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(54) Title: SMALL CRYSTAL ZSM-5, ITS SYNTHESIS AND USE

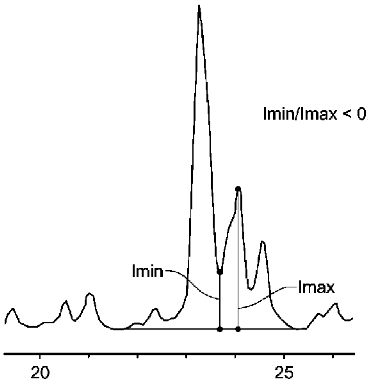

FIG. 1(a)

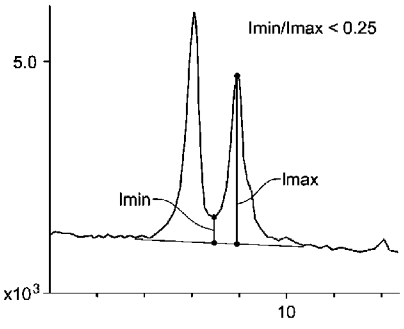

FIG. 1(b)

(57) Abstract: A molecular sieve having the framework structure of ZSM-5 is described comprising crystals having an external surface area in excess of $100 m^2/g$ (as determined by the t-plot method for nitrogen physisorption) and a unique X-ray diffraction pattern.

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SMALL CRYSTAL ZSM-5, ITS SYNTHESIS AND USE

PRIORITY

[0001] The present application claims priority to and the benefit of U.S. Provisional Application No. 61/740,908 filed on 21 December 2012, which is hereby incorporated by reference in its entirety.

FIELD

[0002] This invention relates to small crystal size ZSM-5, its synthesis and its use as an adsorbent and a catalyst for organic conversion reactions.

BACKGROUND

[0003] Crystalline ZSM-5, and its conventional preparation using tetrapropylammonium cations as a structure directing agent, are taught by U.S. Patent No. 3,702,886 and U.S. Patent No. Re. 29,948, the entire disclosures of which are incorporated herein by reference. Conventional ZSM-5 has a distinctive X-ray diffraction pattern which distinguishes it from other known crystalline materials and is a highly versatile catalyst useful in a variety of organic conversion reactions.

[0004] For some acid-catalyzed reactions over zeolites, it is beneficial to reduce diffusion lengths of the reagent and/or product molecules by employing a zeolite with a reduced crystal size and hence an increased external surface area. This may have the effect of reducing the shape selective effects of the zeolite, but for reactions that require only strong activity this may not be important.

[0005] An example of small crystal ZSM-5 is disclosed in U.S. Patent No. 5,240,892, in which the ZSM-5 is in the form of platelets having first and second major dimensions of at least about 0.05 micron, preferably at least about 0.1 micron, and a minor third dimension of less than about 0.02 micron, preferably less than about 0.01 micron. The ZSM-5 has a mesitylene sorption capacity of at least 3.0 weight %, and is produced using precipitated silica as the silica source either in the absence of an organic directing agent or using n-propylamine as the directing agent.

[0006] In addition, in *Chem. Mater.* 21 (2009) 641-654, D. Serrano et al. claim synthesizing ZSM-5 crystals as small as 5 to 10 nm using a dual template of tetrapropylammonium (TPA) ions and phenylaminopropyltrimethoxysilane. In this method, the silanizing agent is introduced after the synthesis gel is pre-heated for short periods of time before the onset of zeolite crystallization. Figure 1 of Serrano et al. shows a schematic representation of the crystallized products, whereas Figure 2 shows TEM images of the product. Although these TEM images show very small particles, the peaks in the powder XRD of the product from this work are not as broad as would be anticipated for 5 to 10 nm crystals.

[0007] Ryoo and coworkers have reported in "Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived, catalysts", *Nature* 461, 246-249 (10 September 2009), the synthesis of a single unit cell-thick version of ZSM-5 by using a single templating agent composed of a 22-carbon atom alkyl chain and two quaternary ammonium groups separated by a methylene chain of 6 carbon atoms. Here the quaternary ammonium groups are located within the single-unit cell nanosheets, which are separated from one another by the long alkyl chains. Figure 3 of Ryoo et al. shows a schematic of the unilamellar and multilamellar version of the ZSM-5 crystals that are a single unit cell in thickness.

[0008] A common problem in the isolation of many nanocrystalline products is that their aggregates are so small that the products must be collected by centrifugation rather than by simple filtration techniques. Large scale-ups are therefore difficult to process.

[0009] According to the present invention, it has now been found that new ultra-small crystal forms of ZSM-5 can be produced. These ultra-small crystal forms of ZSM-5 have unique powder XRD patterns and are also referred to herein as EMM-20. EMM-20 can be made across a wide range of Si/Al ratios (infinity to 10) and is generally produced in highly aggregated form allowing its collection by standard filtration techniques. EMM-20 may be useful as a catalyst in reactions where high acid activity and large surface area are important.

SUMMARY

[0010] In one aspect, the invention resides in a molecular sieve having an X-ray diffraction pattern having at least the following features:

(i) a first peak with a maximum at 8.90 (± 0.30) degrees two-theta which has an intensity above background of $Imax_A$, and which intersects a second peak with a maximum at 7.96 (± 0.30) degrees two-theta to form a local minimum which has an intensity above background of $Imin_A$, such that the $Imin_A/Imax_A$ ratio is > 0.33; and

(ii) a third peak with a maximum at 24.0 (± 0.30) degrees two-theta.

[0011] In one embodiment, the third peak has an intensity above background of $Imax_B$, and intersects a fourth peak with a maximum at 23.2 (± 0.20) degrees two-theta, such that the intersection of the third and the fourth peaks exhibits an inflection point or forms a local minimum which has an intensity above background of $Imin_B$, such that the $Imin_B/Imax_B$ ratio is > 0.90.

[0012] In a further aspect, the invention resides in a molecular sieve having the framework structure of ZSM-5 and comprising crystals having an external surface area in excess of 100 m^2/g as determined by the t-plot method for nitrogen physisorption, and an X-ray diffraction pattern having a composite peak with a maximum at 24.0 ($\pm$ 0.30) degrees two-theta, which has an intensity above background of $Imax_B$, and which intersects a composite peak with a maximum at 23.2 ($\pm$ 0.20) degrees two-theta to form a local minimum, which has an intensity above background of $Imin_B$, such that the $Imin_B/Imax_B$ ratio is > 0.90.

[0013] In yet a further aspect, the invention resides in a molecular sieve having the framework structure of ZSM-5 and comprising crystals having an external surface area in excess of 200 m^2/g as determined by the t-plot method for nitrogen physisorption and an X-ray diffraction pattern with a single diffuse composite feature in the two-theta range from 21.5 to 26° two-theta.

[0014] In one embodiment, the crystals have an external surface area in excess of 250 m^2/g and a total surface area in excess of 525 m^2/g. In some cases, the crystals have an external surface area greater than their internal surface area.

[0015] In one embodiment, the molecular sieve has a composition comprising the molar relationship:

$$X_2O_3:(n)YO_2,$$

wherein n is at least about 20, X is a trivalent element, such as aluminum, and Y is a tetravalent element, such as silicon and/or germanium.

[0016] In another aspect, the invention resides in a process for converting a feedstock comprising an organic compound to a conversion product, the process comprising contacting said feedstock at organic compound conversion conditions with a catalyst comprising an active form of the molecular sieve material described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Figures 1 (a) and (b) show the portions of the X-ray pattern of a conventional ZSM-5 product made according to US Patent No. 5,240,892 in the regions 19 to 26 degree two-theta and 5 to 12 degrees two-theta respectively.

[0018] Figure 2 compares the X-ray diffraction patterns of the as-synthesized product of Example 2 after crystallization for 3 days (top pattern), 3 days and 22 hours (middle pattern), and 4 days (bottom pattern).

[0019] Figure 3 compares the X-ray diffraction patterns of the product of Example 2 after crystallization for 4 days before calcination (top pattern) and after calcination (bottom pattern).

[0020] Figure 4 provides scanning electron microscope (SEM) images of the as-synthesized product of Example 2.

[0021] Figure 5 shows the X-ray diffraction pattern of the as-synthesized product of Example 3.

[0022] Figure 6 compares the X-ray diffraction patterns of the as-synthesized product of Example 4 after crystallization for 24 hours (bottom pattern) and 30 hours (top pattern).

[0023] Figure 7 compares the X-ray diffraction patterns of the as-synthesized product of Example 5 after crystallization for 1 day (top pattern), 2 days (middle pattern) and 6 days (bottom pattern).

[0024] Figure 8 compares the X-ray diffraction patterns of the as-synthesized products of Example 6.

[0025] Figure 9 shows the ^{27}Al MAS NMR of the product of the fourth experiment of Example 6 prepared with pre-dissolved fumed alumina.

[0026] Figure 10 provides SEM images of the product of the fourth experiment of Example 6.

[0027] Figure 11 shows transmission electron micrograph (TEM) images of a microtomed specimen of a sample of the fourth experiment product of Example 6.

[0028] Figure 12 is a bar graph showing the distribution of crystal dimensions for each of the crystallographic edges of a sample of the fourth experiment product of Example 6.

[0029] Figures 13 (a) to (e) show the X-ray diffraction patterns of the as-synthesized products of Examples 7 to 11, respectively.

[0030] Figures 14 (a) to (f) show the X-ray diffraction patterns of the as-synthesized products of Examples 12 to 17, respectively.

[0031] Figures 15 (a) to (e) show the X-ray diffraction patterns of the as-synthesized products of Examples 19 to 23, respectively.

[0032] Figure 16 provides scanning electron microscope (SEM) images of the as-synthesized product of Example 22.

[0033] Figure 17 shows the ^{27}Al MAS NMR of the product of Example 22.

[0034] Figure 18 shows SEM images of the product of Example 23.

[0035] Figure 19 shows the ^{27}Al MAS NMR of the product of Example 23.

[0036] Figure 20 (a) to (c) show the X-ray diffraction pattern of the as-synthesized product of Examples 24 to 26, and Figures 20 (d) and (e) show the X-ray diffraction pattern of the as-synthesized and as-calcined products of Example 27.

[0037] Figure 21 shows SEM images of the product of Example 24.

[0038] Figures 22 (a) to (c) show the X-ray diffraction patterns of the as-synthesized products of Examples 28, 29 and 31, respectively.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0039] Described herein is a new ultra-small crystal form of ZSM-5 which exhibits a unique X-ray diffraction pattern, such that it has been given the designation EMM-20.

[0040] As conventionally synthesized, for example, in the presence of tetrapropylammonium cations as taught by U.S. Patent No. 3,702,886 and U.S. Patent No. Re. 29,948, a typical preparation of ZSM-5 has an X-ray diffraction pattern including the characteristic lines listed in Table 1 below:

Table 1

Interplanar d-Spacing (Å)	Degrees two-theta	Relative Intensity ($100xI/I_o$)
11.10±0.25	7.98±0.17	s-vs
9.85±0.30	9.03±0.28	m-vs
6.70±0.10	13.22±0.20	w
6.34±0.10	14.06±0.22	w
5.98±0.10	14.81±0.25	w
5.57±0.10	15.91±0.29	w
5.00±0.10	17.74±0.36	w
4.36±0.10	20.38±0.48	w
4.25±0.08	20.90±0.40	w
4.08±0.05	21.79±0.27	w
3.85±0.07	23.08±0.46	m-vs
3.71±0.05	23.99±0.33	w-m
3.62±0.04	24.59±0.27	w
3.04±0.03	29.39±0.30	w
2.99±0.02	29.89±0.21	w

[0041] The X-ray diffraction data reported herein were collected with a Panalytical X'Pert Pro diffraction system with an Xcelerator multichannel detector, equipped with a germanium solid state detector, using copper K-alpha radiation. The diffraction data were recorded by step-scanning at 0.02 degrees two-theta, where theta is the Bragg angle, and using an effective counting time of 2 seconds for each step. The interplanar spacings, d-spacings, were calculated in Angstrom units, and the relative intensities of the lines, I/I_o is the ratio of the peak intensity to that of the intensity of the strongest line, above background. The intensities are uncorrected for Lorentz and polarization effects. The relative intensities are given in terms of the symbols vs=very strong (75-100), s=strong (50-74), m=medium (25-49) and w=weak (0-24).

