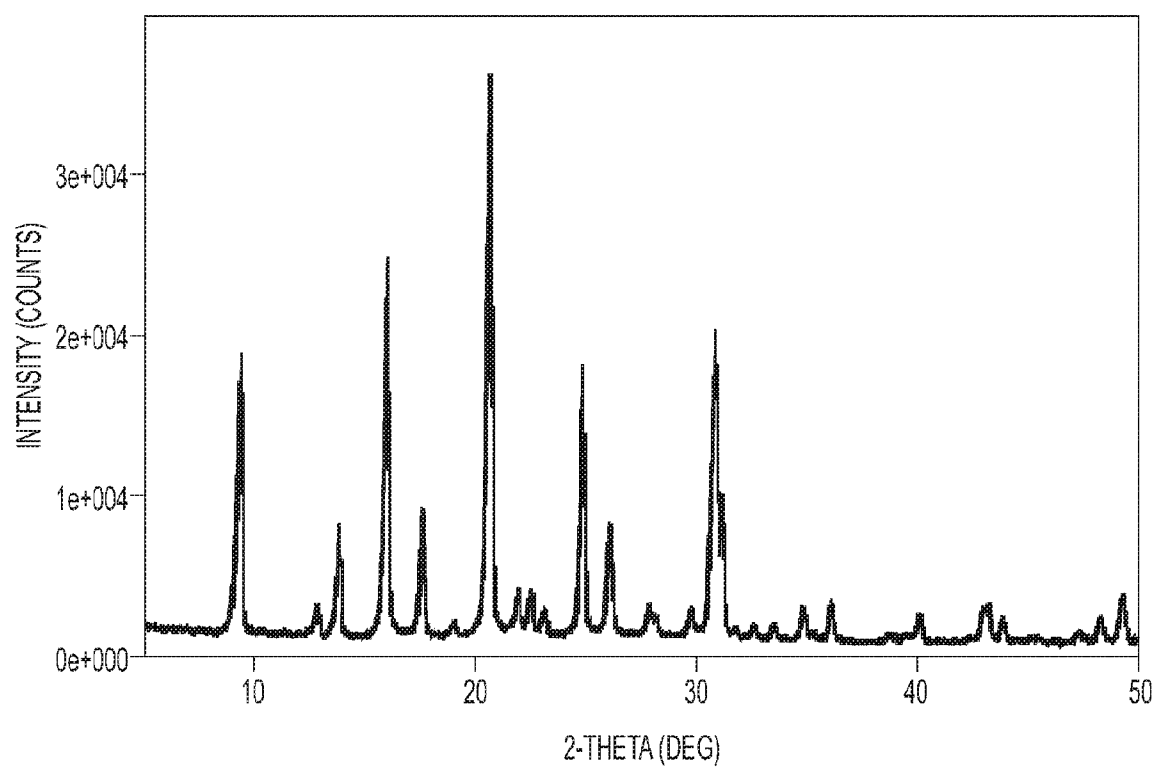
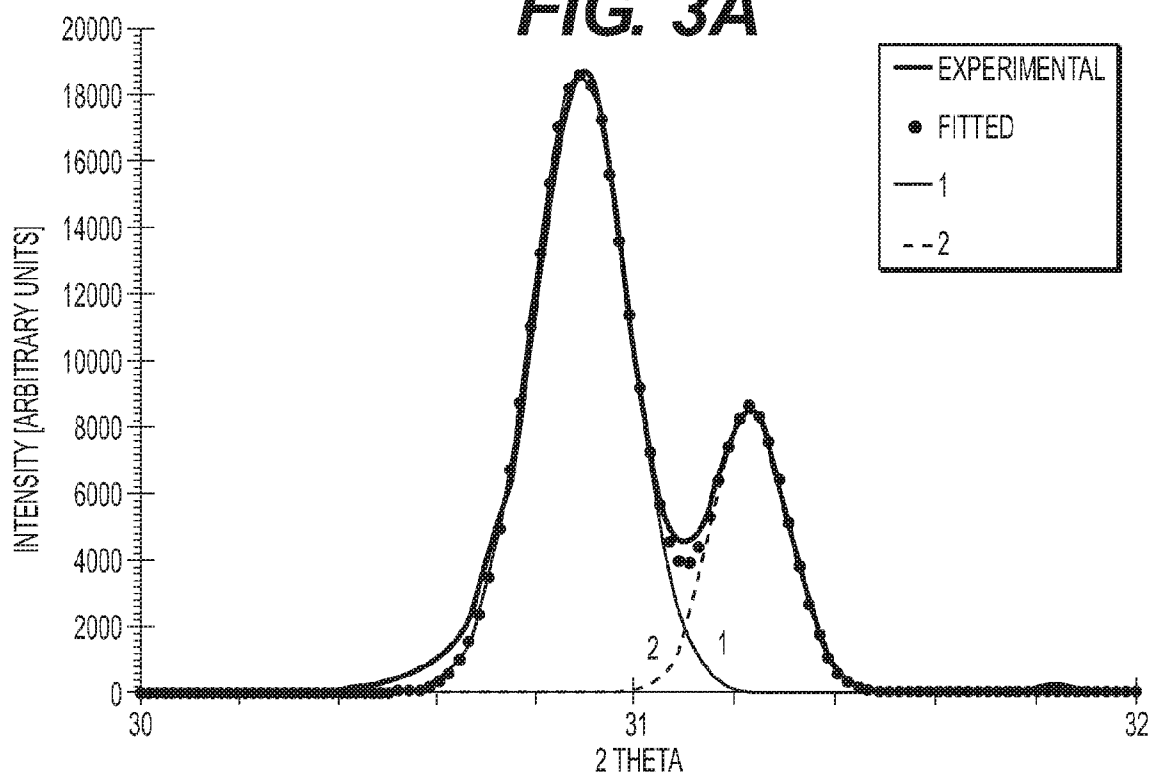
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**FIG. 1A****FIG. 1B**