[0042] It is known that certain lines in the X-ray patterns of zeolites tend to broaden as the relevant dimension of the zeolite crystal decreases so that adjacent lines may begin to overlap and thereby appear as only partially resolved peaks or as unresolved broad peaks. In certain embodiments of the ZSM-5 described herein, this line broadening results in there being only a single diffuse composite feature in the range from 21.5 to 26 degrees two-theta (d-spacing range from 4.13 to 3.42 Å) of the X-ray pattern. In such cases, the maximum of the composite peak near 24.0 ± 0.30 degrees two-theta and the maximum of the composite peak near 24.4 ± 0.30 degrees two-theta either appear as shoulders or form part of a large diffuse composite peak with a maximum near 23.2 (± 0.20) degrees two-theta.

[0043] In a powder XRD pattern of a typical (larger crystallite) ZSM-5 sample, the composite peak with a maximum near 23.2 degrees two-theta and the composite peak near 24.0 degrees two-theta will intersect to form a clearly visible local minimum [See Figure 1(a)]. In these typical ZSM-5 preparations, the ratio of the relative background-subtracted intensity of this local minimum (Imin) to the relative background-subtracted intensity of the composite peak near 24.0 degrees two-theta (Imax) will be less than 0.40 in both the as-made and calcined forms of the zeolite. In one embodiment of the present ultra-small crystal material, the local minimum may still be clearly discerned from the composite peak near 24.0 degrees two-theta [e.g., Figure 3 for Example 2], but in this example the Imin/Imax ratio is > 0.90. In another embodiment, the crystals become so small and the peaks are so severely broadened that the peak maximum near 24.0 degrees either appears as an inflection point of the large diffuse composite peak with a maximum near 23.2 (± 0.20) degrees two-theta [e.g., bottom pattern in Figure 7] or no local maximum or inflection point is discerned for the composite peak near 24.0 (± 0.30) degrees two-theta [top pattern in Figure 8]. In these extreme cases the Imin / Imax ratio approaches 1.0.

[0044] Similarly, in typical ZSM-5 preparations, the composite peak with a maximum near 7.96 (± 0.30) degrees two-theta and the composite peak with a maximum near 8.90 (± 0.30) degrees two-theta intersect to form a clearly visible local minimum [see Figure 1(b)], in which the ratio of the relative background-subtracted intensity of this local minimum (Imin) to the relative background-subtracted intensity of the composite peak near 8.90 degrees two-theta (Imax) will be less than 0.20 in both the as-made and calcined forms of the zeolite. In contrast, in the present ultra-small crystal material produced in Example 2 (see X-ray pattern of Figure 3) the Imin/Imax ratio is > 0.33. In another embodiment (with ultra small crystals), the Imin/Imax ratio will be at least 0.40. It should be borne in mind that in cases where preferred orientation effects may be present, care should be taken to minimize their effects on X-ray patterns.

[0045] In the ultra small crystal embodiments of the present invention, the ZSM-5 crystals typically have an external surface area in excess of 200 m^2/g, in some cases in excess of 250 m^2/g, even in excess of 300 m^2/g and a total surface area in excess of 500 m^2/g, in some cases in excess of 600 m^2/g, even in excess of 650 m^2/g. In one embodiment, the ZSM-5 crystals have an external surface area greater than their internal surface area. All surface area values given herein are determined from nitrogen physisorption data using the t-plot method. Details of this method can be found in Lippens, B.C. and deBoer, J.H., "Studies on pore systems in catalysts: V. The *t* method", J. Catal., 4, 319 (1965), the entire contents of which are incorporated herein by reference.

[0046] It will be appreciated that, with such ultra-small crystal materials, X-ray diffraction may not be sufficient to identify the material as having the ZSM-5 structure, in which case other analytical methods, such as high resolution transmission electron microscopy and electron diffraction, may be necessary to confirm the identity of the material as ZSM-5.

[0047] The ZSM-5 crystals described herein have a composition comprising the molar relationship:

$$X_2O_3{:}(n)YO_2,$$

wherein n is at least about 20, X is a trivalent element in which X is desirably aluminum, and Y is a tetravalent element in which Y is desirably silicon and/or germanium.

[0048] The ZSM-5 crystals described herein can be produced from a synthesis mixture comprising sources of water, an alkali or alkaline earth metal (M), hydroxide ions, an oxide of a tetravalent element Y, optionally a trivalent element X, and a structure directing agent (Q) selected from one or more of 1,4-bis(N-pentylpyrrolidinium)butane dications, 1,5-bis(N-pentylpyrrolidinium)pentane dications, or 1,6-bis(N-pentylpyrrolidinium)hexane dications, the synthesis mixture having a composition, in terms of mole ratios of oxides, within the following ranges:

Reactants	Useful	Preferred
YO_2/X_2O_3	at least 20	at least 24
H_2O/YO_2	10 - 60	20 - 50
OH^-/YO_2	0.2 – 0.6	0.25 – 0.50
M/YO_2	0.05 - 0.40	0.1 – 0.40

Q/YO_2	0.05 - 0.20	0.05 – 0.20

[0049] Suitable sources of the tetravalent element Y depend on the element Y selected but in the preferred embodiments, in which Y is silicon and/or germanium, include colloidal suspensions of silica, fumed silicas, precipitated silicas, alkali metal silicates, tetraalkyl orthosilicates and germanium oxide. If present, the trivalent element X is normally aluminum, and suitable sources of aluminum include hydrated alumina and water-soluble aluminum salts, such as aluminum nitrate. Combined sources of aluminum and silicon may include clays or treated clays, such as metakaolin. Other combined sources of X and Y, including aluminosilicate zeolites such as zeolite Y, may also be used.

[0050] Suitable sources of Q are the hydroxides and/or salts of the relevant diquaternary ammonium compounds. Although the compounds themselves are believed to be novel, they can readily be synthesized by reaction of N-pentylpyrrolidine with 1,4-dibromobutane, 1,5-dibromopentane or 1,6-dibromohexane.

[0051] In some embodiments, the synthesis mixture may also use seeds of a molecular sieve material, such as ZSM-5 from a previous synthesis, desirably in an amount from 0.01 ppm by weight to 10,000 ppm by weight, such as from 100 ppm by weight to 5,000 ppm by weight of the synthesis mixture.

[0052] Crystallization of ZSM-5 from the above synthesis mixture can be carried out at either static or stirred conditions in a suitable reactor vessel, such as for example, polypropylene jars or teflon lined or stainless steel autoclaves, at a temperature of about 80°C to about 200°C for a time sufficient for crystallization to occur at the temperature used, e.g., from about 1 to about 21 days. Thereafter, the crystals are separated from the liquid and recovered.

[0053] To the extent desired and depending on the X_2O_3/YO_2 molar ratio of the material, any alkali or alkaline earth metal cations in the as-synthesized ZSM-5 can be replaced in accordance with techniques well known in the art by ion exchange with other cations. Preferred replacing cations include metal ions, hydrogen ions, hydrogen precursor, e.g., ammonium ions and mixtures thereof. Particularly preferred cations are those which tailor the catalytic activity for certain hydrocarbon conversion reactions. These include hydrogen, rare earth metals and metals of Groups 2 to 15 of the Periodic Table of the Elements. As used herein, the numbering scheme for the Periodic Table Groups is as disclosed in Chemical and Engineering News, 63(5), 27 (1985).

[0054] The as-synthesized ZSM-5 may also be subjected to treatment to remove part or all of the organic directing agent Q used in its synthesis. This is conveniently effected by thermal treatment in which the as-synthesized material is heated at a temperature of at least about 370°C for at least 1 minute and generally not longer than 20 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. The thermal treatment can be performed at a temperature up to about 925°C. Alternatively, the organic directing agent Q can be removed by treatment with ozone (*see,* e.g., Parikh et al., Microporous and Mesoporous Materials 76 (2004) 17–22). The organic-free product, especially in its metal, hydrogen and ammonium forms, is particularly useful in the catalysis of certain organic, e.g., hydrocarbon, conversion reactions.

[0055] The present molecular sieve may be intimately combined with a hydrogenating component, such as molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal, such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such component can be in the composition by way of (1) cocrystallization, (2) exchanged into the composition to the extent a Group IIIA element, e.g., aluminum, is in the structure, (3) impregnated therein, or (4) intimately physically admixed therewith. Such component can be impregnated in, or on to it, such as, for example, by, in the case of platinum, treating the silicate with a solution containing a platinum metal-containing ion. Thus, suitable platinum compounds for this purpose include chloroplatinic acid, platinous chloride and various compounds containing the platinum amine complex.

[0056] The present molecular sieve, when employed either as an adsorbent, or as a catalyst, should be dehydrated, at least partially. This can be done by heating to a temperature in the range of 200°C to about 370°C in an atmosphere such as air, nitrogen, etc., and at atmospheric, subatmospheric or superatmospheric pressures for between 30 minutes and 48 hours. Dehydration can also be performed at room temperature merely by placing the ZSM-5 in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

[0057] The ZSM-5 described herein, can be used as an adsorbent or, particularly in its aluminosilicate form, as a catalyst to catalyze a wide variety of organic compound conversion processes including many of present commercial/industrial importance. Examples of chemical conversion processes which are effectively catalyzed by the present ZSM-5 are those where high acid activity and large surface area are important.

[0058] As in the case of many catalysts, it may be desirable to incorporate the present ZSM-5 with another material resistant to the temperatures and other conditions employed in organic conversion processes. Such materials include active and inactive materials, and synthetic or naturally occurring zeolites, as well as, inorganic materials such as clays, silica and/or metal oxides such as alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the present ZSM-5, i.e., combined therewith or present during synthesis of the new crystal, which is active, tends to change the conversion and/or selectivity of the catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained in an economic and orderly manner without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. Said materials, i.e., clays, oxides, etc., function as binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay and/or oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

[0059] Naturally occurring clays which can be composited with the present ZSM-5 include the montmorillonite and kaolin family, which families include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays can be used in the raw state as originally mined, or initially subjected to calcination, acid treatment or chemical modification. Binders useful for compositing with ZSM-5 also include inorganic oxides, such as silica, zirconia, titania, magnesia, beryllia, alumina, and mixtures thereof.

[0060] In addition to the foregoing materials, the present ZSM-5 can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as, ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia silica-alumina-magnesia and silica-magnesia-zirconia.

[0061] The relative proportions of ZSM-5 and inorganic oxide matrix may vary widely, with the ZSM-5 content ranging from about 1 to about 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of about 2 to about 80 weight percent of the composite.

[0062] The invention will now be more particularly described with reference to the following Examples and the accompanying drawings.

Example 1: Preparation of the C4 diquat of N-pentylpyrrolidine

[0063] N-pentylpyrrolidine is initially prepared by the reductive amination of pentanal with pyrrolidine according to the following procedure.

[0064] 500 mL tetrahydrofuran (THF) was placed in a 1-L suction flask equipped with a nitrogen gas flow. 31.9 g pentanal (0.37 mol) and then 24.9 g pyrrolidine (0.35 mol) were mixed into the THF. With the nitrogen flow turned off, 100 g of sodium triacetoxyborohydride powder was then added in 5-10 g increments to the solution. During the addition, vigorous stirring was used to ensure that the powder did not clump at the bottom of the flask and to ensure the efficient mixing of the suspension. After each addition of the sodium triacetoxyborohydride powder, adequate time was provided to form a uniform slurry before the next addition of the powder. Once all of the powder had been added, the nitrogen flow was then turned on. After two days the product was worked up by quenching the suspension with the slow addition of 275 g of a 24% potassium hydroxide (KOH) solution. The product was then extracted from the resultant solution with pentane. The organic fraction was then collected with a separatory funnel and dried with anhydrous magnesium sulfate. The amine product was then isolated by rotary evaporation of the THF and pentane solvents under reduced pressure.

[0065] The C4 diquat was formed by the reaction between N-pentylpyrrolidine and 1,4-dibromobutane. 20.0 g N-pentylpyrrolidine (0.14 mol) was added to 65 mL acetonitrile inside a 125-mL Teflon liner. 13.93 g 1,4-dibromobutane (0.064 mol) was added to the mixture. The liner was then capped, sealed inside a Parr steel autoclave, and then heated at 80 °C for 4 days. The solid precipitates were then collected by filtration and washed with acetone. After the acetone wash, additional product precipitated within the filtrate. The combined solids were then washed with ether and allowed to dry. The total yield of clean product was 18.8 g. ^{1}H and ^{13}C NMR showed the product to be pure. The dibromide salt was then ion-exchanged into the hydroxide form by dissolving it in water and passing it through a column of Dowex LC NG hydroxide exchange resin. The concentration of the aqueous solution was determined by titration with a standard solution of 0.1 N hydrochloric acid (HCl).