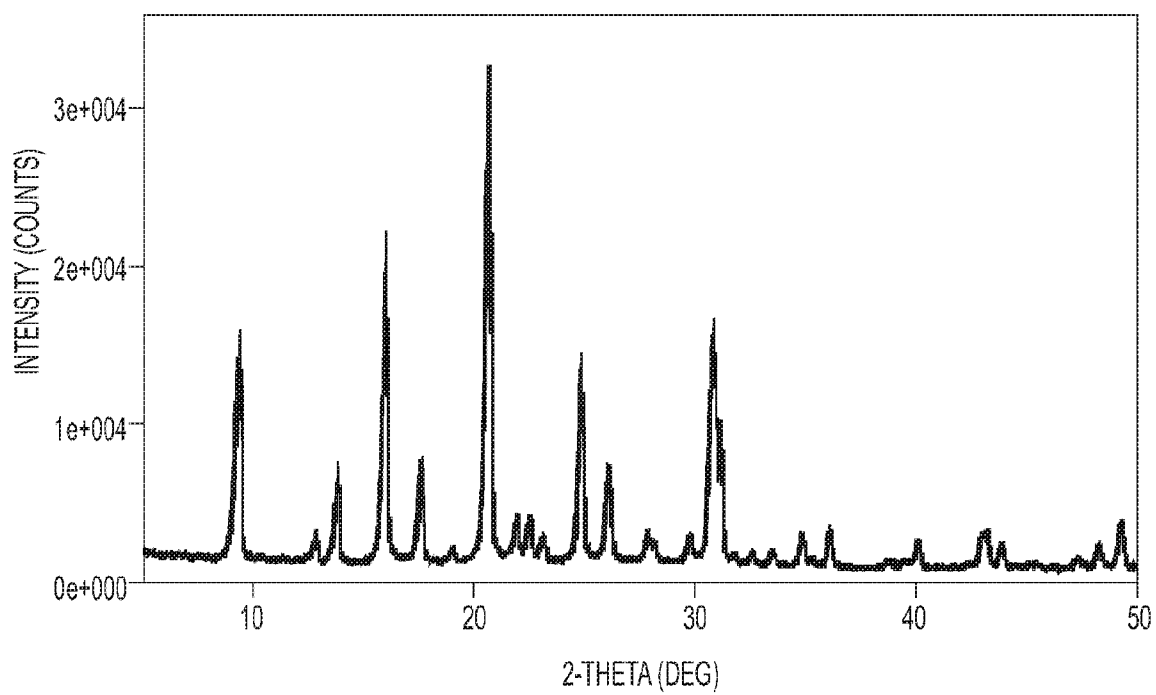
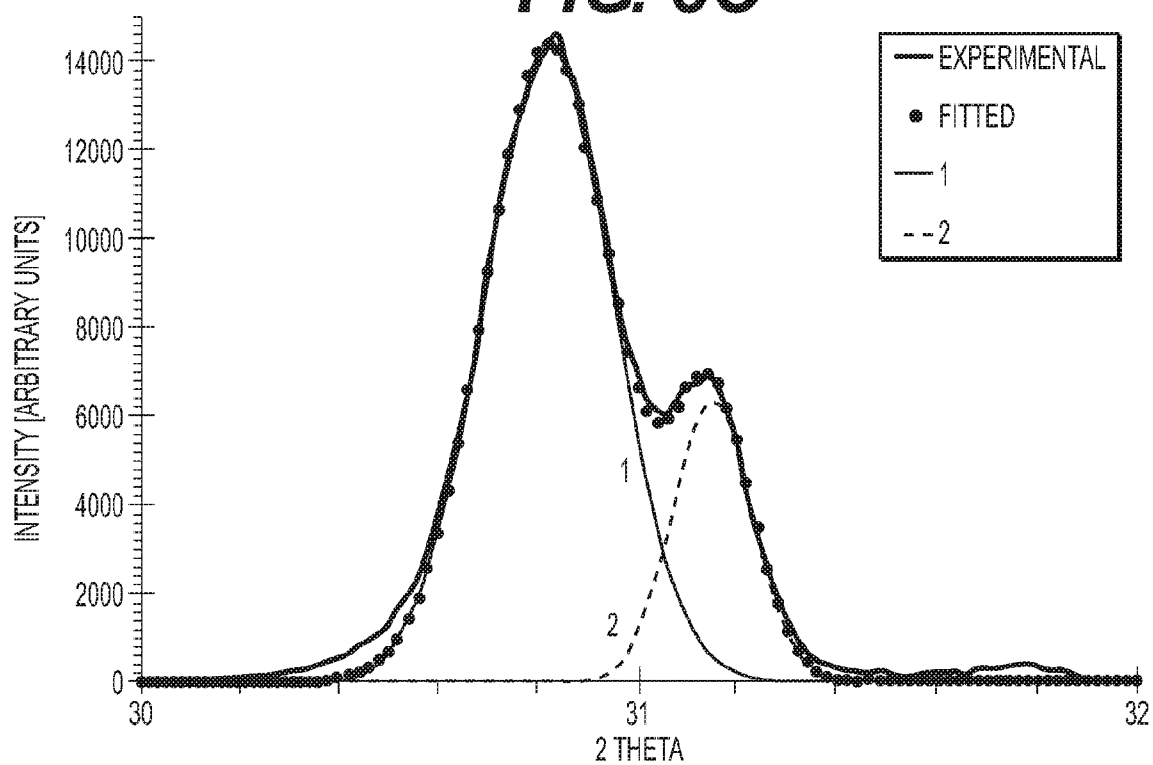
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**FIG. 2A****FIG. 2B**