[0066] The C5 and C6 diquat salts of N-pentylpyrrolidine were prepared in similar fashion by using 1,5-dibromopentane and 1,6-dibromohexane, respectively, in place of the 1,4-dibromobutane.

Example 2: Synthesis of ZSM-5 with the C4 diquat of N-pentylpyrrolidine

[0067] This synthesis was performed with a hydroxide-exchanged form of the C4 diquat of N-pentylpyrrolidine (prepared from the reaction of 1,4-dibromobutane with N-pentylpyrrolidine). 55.1 g of the diquat solution ([OH$^-$] = 1.02 mmol/g) were mixed with 49.1 g 1 N KOH and 22.4 g deionized water. 1.59 g fumed alumina was added and the mixture was thoroughly mixed to create a uniform suspension. 41.6 g Ludox AS-40 colloidal silica was then mixed into the suspension. The mixture was placed inside a Teflon liner and sealed inside a 300-mL capacity Parr autoclave with an overhead stirrer. The overhead stirrer was set at 150 rpm. The gel was heated to 160 °C over a 4-hr period. After 3 days a sample was removed (online) from the autoclave and worked up for powder X-ray diffraction (XRD) analysis. The product was predominantly a layered phase with an intense peak around 4.5 degrees two-theta with a trace amount of the ultra-small ZSM-5. At this point the temperature was decreased to 150 °C. After an additional 22 hours at 150 °C, the product was ultra-small ZSM-5 with a small amount of the layered impurity. After a further 2 hours, the product was pure ZSM-5. Figure 2 compares the powder XRD patterns of the sequence of sampling points taken at 3 days, at 2 hours before completion, and at completion after 4 days.

[0068] The product of the 4 day synthesis was then recovered by filtration, washed with at least 500 mL deionized water, washed with acetone, and dried in a vacuum oven at 60 °C overnight. The zeolite was then calcined in a muffle furnace by heating in a nitrogen stream from ambient temperature to 400 °C over a 2-hr period, maintaining this temperature for 15 minutes, switching the gas stream to air, increasing the temperature from 400 °C to 600 °C over a 2-hr period, maintaining the temperature at 600 °C for 2 hours, and then allowing the furnace to cool to ambient conditions. Figure 3 compares the powder XRD patterns of the as-made and calcined products.

[0069] Scanning electron microscope (SEM) images of the as-made product of the 4 day synthesis are shown in Figure 4 and demonstrate the bulk material to be crystalline. Transmission electron microscopy (TEM) shows the crystals are in the form of ultra-small primary crystallites with plate-like morphologies about 20- 60 nm on their edges. Microtomy of these crystals shows that the particles are less than 100 Å in thickness. The crystallites are aggregated into larger secondary particles having an average size of about 1 micron.

[0070] The calcined product of the 4 day synthesis was ion-exchanged into the ammonium form by adding 7.0 g zeolite to a solution containing an equal mass of ammonium nitrate (7.0 g) and a 10-fold mass of deionized water (70 g). The slurry was placed in a polypropylene bottle and heated within a steambox overnight at 98 °C. The zeolite was then filtered and washed with at least 300 mL deionized water. The zeolite was converted to the acidic form by calcining the zeolite from ambient conditions to 500 °C over a 2-hour period, maintaining that temperature for 4 hours, and then allowing the furnace to cool to near-ambient conditions. Analysis of nitrogen physisorption data by the t-plot method showed that the preparation had 124 m^2/g external surface area and 0.13 cc/g micropore volume (318 m^2/g internal surface area).

Example 3: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0071] This synthesis was performed with a hydroxide-exchanged form of the C5 diquat of N-pentylpyrrolidine (prepared from the reaction of 1,5-dibromobutane with N-pentylpyrrolidine). 87.2 g of the diquat solution ($[OH^-]$ = 0.58 mmol/g) were mixed with 44.03 g 1 N KOH. 1.05 g fumed alumina was added and the mixture was thoroughly mixed to create a uniform suspension. 37.7 g Ludox AS-40 colloidal silica was then mixed into the suspension. The mixture was placed inside a Teflon liner and sealed inside a 300-mL capacity Parr autoclave with an overhead stirrer. The overhead stirrer was set at 150 rpm. The gel was heated to 160 °C over a 4-hr period. After 24 hours, a sample was removed (online) from the autoclave and worked up for powder XRD analysis. The product was pure (by XRD) ultra-small ZSM-5. Figure 5 shows the powder XRD of the product.

Example 4: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0072] 5.21 g of the diquat solution used in Example 3 ($[OH^-]$ = 0.58 mmol/g) were mixed with 2.63 g 1 N KOH. 0.063 g SpectrAl fumed alumina (Cabot) was added and the mixture was thoroughly mixed to create a uniform suspension. 2.25 g Ludox AS-40 colloidal silica was then mixed into the suspension. The mixture was placed inside a Teflon liner and sealed inside a 23-mL capacity Parr autoclave. The autoclave was placed inside an oven at 150 °C with a rotisserie and tumbled at 50 rpm. The gel was heated for 24 hours and then removed and sampled. The autoclave was then placed back in an oven and heated an additional 6 hours. The product, after 30 total hours of heating, was ultra-small ZSM-5 with some remaining amorphous material. Figure 6 shows the powder XRD of the products.

Example 5: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0073] Example 3 was repeated, except the synthesis temperature was maintained at 130°C. After 24 hours, the reaction was sampled and the product was amorphous by XRD. After 2 days, the product was still mostly amorphous, but some ZSM-5 appeared. The reaction was then sampled again after 6 total days of heating. The XRD of the product showed it to be pure ultra-small ZSM-5. Figure 7 shows the powder XRD for the samples taken after 1, 2 and 6 days of heating.

Example 6: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0074] Four further repeat experiments of the process of Example 3 were conducted. In the first experiment crystallization was carried out at 160 °C for 66 hours, whereas in the second and third experiments crystallization was carried out at 150 °C for 30 hours and 130 °C for 5 days, respectively. In the fourth experiment, fumed alumina was pre-dissolved in the KOH/diquat solution by heating the mixture at 160 °C for about 45 minutes before adding the silica. Crystallization was then conducted by heating at 130 °C for 7 days followed by heating at 150 °C for 6 days. The results are shown in Figure 8 and demonstrate that reducing the temperature resulted in products having significantly decreased crystal size as inferred from the peak broadening in the powder XRD patterns.

[0075] The product of the fourth experiment was calcined as in Example 1 and was subjected to nitrogen physisorption measurements. Analysis of the data by the t-plot method showed the product to possess 247 m^2/g internal surface area (0.107 cc/g micropore volume) and 370 m^2/g external surface area. ^{27}Al MAS NMR spectrum of the product of the fourth experiment is given in Figure 9 and shows that the calcined product has >95% tetrahedral aluminum. In contrast, the product obtained from the synthesis without pre-dissolution of the fumed alumina (see Example 4) contains only about 10% tetrahedral aluminum.

[0076] SEM images of the product of the fourth experiment are shown in Figure 10. The TEM images in Figures 11(a) and (b) demonstrate that many of the crystals are elongated with lengths that are generally less than 30 nm and widths that are less than 10 nm. Other TEM images (Figure 11(c)) show more isotropically shaped crystals with shorter lengths (10-20 nm) than those in Figures 11(a) and (b). The mean and median crystal lengths were 15 and 14 nm, respectively and the mean and median widths were 8.2 and 8.0 nm, respectively.

[0077] Figure 11(d) shows a TEM image of a microtomed specimen of a sample of fourth experiment product. The images of the microtomed crystals reveal the thickness of the crystals; the crystal dimensions here are mostly 5 – 7 nm. The mean and median thicknesses were 6.4 and 6.0 nm, respectively. The bar graphs in Figure 12 show the distribution of crystal dimensions for each of the crystallographic edges.

Example 7: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0078] A solution was prepared by mixing 5.21 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.58 mmol/g) with 2.63 g 1 N KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 0.063 g SpectrAl fumed alumina (Cabot) was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 23 mL autoclave, and heated at 160 °C under tumbling conditions (~50 rpm) inside a convection oven for about 45 minutes in order to dissolve most of the alumina. The reactor was then cooled and 2.25 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for 8 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. Figure 13(a) shows the powder XRD of the product.

Example 8: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0079] The process of Example 7 was repeated except that 0.04 g of seeds from that preparation were added and the gel was heated for a total of 6 days instead of 8. The powder XRD shown in Figure 13(b) is consistent with the product being ultra-small ZSM-5 with a trace level of MCM-68.

Example 9: Synthesis of ZSM-5 with the C6 diquat of N-pentylpyrrolidine

[0080] A solution was prepared by mixing 3.51 g of a hydroxide solution of the C6 diquat of N-pentylpyrrolidine ([OH] = 0.86 mmol/g) with 2.63 g 1 N KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 0.063 g SpectrAl fumed alumina (Cabot) was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 23 mL autoclave, and heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for about 45 minutes in order to dissolve most of the alumina. The reactor was then cooled and 2.25 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 125°C under tumbling conditions (~50 rpm) inside a convection oven for 9 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. Figure 13(c) shows the powder XRD of the product.

[0081] The zeolite was heated inside a muffle furnace from ambient temperature to 400°C at 4°C/min under a nitrogen atmosphere, then heated to 600 °C at 4 °C/min in air, and maintained at 600 °C in air for 2 hours. After the sample cooled to ambient temperature, it was ammonium-exchanged by adding the zeolite to a 10-fold mass of water and adding an equivalent mass of ammonium nitrate. The ammonium-exchange was carried out overnight in a steam box at a temperature of 98-99 °C. The zeolite was then filtered and washed exhaustively with deionized water to remove excess salt. The zeolite was then calcined to 500 °C to obtain the fully acidic form of the zeolite. Analysis by the t-plot method of nitrogen physisorption shows the sample possesses 222 m^2/g external surface area and 0.14 cc/g micropore volume (326 m^2/g internal surface area).

Example 10: Synthesis of ZSM-5 with the C6 diquat of N-pentylpyrrolidine

[0082] A solution was prepared by mixing 3.51 g of a hydroxide solution of the C6 diquat of N-pentylpyrrolidine ([OH] 0.86 mmol/g) with 0.15 g 50% KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 0.063 g SpectrAl fumed alumina (Cabot) was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for about 45 minutes in order to dissolve most of the alumina. The reactor was then cooled and 2.25 g Ludox AS-40 was then mixed into the suspension. 0.04 g seeds from Example 7 were added. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 125°C under tumbling conditions (~50 rpm) inside a convection oven for 14 days and then at 140°C for an additional 4 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. The powder XRD of the product is shown in Figure 13(d).

Example 11: Synthesis of ZSM-5 with the C6 diquat of N-pentylpyrrolidine

[0083] A solution was prepared by mixing 3.51 g of a hydroxide solution of the C6 diquat of N-pentylpyrrolidine ([OH] = 0.86 mmol/g) with 2.63 g 1 N KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 0.097 Alcoa-C31 alumina trihydrate was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 160 °C under tumbling conditions (~50 rpm) inside a convection oven for about 45 minutes in order to dissolve the alumina, The reactor was then cooled and 2.25 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 140 °C under tumbling conditions (~50 rpm) inside a convection oven for 7 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. The powder XRD of the product is shown in Figure 13(e).

Example 12: Synthesis of borosilicate ZSM-5 with the C6 diquat of N-pentylpyrrolidine

[0084] A solution was prepared by mixing 3.51 g of a hydroxide solution of the C6 diquat of N-pentylpyrrolidine ([OH] 0.86 mmol/g) with 2.63 g of 1N KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 0.046 g boric acid was then dissolved in the hydroxide solution. 2.25 g Ludox AS-40 was then added and mixed to create a uniform suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 100 °C under static conditions inside a convection oven for 9 days. The solids were then recovered by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100 °C. The powder XRD of the product is shown in Figure 14(a).

Example 13: Synthesis of borosilicate ZSM-5 with the C6 diquat of N-pentylpyrrolidine

[0085] The process of Example 12 was repeated at 125°C under tumbling conditions (50 rpm) for 6 days. Figure 14(b) shows the powder XRD of the product.

Example 14: Synthesis of All Silica ZSM-5 with the C6 diquat of N-pentylpyrrolidine

[0086] A solution was prepared by mixing 3.51 g of a hydroxide solution of the C6 diquat of N-pentylpyrrolidine ([OH] = 0.86 mmol/g) with 2.63 g 1 N KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 2.25 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 100°C under static conditions inside a convection oven for 4 days. The solids were then isolated by centrifugation and washing three times, and drying in an oven at 100°C. The powder XRD of the product is shown in Figure 14(c).

Example 15: Synthesis of All Silica ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0087] A solution was prepared by mixing 4.92 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.61 mmol/g) with 2.63 g 1 N KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 2.25 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 100°C under static conditions inside a convection oven for 5 days. The solids were then isolated by centrifugation and washing three times, and drying in an oven at 100°C. The powder XRD of the product is shown in Figure 14(d).

Example 16: Synthesis of BZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0088] A solution was prepared by mixing 4.92 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.61 mmol/g) with 2.63 g 1 N KOH inside a Teflon liner for a 23-mL steel Paar autoclave. 0.046 g boric acid was then dissolved in the hydroxide solution. 2.25 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 125 °C under tumbling conditions (50 rpm) inside a convection oven for 13 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. The powder XRD of the product is shown in Figure 14(e).

Example 17: Synthesis of BZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0089] The process of Example 16 was repeated but the reaction mixture was heated at 140 °C for 11 days. Figure 14(f) shows the powder XRD pattern of the product.

Example 18: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0090] A solution was prepared by mixing 4.93 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.61 mmol/g) with 2.63 g 1 N KOH inside a Teflon liner for a 23-mL steel Parr autoclave. 0.063 g SpectrAl fumed alumina (Cabot) was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 23- mL autoclave, and heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for about 45 minutes in order to dissolve most of the alumina. The reactor was then cooled and 2.25 g Ludox AS-40 was then mixed into the suspension. 0.04 g seeds from Example 7 were then added. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 175°C under tumbling conditions (~50 rpm) inside a convection oven for 3 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. Powder XRD showed the product to be a mixture of ZSM-5 and MCM-68.

Example 19: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0091] The process of Example 18 was repeated except only 0.032 g fumed alumina was added and the reaction mixture was heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for 9 days. Figure 15(a) shows the powder XRD of the product.

Example 20: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0092] A solution was prepared by mixing 3.95 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.76 mmol/g) with 2.63 g 1 N KOH and 0.88 g deionized water inside a Teflon liner for a 23-mL steel Parr autoclave. 0.015 g SpectrAl fumed alumina (Cabot) was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for about 45 minutes in order to dissolve most of the alumina. The reactor was then cooled and 2.12 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 110°C under tumbling conditions (~50 rpm) inside a convection oven for 11 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. The powder XRD pattern in Figure 15(b) is consistent with the product being pure ultra-small ZSM-5.

Example 21: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0093] A solution was prepared by mixing 35.96 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.76 mmol/g) with 23.91 g 1 N KOH and 11.4 g deionized water inside a Teflon liner for a 125-mL steel Parr autoclave. 0.57 g SpectrAl fumed alumina (Cabot) was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 125-mL autoclave, and heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for about 45 minutes in order to dissolve most of the alumina. The reactor was then cooled and 20.45 g Ludox AS-40 was then mixed into the suspension. The liner was then capped, sealed inside the 125-mL autoclave, and heated at 150°C under tumbling conditions (~50 rpm) inside a convection oven for 7 days. The solids were then isolated by filtering through a Buchner funnel, washing exhaustively with deionized water (about 1 liter), and drying in an oven at 100°C. The powder XRD pattern in Figure 15(c) is consistent with the product being ultra-small ZSM-5.

<u>Example 22:</u> **Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine**

[0094] A solution was prepared by mixing 3.95 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.76 mmol/g) with 2.63 g 1 N KOH and 0.90 g deionized water inside a Teflon liner for a 23-mL steel Parr autoclave. 2.08 g Ludox AS-40 and 0.13 g metakaolin (Nusheen) were then mixed with the solution. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 140°C under tumbling conditions (~50 rpm) inside a convection oven for 3 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. The powder XRD pattern in Figure 15(d) is consistent with the product being ZSM-5 with a trace level of anatase impurity from the metakaolin reactant (peak at ~25.2 degrees two-theta). SEM images of the product are shown in Figure 16. The product is composed of spheroidal polycrystalline aggregates that are less than 1 micron in size. The size of the individual crystallites cannot be resolved within the resolution of the SEM images. In the lowest magnification image, a few flakes can be observed that are due to some unreacted metakaolin. The presence of unreacted metakaolin is verified by ^{27}A1 MAS NMR (Figure 17), which shows about 27% of the aluminum of the as-made product is non-tetrahedral.

<u>Example 23:</u> **Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine**

[0095] The process of Example 22 was repeated except that only 0.065 g metakaolin was used and the reaction was carried out at 130 °C for 3 days. The powder XRD of the product in Figure 15(e) is somewhat sharper than that of the product from Example 22. Figure 18 shows SEM images of the product. ^{27}Al MAS NMR of the product (Figure 19) shows that 76% of the aluminum from the metakaolin reactant is incorporated into the product as tetrahedral aluminum.

<u>Example 24:</u> **Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine**

[0096] The process of Example 22 was again repeated except that only 0.033 g metakaolin was used and the reaction was carried out at 130°C for 3 days. The peaks of the powder XRD of the product [Figure 20(a)] are somewhat sharper than those of the product from Example 22. SEM images of the product are shown in Figure 21.

Example 25: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0097] The process of Example 22 was again repeated except that the reaction was carried out at 130°C for 4 days. The powder XRD of the product is shown in Figure 20(b).

Example 26: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0098] The process of Example 23 was repeated except the reaction was carried out at 120°C for 3 days. The powder XRD of the product [Figure 20(c)] is broader than the one for the product of Example 23.

Example 27: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[0099] The process of Example 24 was repeated except the reaction was carried out at 120°C for 3 days. The powder XRD of the product [Figure 20(d)] is broader than the one for the product of Example 24. The product was calcined as described in Example 9. Figure 20(e) shows the powder XRD pattern of the calcined material.

Example 28: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[00100] The process of Example 23 was repeated except the reaction was carried out at 110°C for 6 days. Figure 22(a) shows the powder XRD pattern of the product.

Example 29: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[00101] The process of Example 24 was repeated except the reaction was carried out at 110°C for 6 days. Figure 22(b) shows the powder XRD of the product.

Example 30: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[00102] A solution was prepared by mixing 3.95 g of a hydroxide solution of the C5 diquat of N-pentylpyrrolidine ([OH] = 0.76 mmol/g) with 2.63 g 1 N KOH and 0.90 g deionized water inside a Teflon liner for a 23-mL steel Parr autoclave. 0.022 g SpectrAl fumed alumina (Cabot) was mixed into the solution to create a uniform suspension. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 160°C under tumbling conditions (~50 rpm) inside a convection oven for about 30 minutes in order to dissolve most of the alumina. The reactor was then cooled and 2.05 g Ludox AS-40 and 0.092 g metakaolin was then mixed into the solution. The liner was then capped, sealed inside the 23-mL autoclave, and heated at 130°C under tumbling conditions (~50 rpm) inside a convection oven for 22 days. The solids were then isolated by filtering through a Buchner funnel, washing with deionized water, and drying in an oven at 100°C. Powder XRD showed the product to be ultra small crystal ZSM-5.

Example 31: Synthesis of ZSM-5 with the C5 diquat of N-pentylpyrrolidine

[00103] The process of Example 30 was repeated except that only 0.015 g fumed alumina and 0.097 g metakaolin were used and the reaction was carried out for 15 days. Figure 22(c) shows the powder XRD pattern. The broad hump from 10 to 15 degrees two-theta is due to the plastic sample holder used for the powder XRD measurement.

[00104] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS

1. A crystalline molecular sieve having an X-ray diffraction pattern, said molecular sieve having at least the following features:

(i) a first peak with a maximum at 8.90 (± 0.30) degrees two-theta which has an intensity above background of $Imax_A$, and which intersects a second peak with a maximum at 7.96 (± 0.30) degrees two-theta, to form a local minimum which has an intensity above background of $Imin_A$, such that the $Imin_A/Imax_A$ ratio is > 0.33; and

(ii) a third peak with a maximum at 24.0 (± 0.30) degrees two-theta.

2. The molecular sieve of claim 1, wherein said third peak has an intensity above background of $Imax_B$, and intersects a fourth peak with a maximum at 23.2 (± 0.20) degrees two-theta, such that said intersection of said third and said fourth peaks forms a local minimum which has an intensity above background of $Imin_B$, such that the $Imin_B/Imax_B$ ratio is > 0.90.

3. The molecular sieve of claim 1 or claim 2 and comprising crystals having an external surface area (as determined by the t-plot method for nitrogen physisorption) in excess of 100 m^2/g.

4. The molecular sieve of claim 1, wherein said third peak has an intensity above background of $Imax_B$, and intersects a fourth peak with a maximum at 23.2 (± 0.20) degrees two-theta, to form a composite peak exhibiting an inflection point at the intersection of the third and fourth peaks.

5. The molecular sieve of any preceding claim, wherein the $Imin_A/Imax_A$ ratio is at least 0.40.

6. The molecular sieve of any preceding claim, wherein the molecular sieve has the framework structure of ZSM-5.

7. A molecular sieve having the framework structure of ZSM-5, said molecular sieve comprising crystals having an external surface area in excess of 100 m^2/g as determined by the t-plot method for nitrogen physisorption, and an X-ray diffraction pattern having a composite peak with a maximum at 24.0 ($\pm$ 0.30) degrees two-theta, which has an intensity above background of $Imax_B$ and which intersects a composite peak with a maximum at 23.2 ($\pm$ 0.20) degrees two-theta, to form a local minimum, which has an intensity above background of $Imin_B$, such that the $Imin_B/Imax_B$ ratio is > 0.90.

8. The molecular sieve of any preceding claim, said molecular sieve comprising crystals having an external surface area (as determined by the t-plot method for nitrogen

physisorption) in excess of 200 m^2/g.

9. A molecular sieve having the framework structure of ZSM-5, said molecular sieve comprising crystals having an external surface area in excess of 200 m^2/g (as determined by the t-plot method for nitrogen physisorption), and an X-ray diffraction pattern with a single diffuse composite feature in the two-theta range from 21.5 to 26°.

10. The molecular sieve of any preceding claim, said molecular sieve comprising crystals having an external surface area (as determined by the t-plot method for nitrogen physisorption) in excess of 250 m^2/g.

11. The molecular sieve of any preceding claim, said molecular sieve comprising crystals having an external surface area (as determined by the t-plot method for nitrogen physisorption) greater than their internal surface area.

12. The molecular sieve of any preceding claim, said molecular sieve comprising crystals having a total surface area (as determined by the t-plot method for nitrogen physisorption) in excess of 550 m^2/g.

13. The molecular sieve of any preceding claim, wherein said molecular sieve has a composition comprising the molar relationship:

$$X_2O_3:(n)YO_2,$$

wherein n is at least about 20, X is a trivalent element, and Y is a tetravalent element.

14. The molecular sieve of claim 11, wherein X includes aluminum and Y includes silicon and/or germanium.

15. A process for converting a feedstock comprising an organic compound to a conversion product, said process comprising the step of contacting said feedstock at organic compound conversion conditions with a catalyst comprising an active form of the molecular sieve material of any preceding claim, to form said conversion product.