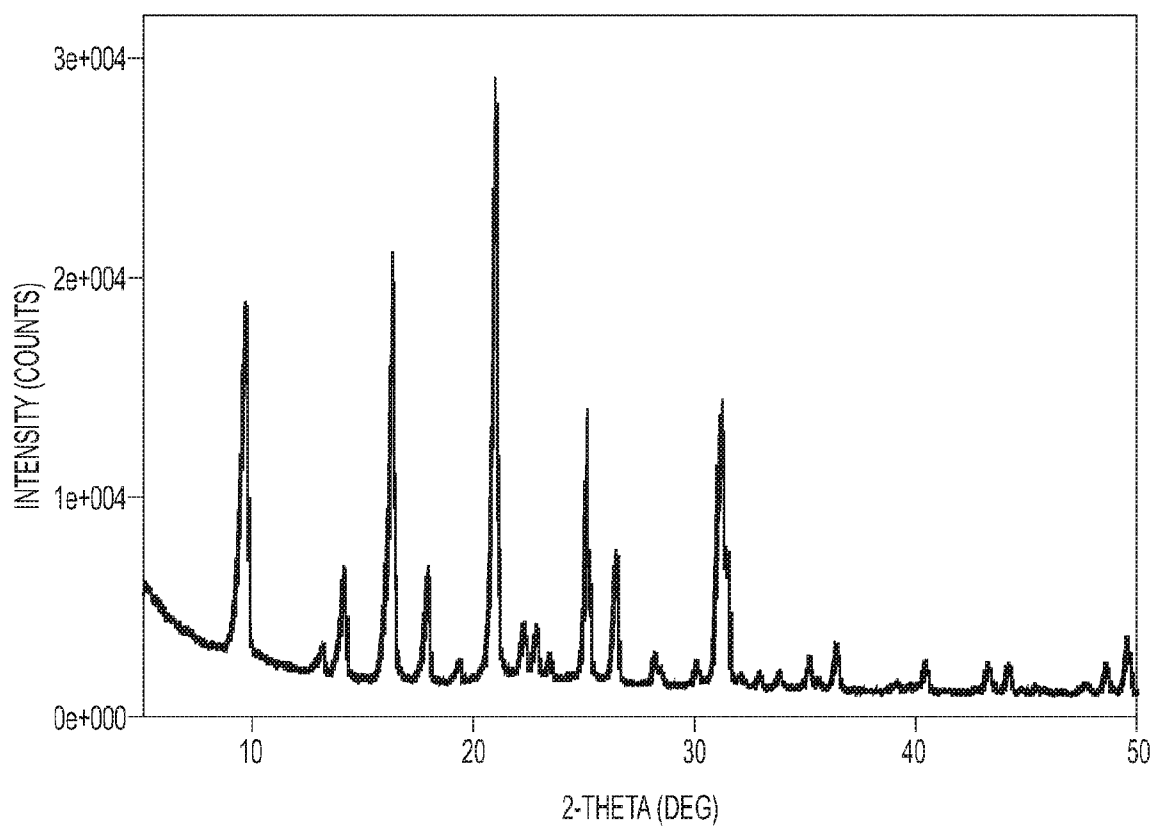
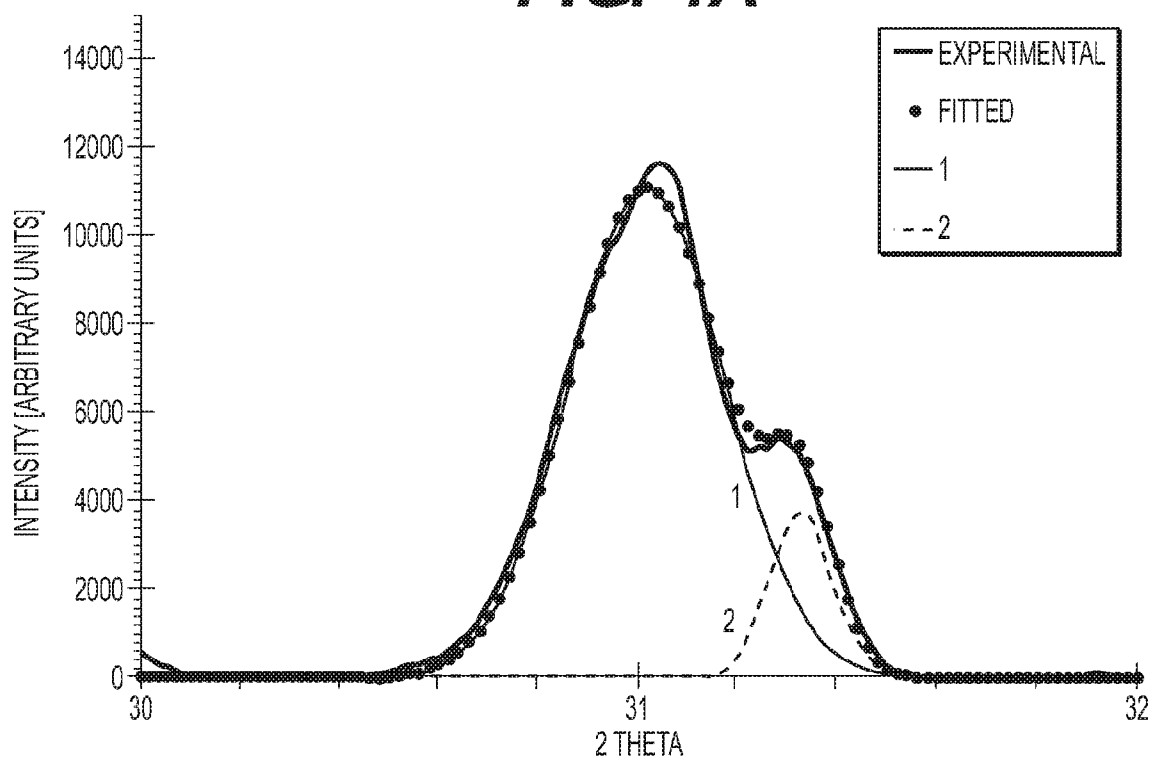
3/13

**FIG. 3A****FIG. 3B**

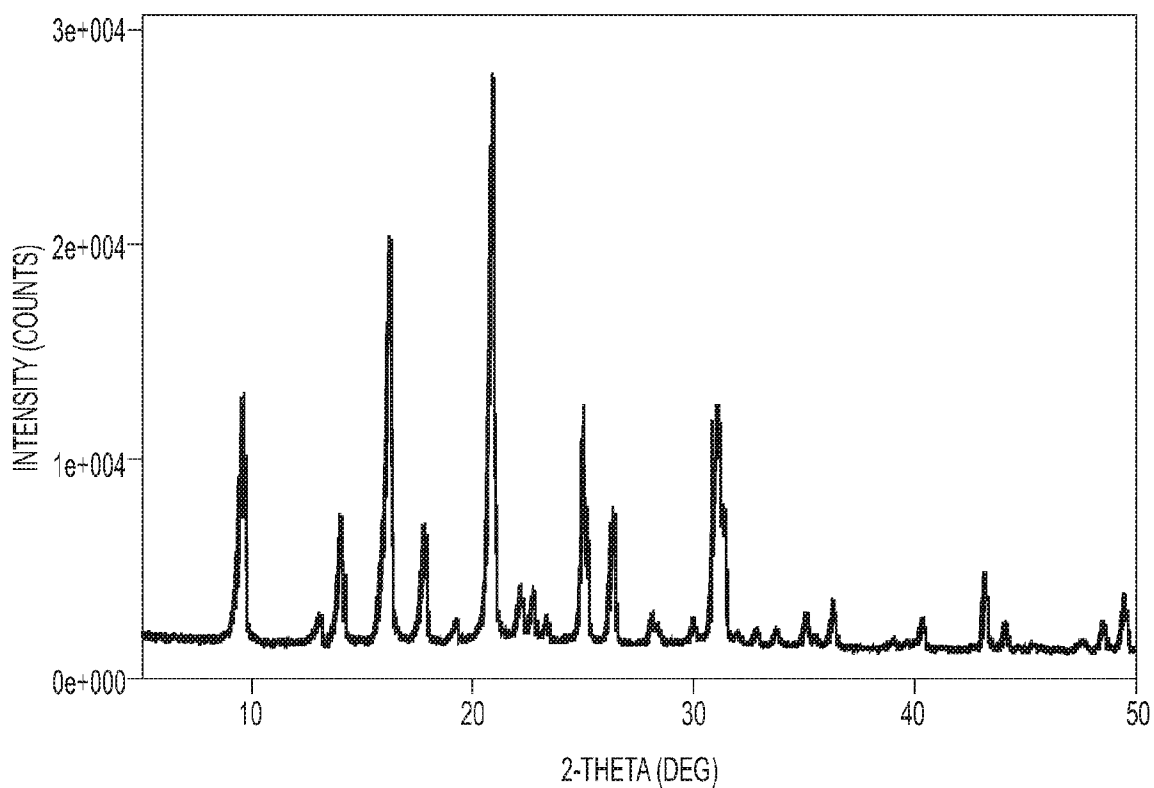
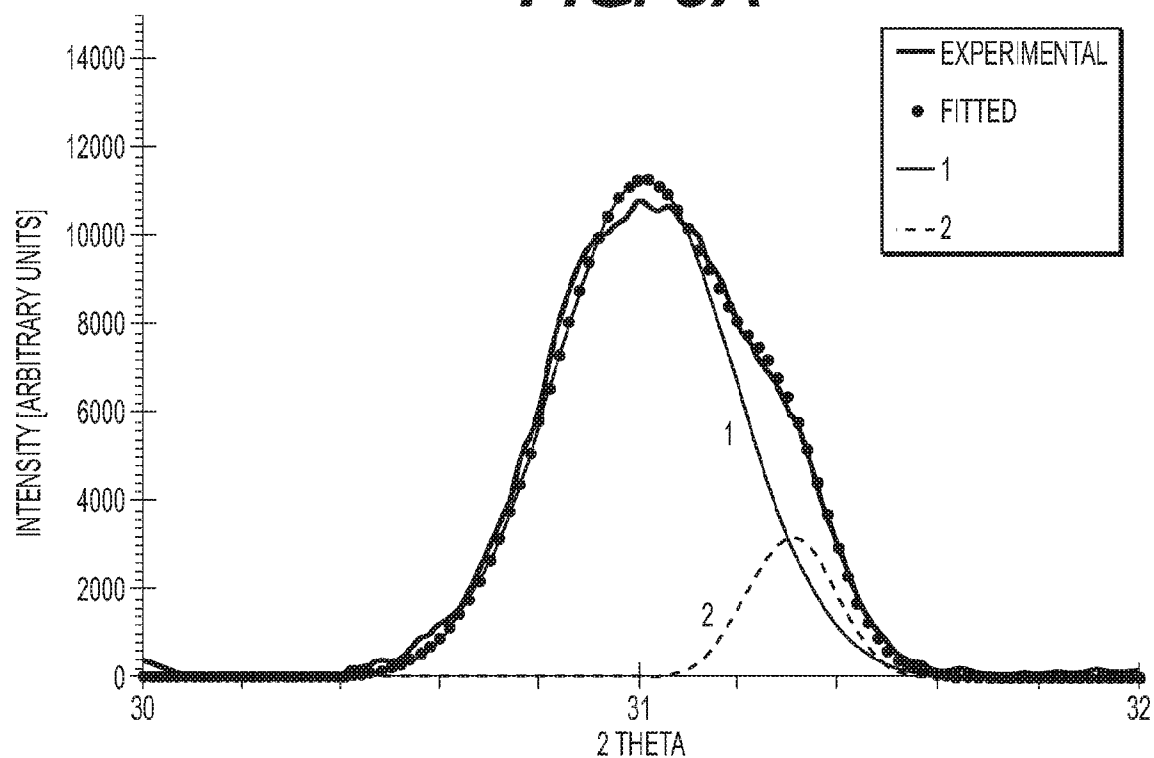
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**FIG. 3C****FIG. 3D**