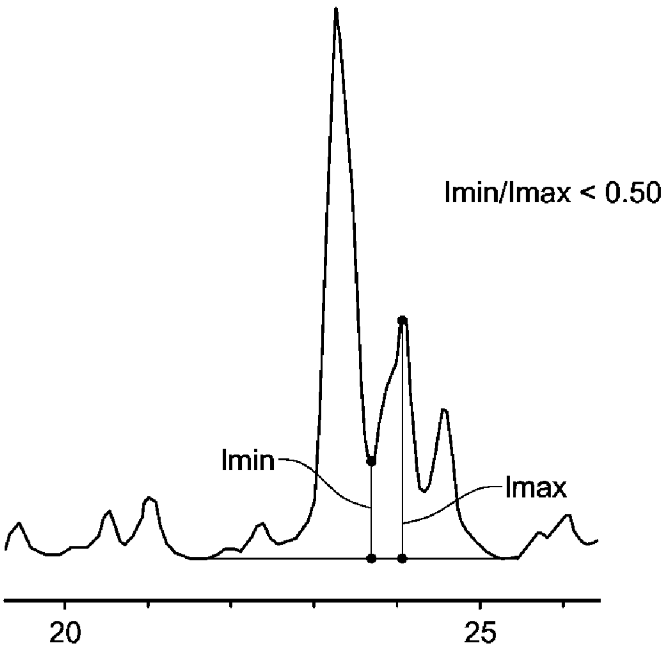

Imin/Imax < 0.50
Imin
Imax
20
25

FIG. 1(a)

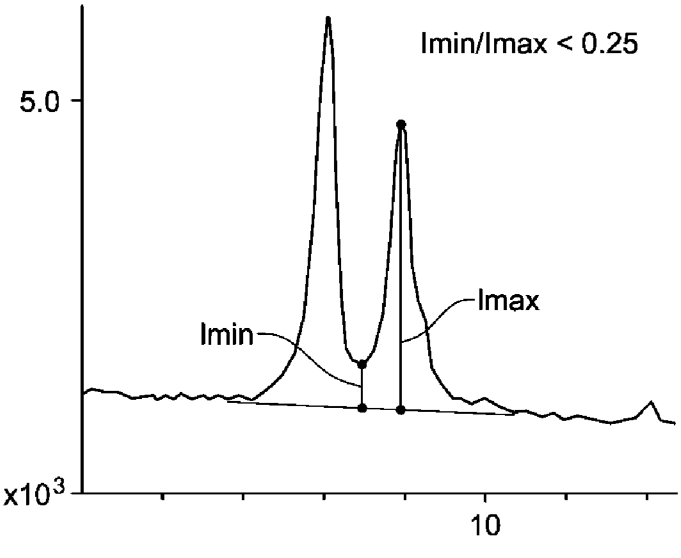

Imin/Imax < 0.25
5.0
Imin
Imax
x10^3
10

FIG. 1(b)

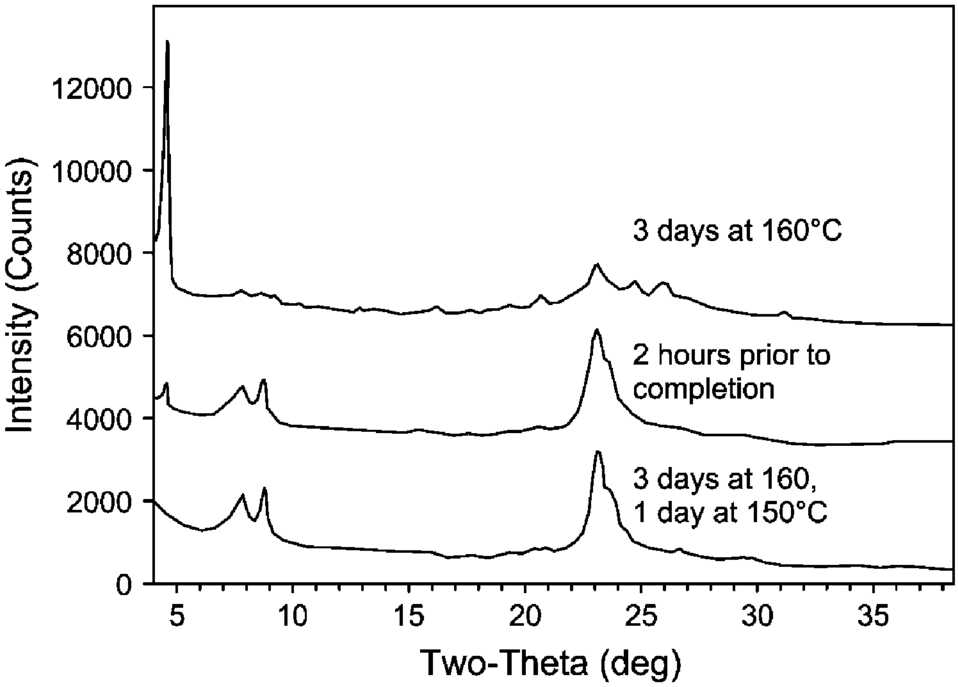

Intensity (Counts)
0
2000
4000
6000
8000
10000
12000
Two-Theta (deg)
5
10
15
20
25
30
35
3 days at 160°C
2 hours prior to completion
3 days at 160, 1 day at 150°C

FIG. 2

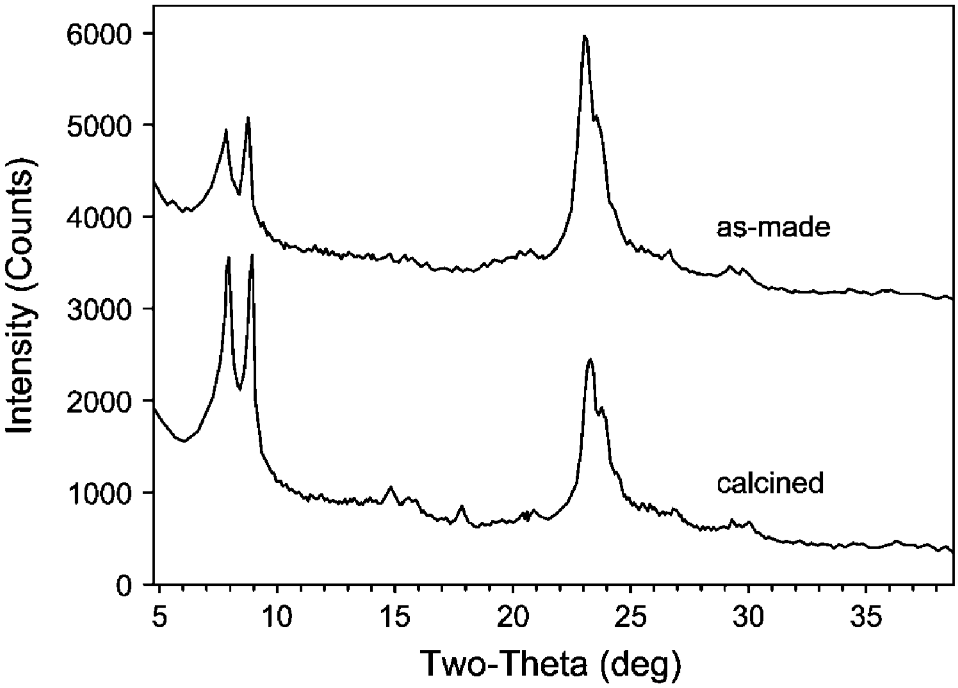

Intensity (Counts)
0
1000
2000
3000
4000
5000
6000
Two-Theta (deg)
5
10
15
20
25
30
35
as-made
calcined

FIG. 3

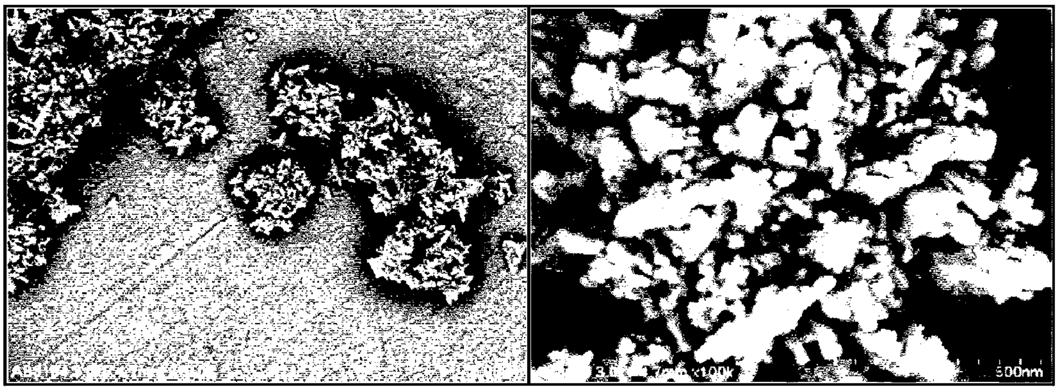

x100k
500nm

FIG. 4

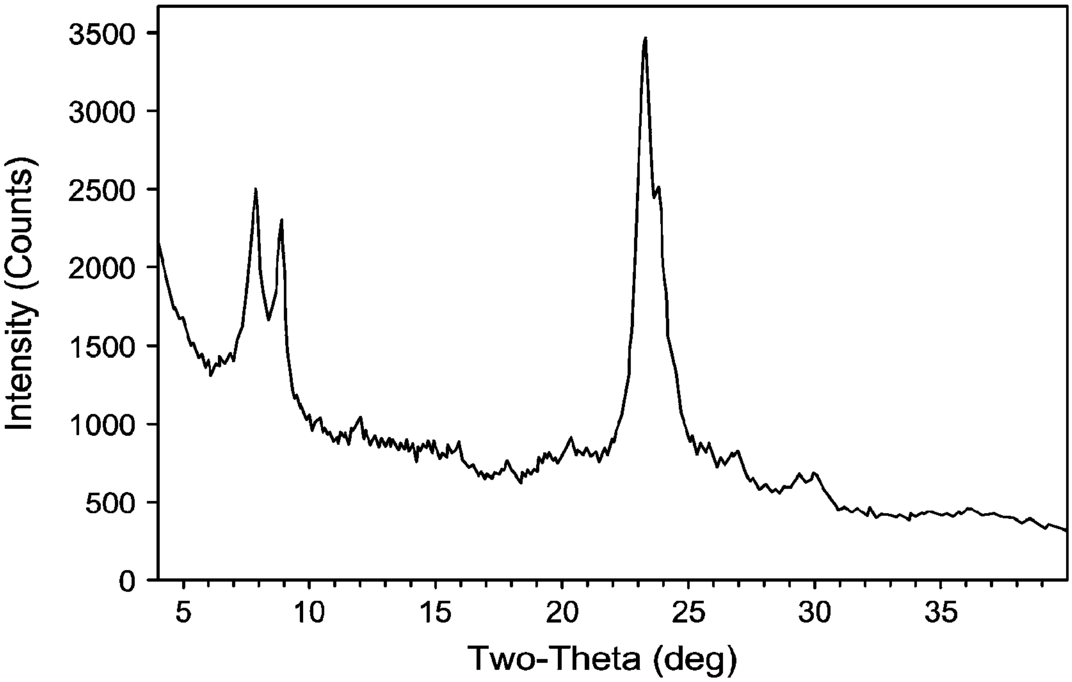

3500
3000
2500
2000
1500
1000
500
0
Intensity (Counts)
5
10
15
20
25
30
35
Two-Theta (deg)

FIG. 5

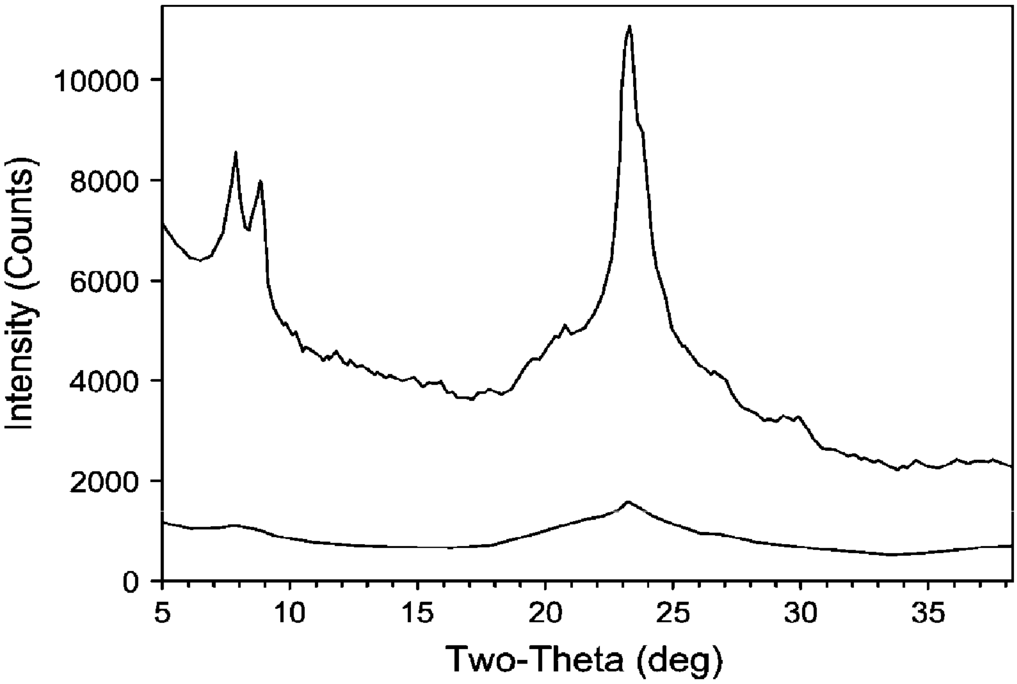

Intensity (Counts)
10000
8000
6000
4000
2000
0
5
10
15
20
25
30
35
Two-Theta (deg)