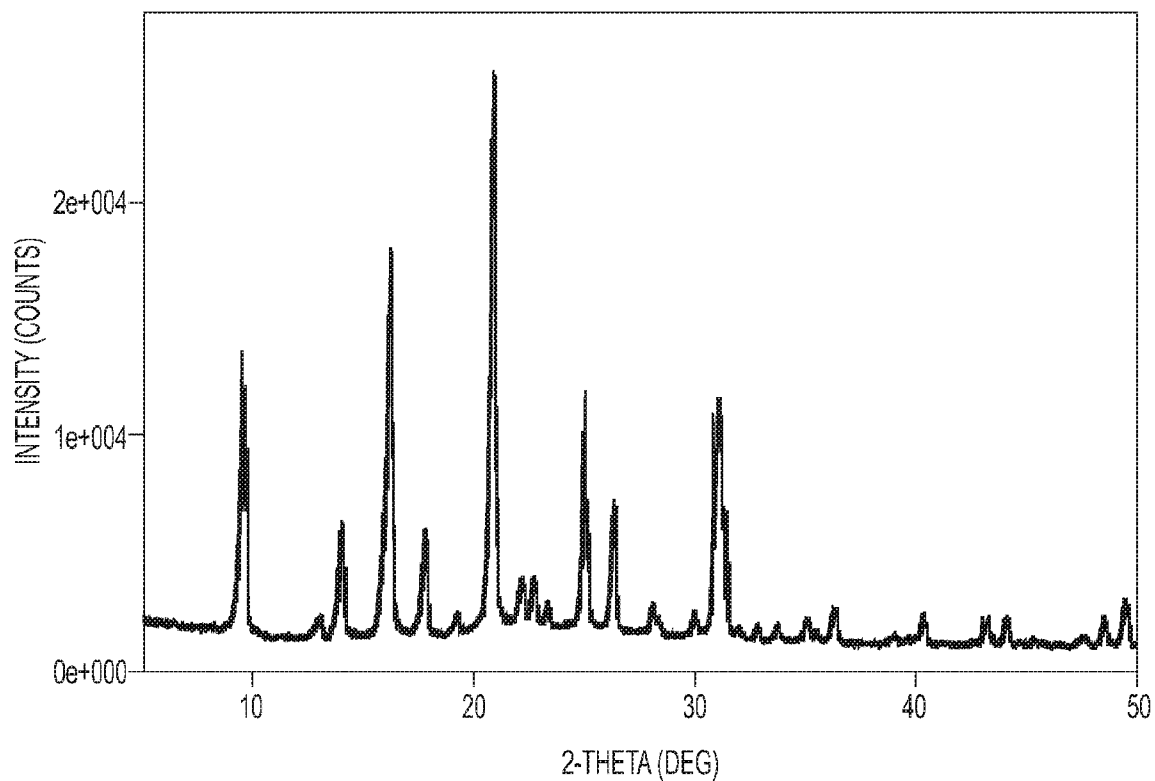
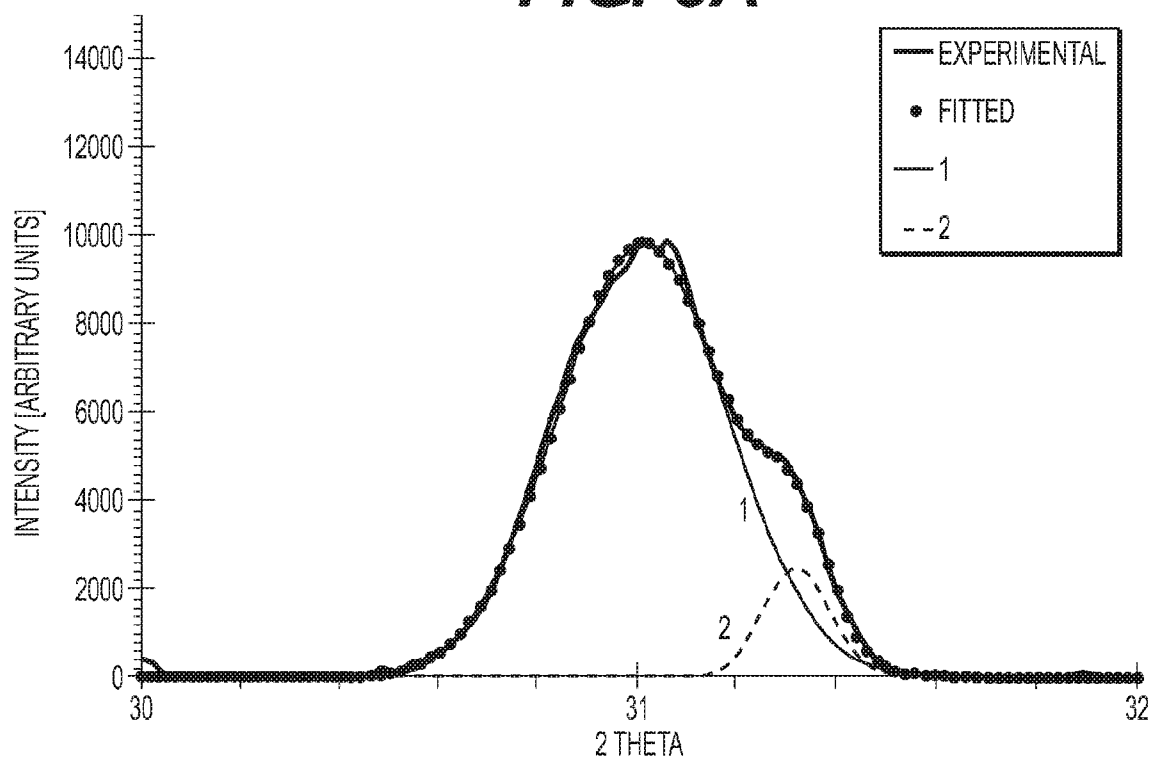
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**FIG. 4A****FIG. 4B**

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**FIG. 5A****FIG. 5B**

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**FIG. 6A****FIG. 6B**

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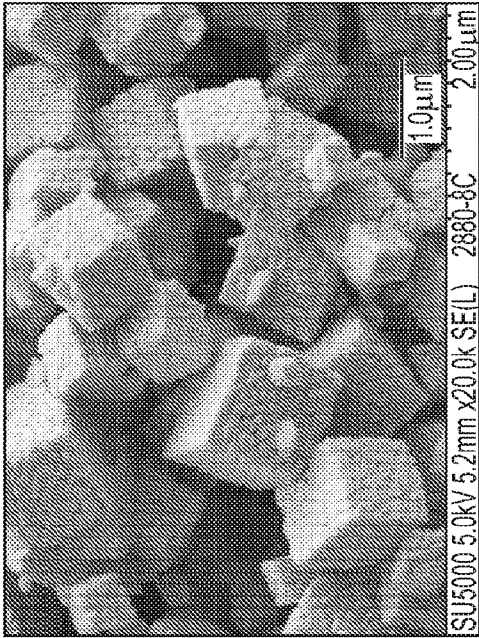


FIG. 7B

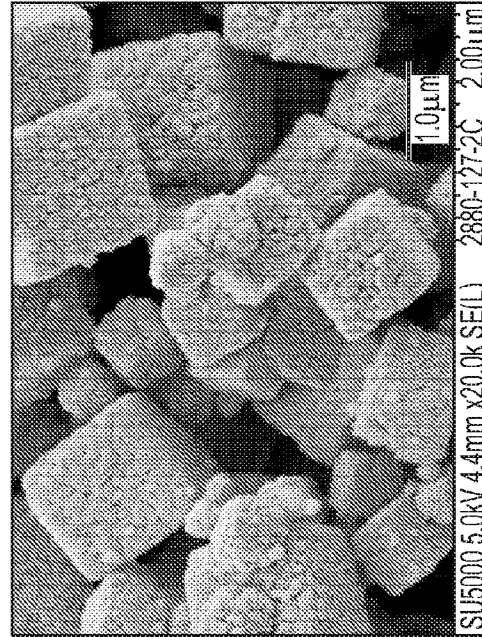


FIG. 8B

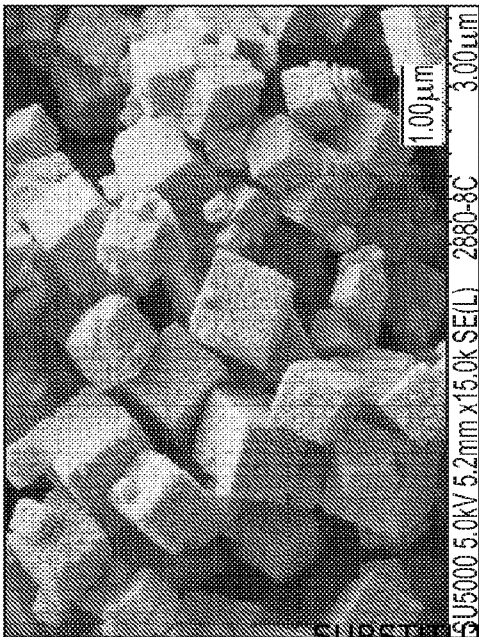