FIG. 6

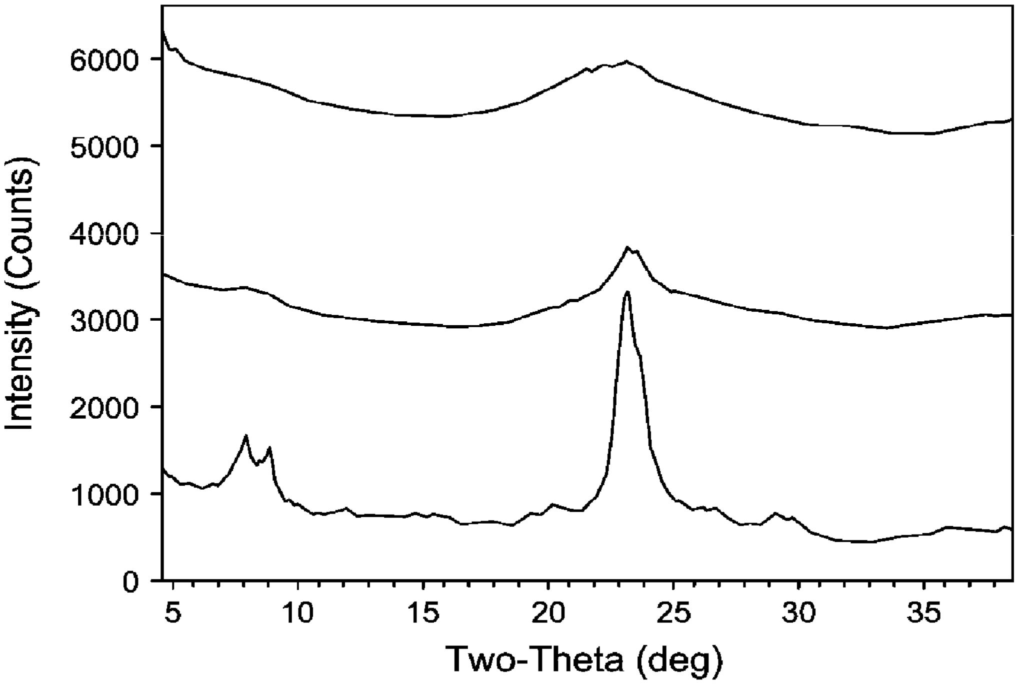

Intensity (Counts)
6000
5000
4000
3000
2000
1000
0
5
10
15
20
25
30
35
Two-Theta (deg)

FIG. 7

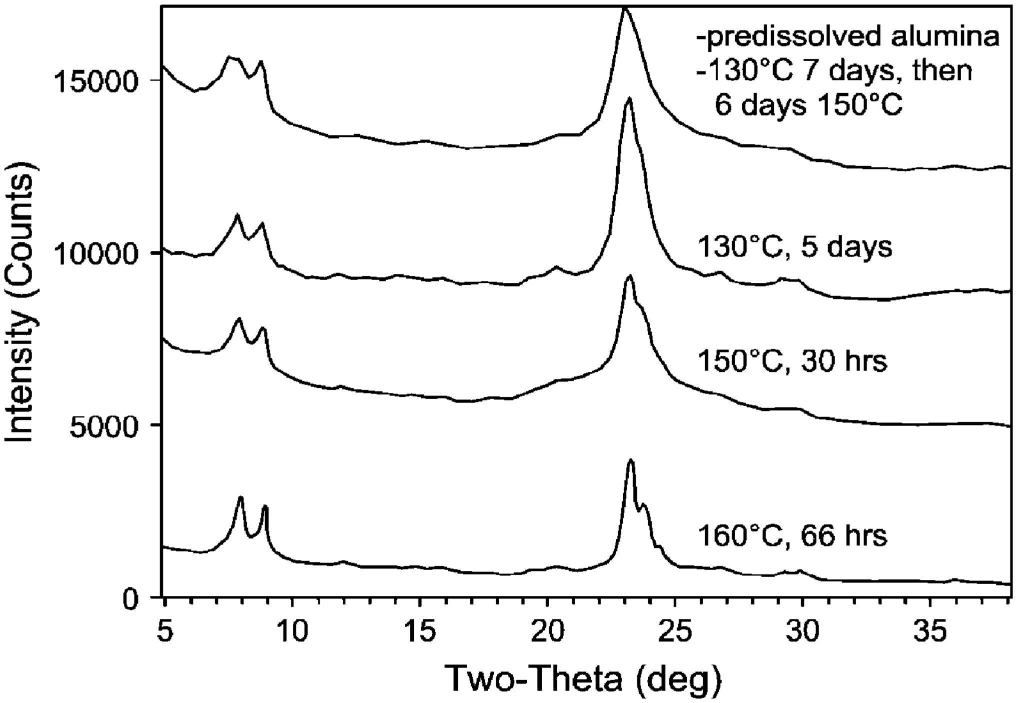

-predissolved alumina
-130°C 7 days, then
6 days 150°C
130°C, 5 days
150°C, 30 hrs
160°C, 66 hrs
Intensity (Counts)
0
5000
10000
15000
5
10
15
20
25
30
35
Two-Theta (deg)

FIG. 8

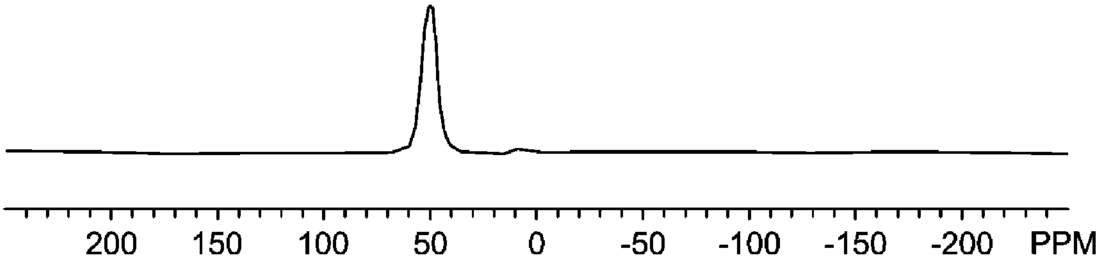

200
150
100
50
0
-50
-100
-150
-200
PPM

FIG. 9

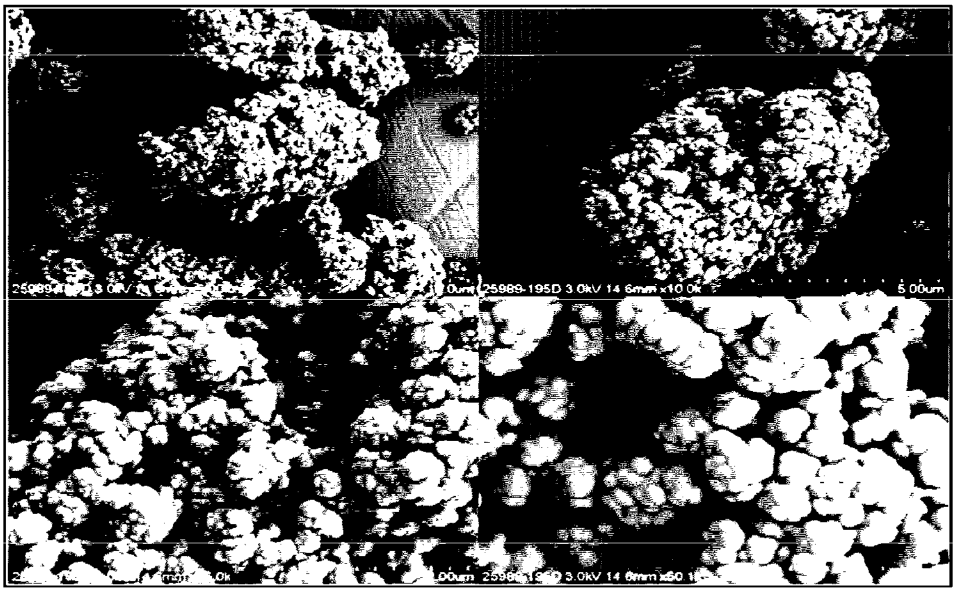


FIG. 10

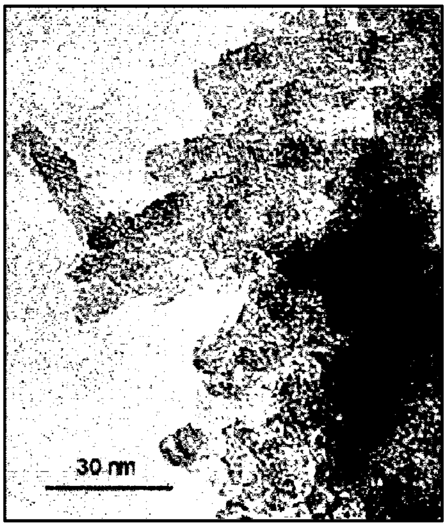


FIG. 11(a)

FIG. 11(b)

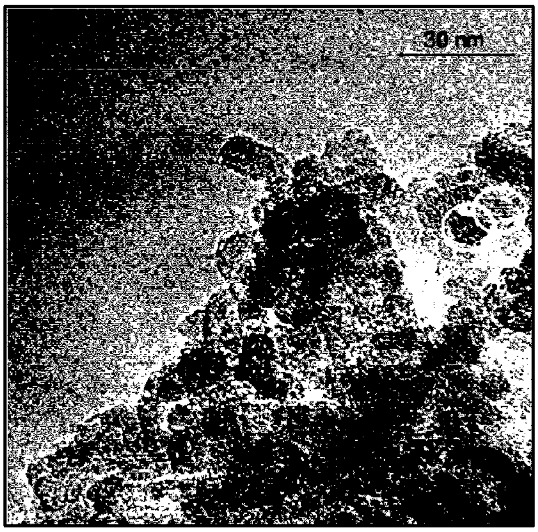


FIG. 11(c)