FIG. 7A

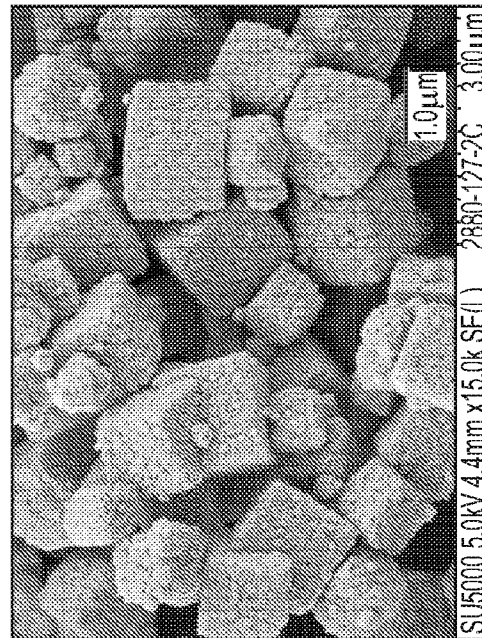


FIG. 8A

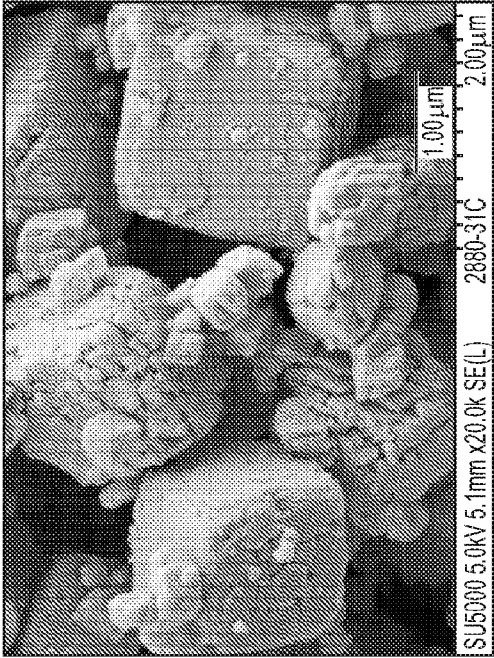


FIG. 9B

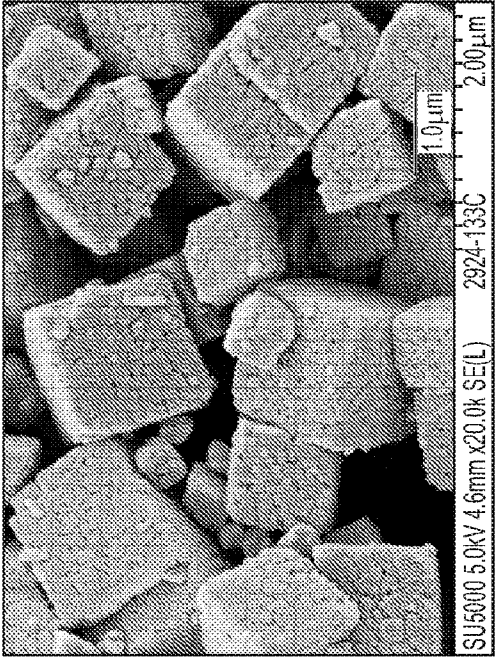


FIG. 9D

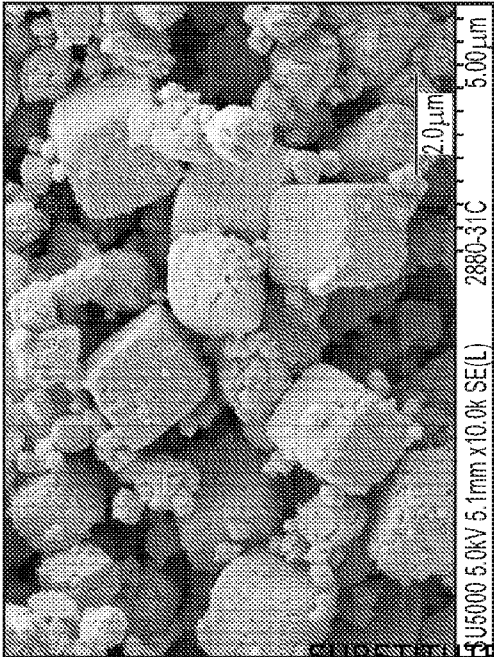


FIG. 9A

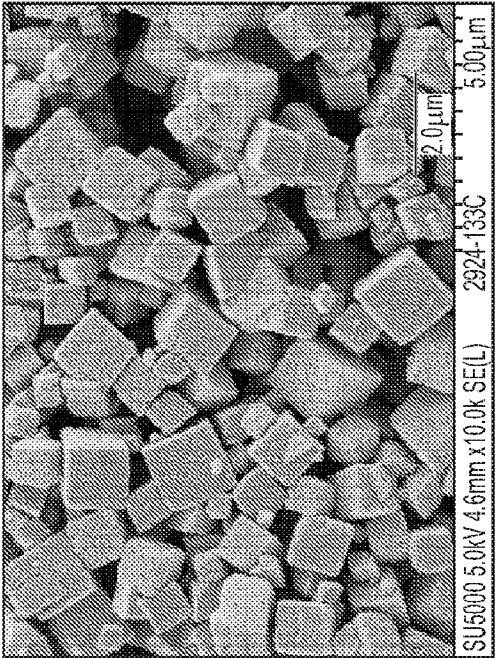


FIG. 9C

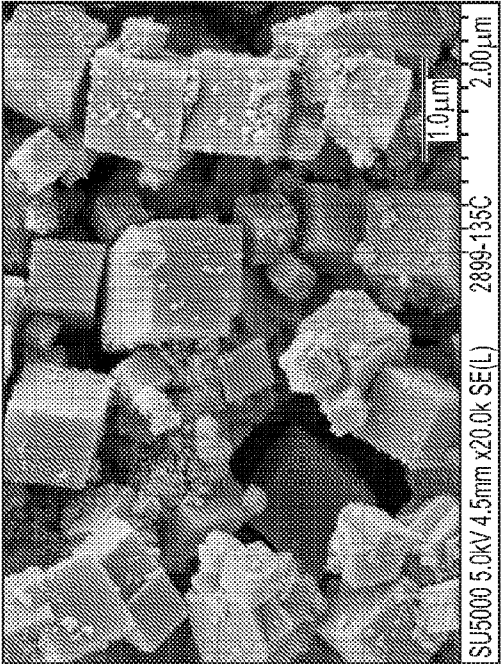


FIG. 10B

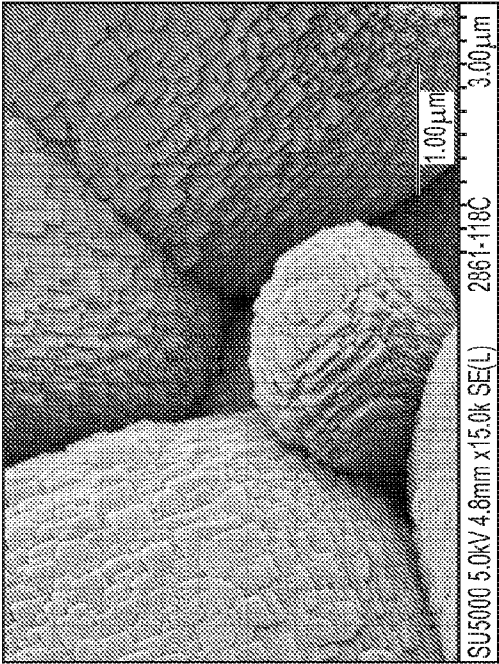


FIG. 11B

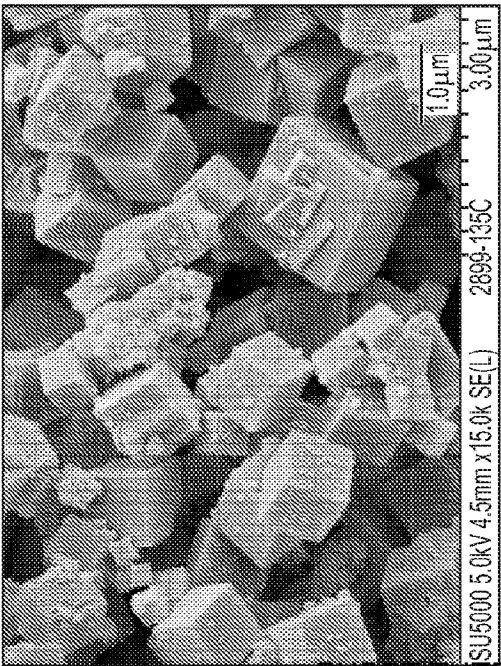


FIG. 10A

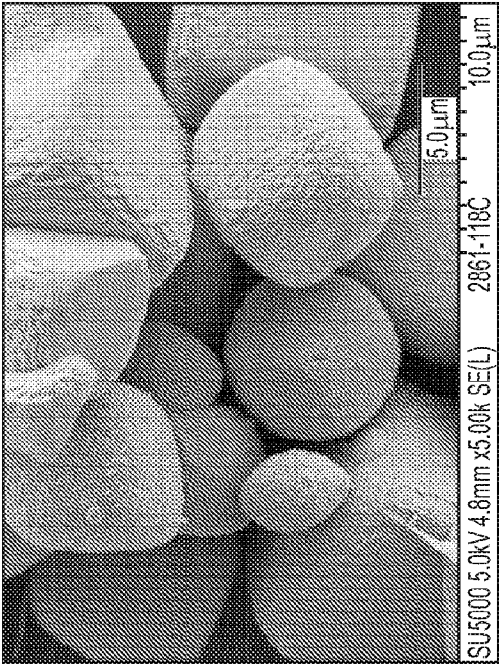


FIG. 11A

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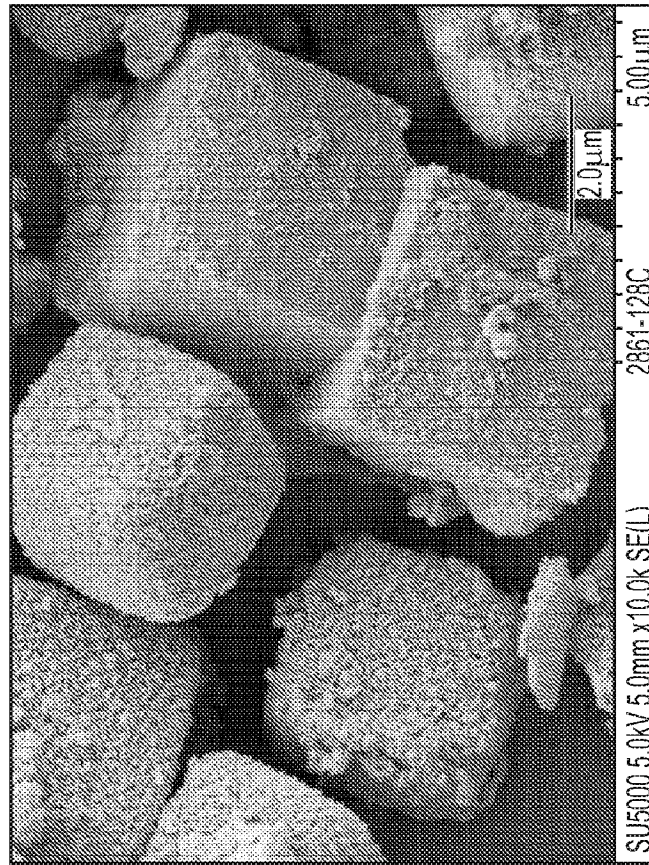


FIG. 12B

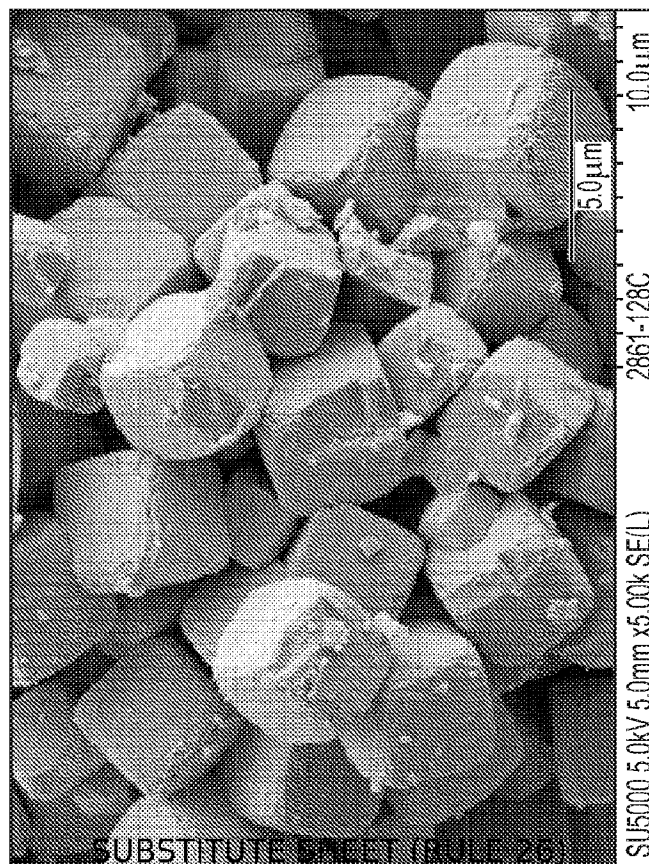
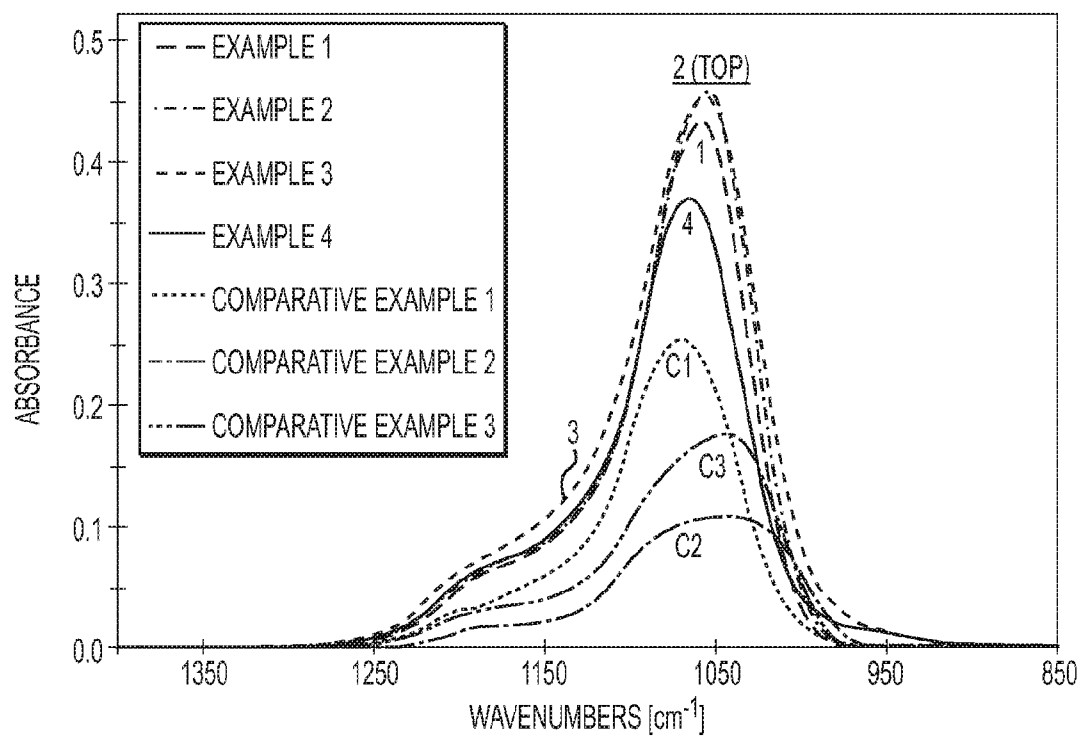
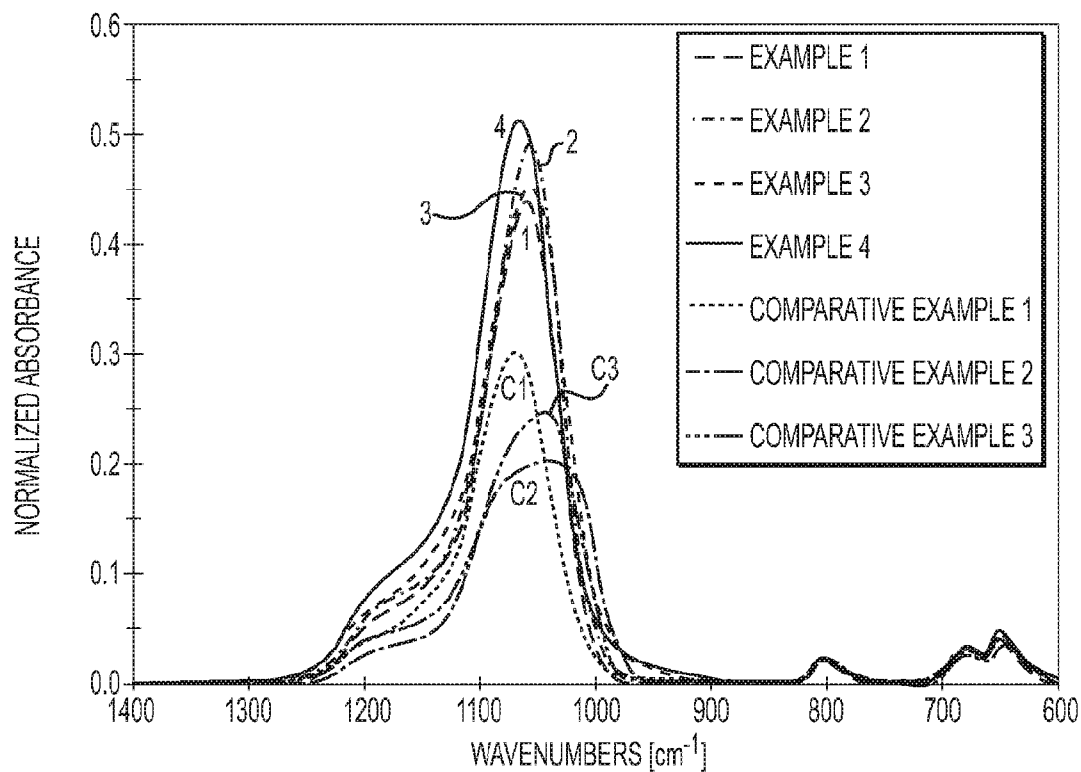