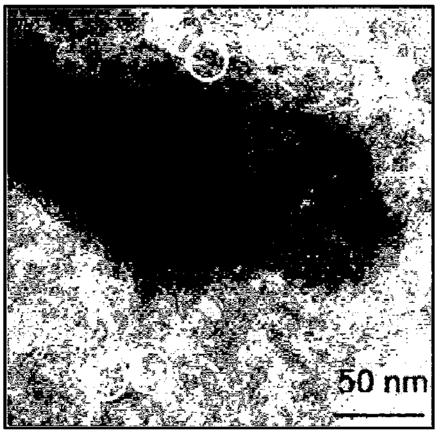
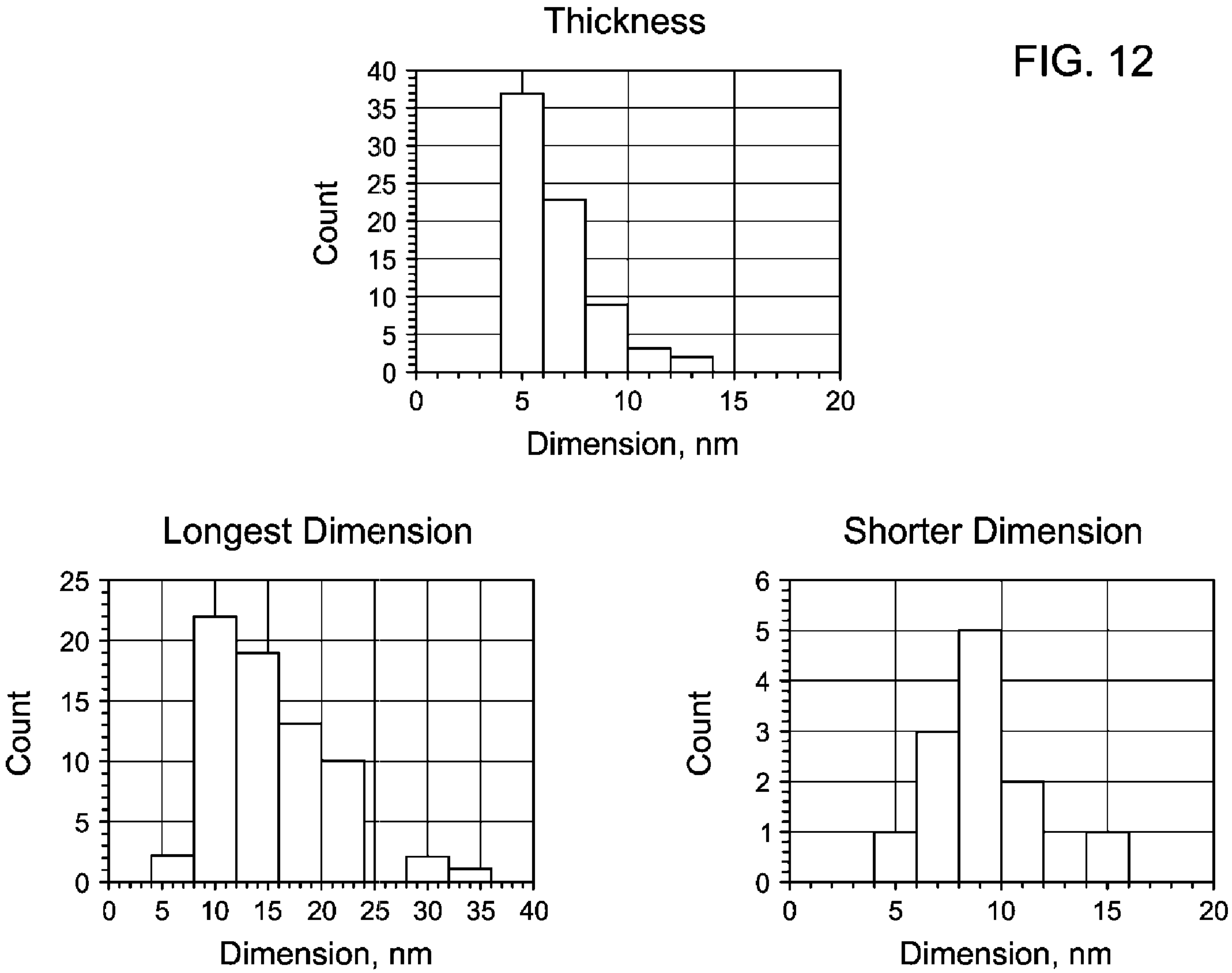


FIG. 11(d)

FIG. 12


Thickness
Count
40
35
30
25
20
15
10
5
0
0
5
10
15
20
Dimension, nm
Longest Dimension
Count
25
20
15
10
5
0
0
5
10
15
20
25
30
35
40
Dimension, nm
Shorter Dimension
Count
6
5
4
3
2
1
0
0
5
10
15
20
Dimension, nm

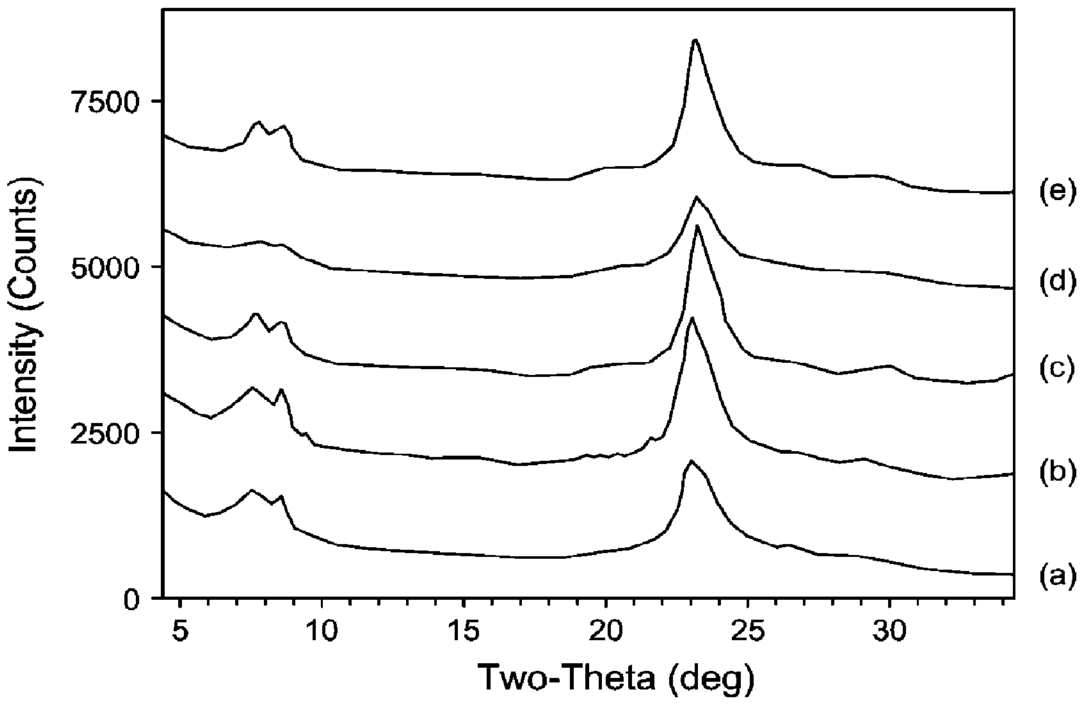

Intensity (Counts)
7500
5000
2500
0
5
10
15
20
25
30
Two-Theta (deg)
(e)
(d)
(c)
(b)
(a)

FIG. 13

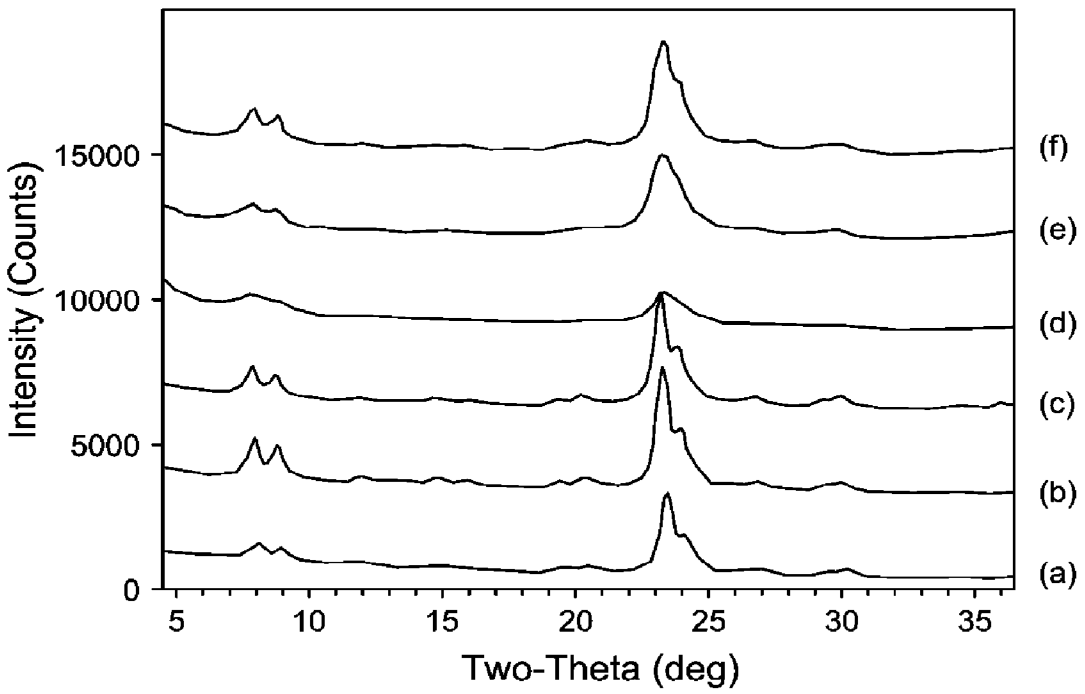

Intensity (Counts)
15000
10000
5000
0
5
10
15
20
25
30
35
Two-Theta (deg)
(f)
(e)
(d)
(c)
(b)
(a)

FIG. 14

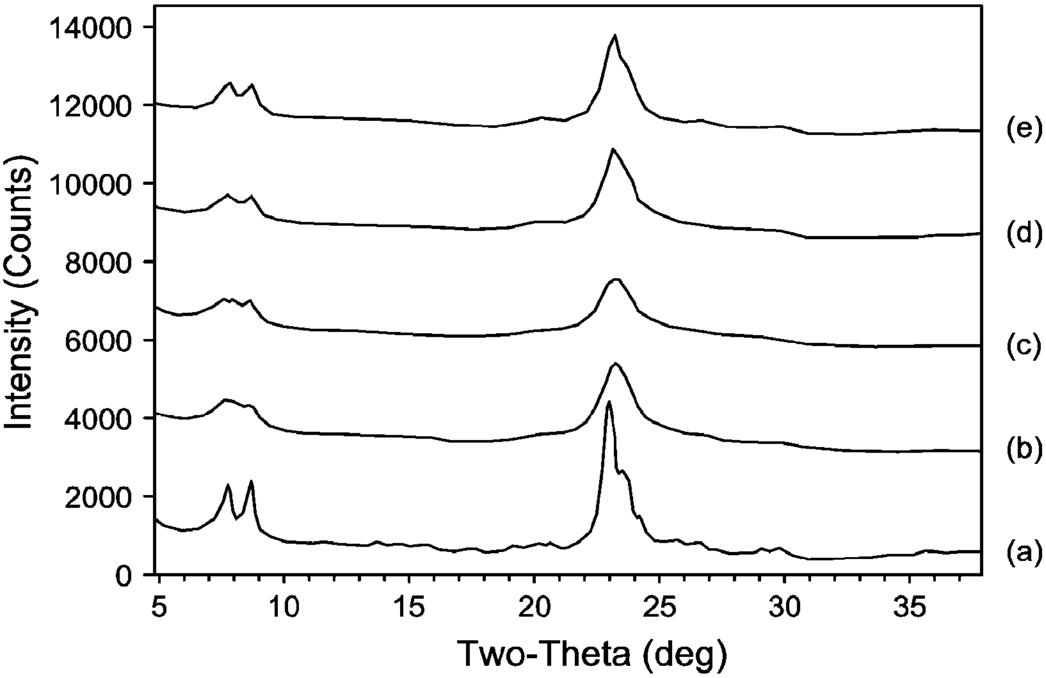

Intensity (Counts)
14000
12000
10000
8000
6000
4000
2000
0
5
10
15
20
25
30
35
Two-Theta (deg)
(e)
(d)
(c)
(b)
(a)