FIG. 12A

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**FIG. 13A****FIG. 13B**

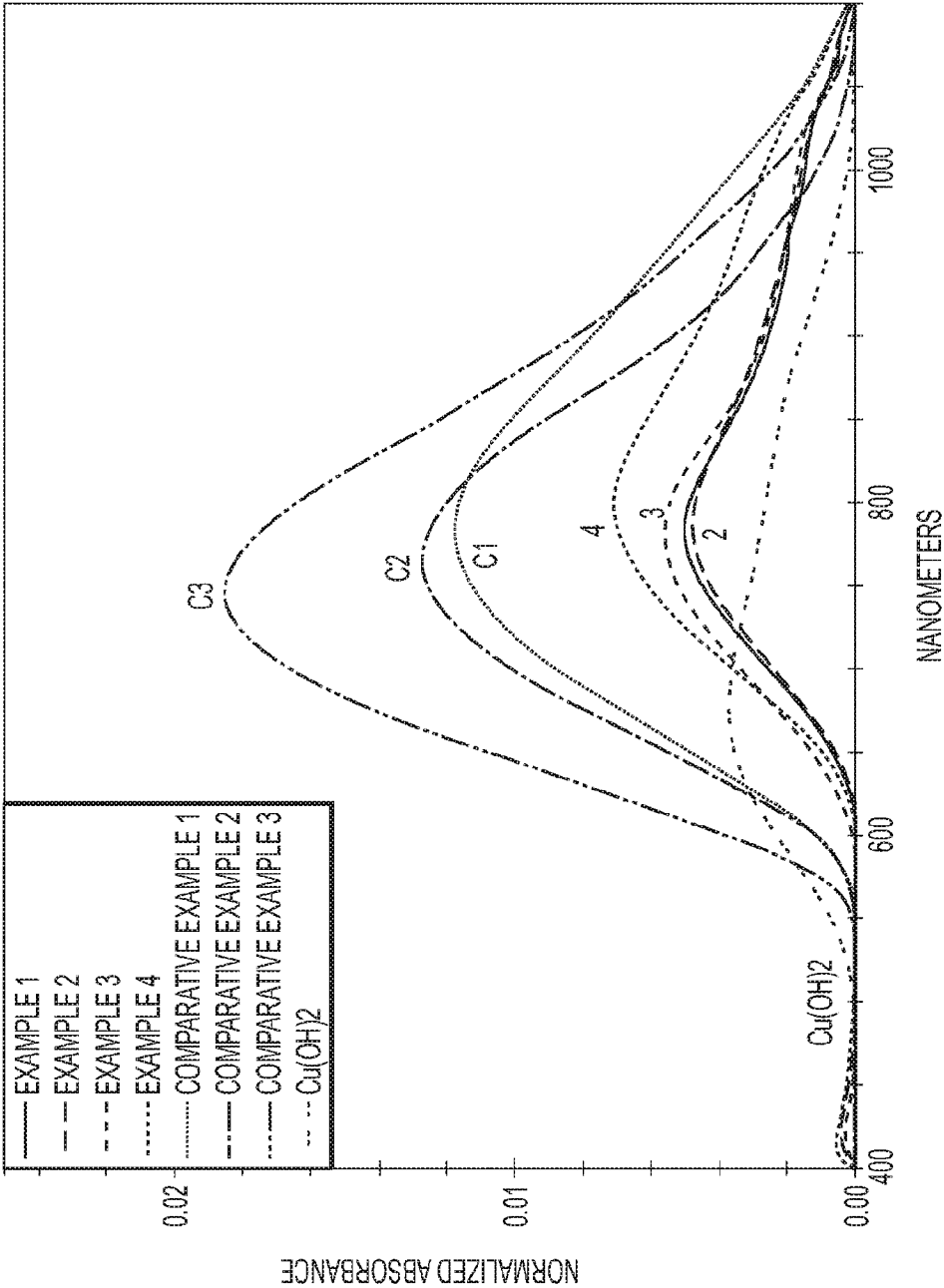


FIG. 14

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/067886

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B39/48 B01J29/76
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B B01J

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)

EP0-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/151286 A1 (RIVAS-CARDONA ALEJANDRA [US] ET AL) 4 June 2015 (2015-06-04) claims 10-18; example 1 paragraph [0027] paragraph [0081] -----	1-13, 15-20
X	WO 2014/090698 A1 (HALDOR TOPSØE AS [DK]) 19 June 2014 (2014-06-19) examples 2-5, 7-10 -----	1-13, 15-20
X	WO 2009/141324 A1 (BASF SE [DE]; TRUKHAN NATALIA [DE]; MUELLER ULRICH [DE]) 26 November 2009 (2009-11-26) examples 1-3 ----- -/--	1-13, 15-20



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 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

20 March 2020

Date of mailing of the international search report

30/03/2020

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/067886

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 3 293 149 A1 (CONSEJO SUPERIOR INVESTIGACION [ES]; UNIV VALENCIA POLITECNICA [ES]) 14 March 2018 (2018-03-14) examples 1-4 -----	1-20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/067886

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.: 1-20(partially)
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:
see FURTHER INFORMATION sheet PCT/ISA/210
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:

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 an 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.:

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-20(partially)

1. Present claims 1-20 relate to a extremely large number of possible products and starting materials for a method. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only only a very small proportion of the mentioned starting materials, see paragraphs [006] - [009] and [060] - [068].

It is commonly accepted that claims are generalizations from one or more particular examples, but the extend of the generalization permissible is a matter which must be judged in the light of the relevant prior art.

The art of zeolite synthesis is a technical field in which generalization of the disclosure of specific examples towards other elements is really unpredictable.

The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extend of the search claims 1-20 (PCT Guidelines 9.19 and 9.23).

2. The search of the claims 1-20 was restricted to those claimed compounds and starting materials wich appear to be supported:

1.

Regarding the product, the search was carried out for a copper-containing chabazite zeolite.

2. Regarding the process, the search was carried out for a process where the reaction mixture contains a combination of the following 3 structure directing agents: Cu-TEPA, TMAdOH and TMAOH.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2019/067886

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