FIG. 15

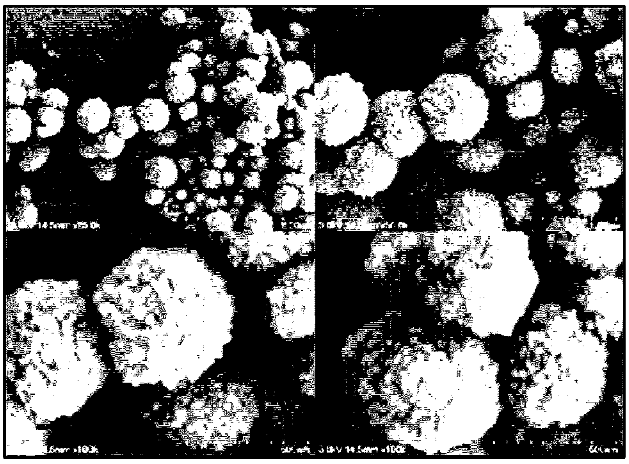


FIG. 16

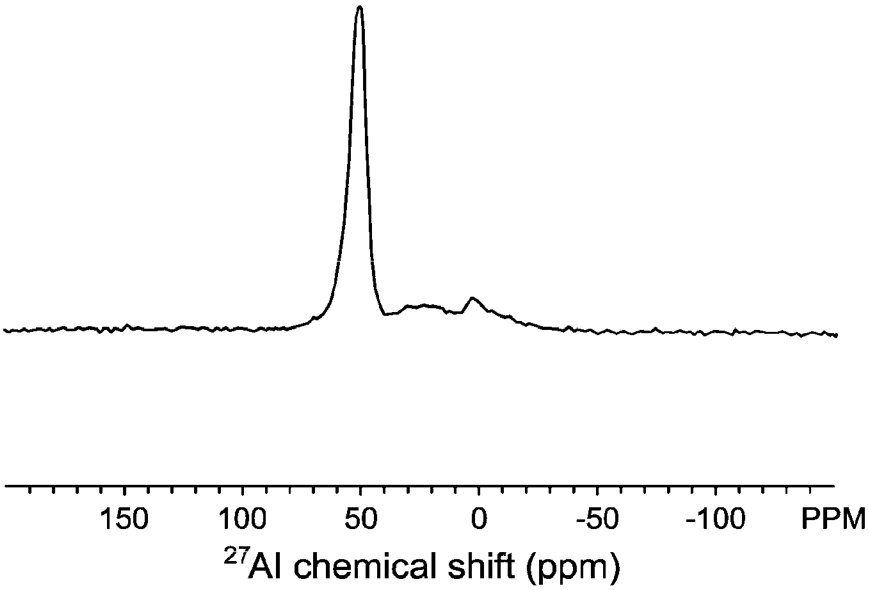


FIG. 17

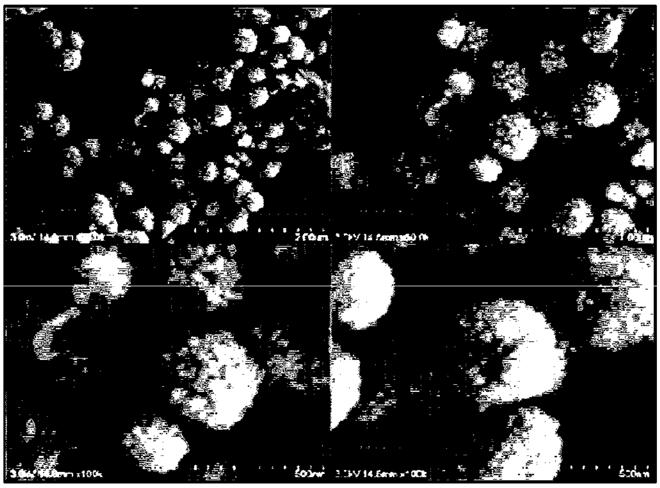


FIG. 18

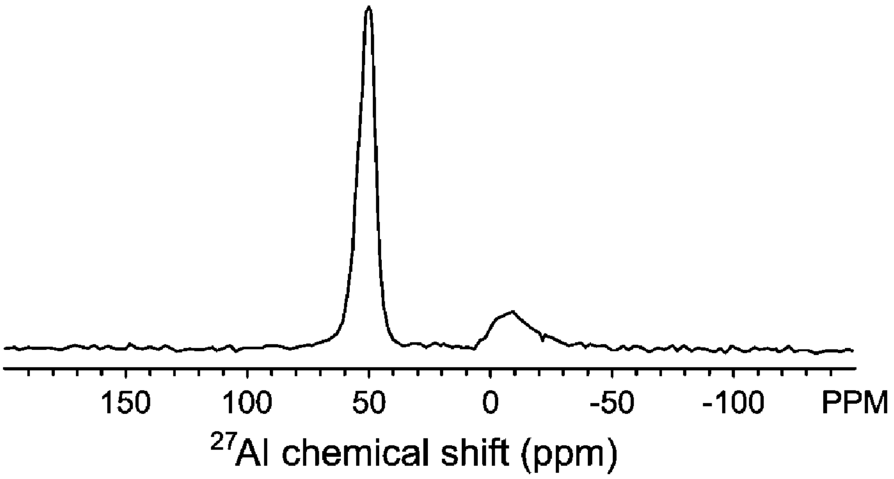

150
100
50
0
-50
-100
PPM
^{27}Al chemical shift (ppm)

FIG. 19

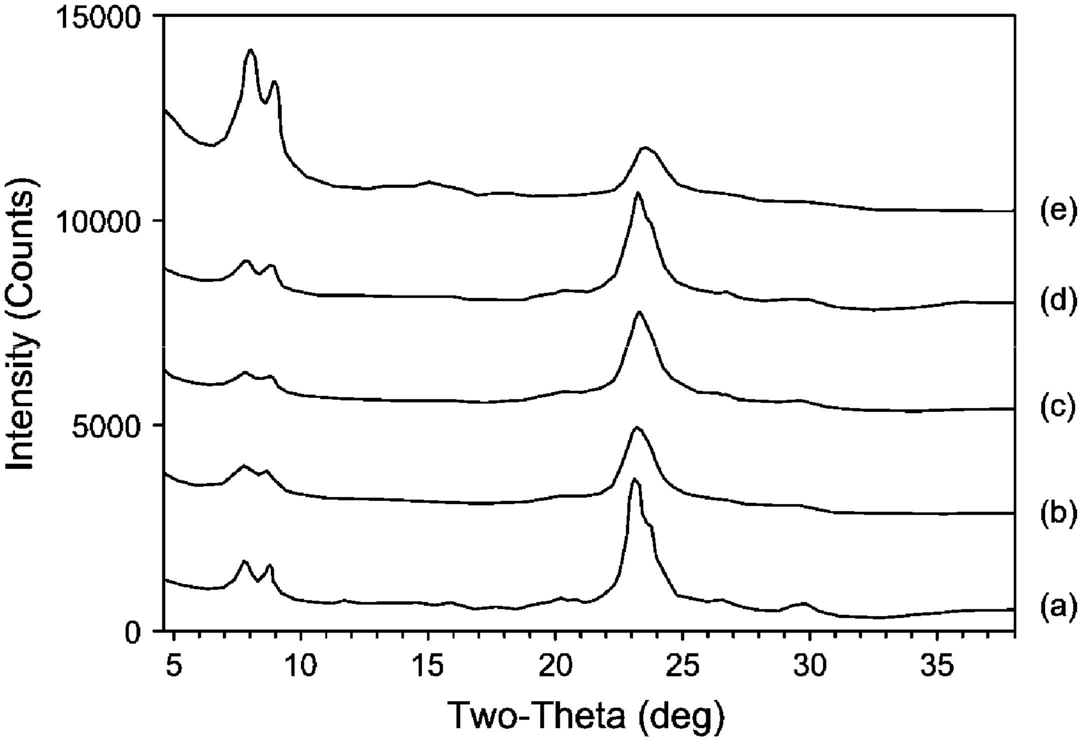

15000
10000
5000
0
Intensity (Counts)
5
10
15
20
25
30
35
Two-Theta (deg)
(e)
(d)
(c)
(b)
(a)

FIG. 20

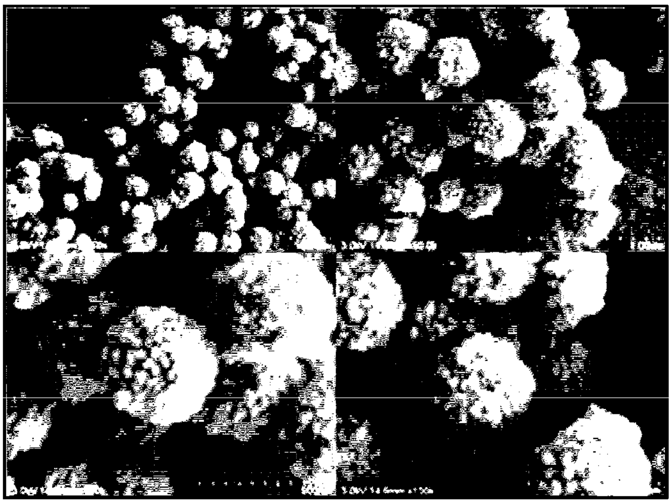


FIG. 21

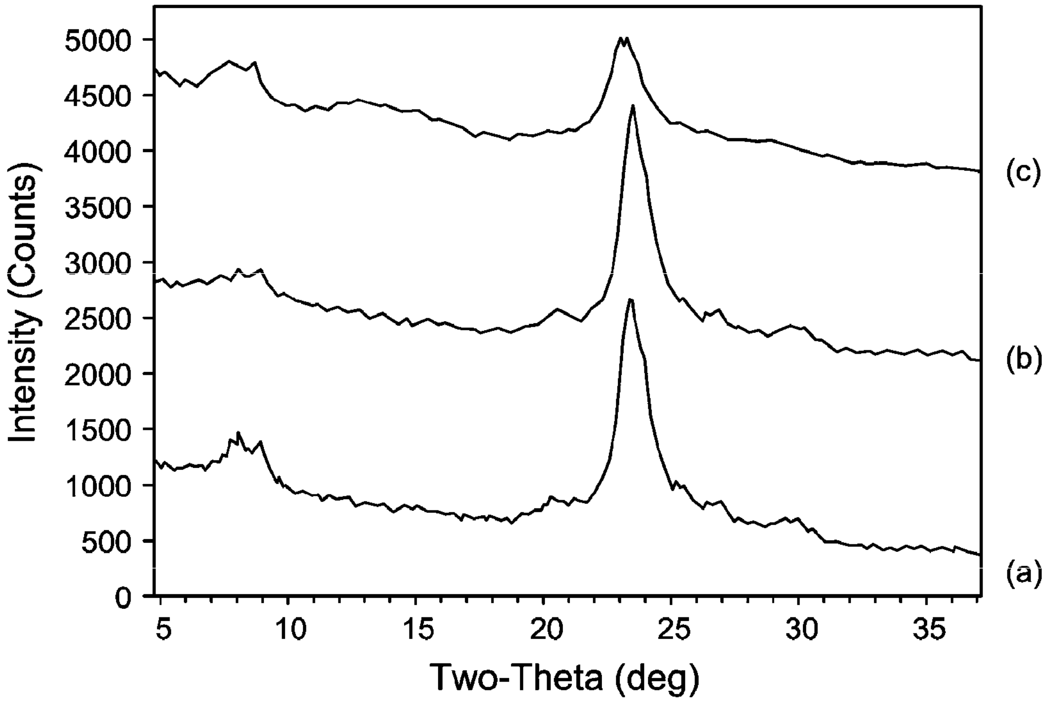

Intensity (Counts)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Two-Theta (deg)
5
10
15
20
25
30
35
(c)
(b)
(a)

FIG. 22

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/071456

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B37/02 C01B39/12 C01B39/40
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

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)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/087633 A2 (KOREA ADVANCED INST SCI & TECH [KR]; RYOO RYONG [KR]; CHOI MINKEE [KR]) 5 August 2010 (2010-08-05)	1,5,6,15
A	figure 10; example 4 abstract the whole document -----	2-4,7-12
X	US 2012/027673 A1 (LARSEN SARAH [US] ET AL) 2 February 2012 (2012-02-02)	7,13,14
A	paragraphs [0024], [0028], [0133]; figure 1; examples D,E; table 1 the whole document -----	1-6, 8-10,15
A,P	WO 2013/019462 A1 (EXXONMOBIL CHEM PATENTS INC [US]; BURTON ALLEN W [US]; STROHMAIER KARL) 7 February 2013 (2013-02-07) the whole document -----	1-15
	-/--	

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

☒ See patent family annex.

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"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 14 February 2014	Date of mailing of the international search report 20/02/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Follens, Lana

2

International application No
PCT/US2013/071456

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 0 514 715 A1 (ASAHI CHEMICAL IND [JP]) 25 November 1992 (1992-11-25) the whole document -----	1-13
A	WO 01/49607 A1 (EXXON CHEMICAL PATENTS INC [US]) 12 July 2001 (2001-07-12) the whole document -----	1-15

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/071456

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010087633 A2	05-08-2010	KR 20100088813 A	11-08-2010
		WO 2010087633 A2	05-08-2010
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		EP 0514715 A1	25-11-1992
		JP H05310415 A	22-11-1993
		US 5268162 A	07-12-1993
WO 0149607 A1	12-07-2001	AT 356083 T	15-03-2007
		AU 2763701 A	16-07-2001
		DE 60127095 T2	15-11-2007
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		WO 0149607 A1	12-07-2001