



(51) International Patent Classification:

C01B 39/14 (2006.01) C01B 39/22 (2006.01)

(21) International Application Number:

PCT/IN2019/050202

(22) International Filing Date:

13 March 2019 (13.03.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201841017881 11 May 2018 (11.05.2018) IN

(71) Applicant: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT MADRAS)** [IN/IN]; Dean, ICSR, Indian Institute of Technology Madras, IIT P.O., CHENNAI 600036 (IN).

(72) Inventors: **SELVAM, Parasuraman**; National Centre for Catalysis Research, Department of Chemistry, IIT Madras,

Chennai 600036 (IN). **PARSAPUR, Rajesh Kumar**; National Centre for Catalysis Research, Department of Chemistry, IIT Madras, Chennai 600036 (IN).

(74) Agent: **VENKATARAMAN, Shankar**; Maxval IP Services Pvt. Ltd, Indialand Techpark, Chil Sez, Saravanampatty PO, Coimbatore 641035 (IN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(54) Title: ORDERED AND HIERARCHICALLY POROUS ZEOLITE CRYSTAL AND A METHOD FOR PREPARATION THEREOF

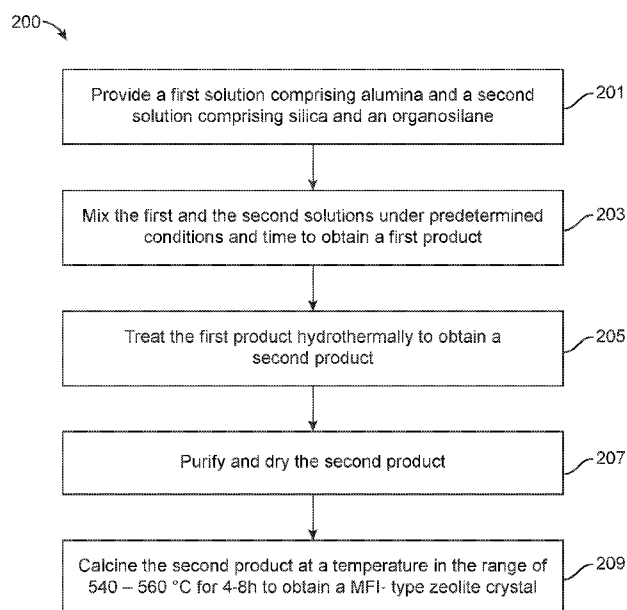


FIG. 2A

(57) Abstract: Ordered and hierarchically porous zeolite crystal catalyst showing enhanced selectivity towards phenol conversion and a method for preparation of the catalyst are disclosed. A solution containing alumina, silica and an organosilane are mixed and treated at a particular temperature for a particular period of time under pre-determined conditions to obtain a highly crystalline zeolite. A MFI-type, FAU-type and LTA-type zeolites are obtained. The zeolite catalyst exhibits a hierarchically porous structure with ordered mesopores. The surface area of the zeolite is in the range of micropores is in the range of 2- 374 m² g⁻¹ and the size of the mesopores is in the range of 89 - 499 m² g⁻¹. The lifetime of the crystal is at least 20 h.



(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

**ORDERED AND HIERARCHICALLY POROUS ZEOLITE CRYSTAL AND A
METHOD FOR PREPARATION THEREOF**

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims priority to Indian patent application no. 201841017881 entitled “ORDERED AND HIERARCHICALLY POROUS ZEOLITE CRYSTAL AND A METHOD FOR PREPARATION THEREOF” filed on May 11, 2018.

FIELD OF THE INVENTION

[0002] The disclosure relates to a zeolite and a method of preparation thereof, and in particular to zeolite for catalytic conversion of phenol.

DESCRIPTION OF THE RELATED ART

[0003] There is a huge demand for improved zeolite catalysts for selective butylation of phenol with high conversion rates. The remarkable success of zeolites as solid acid catalysts is attributed to their exceptional physicochemical properties. Among the plethora of zeolites employed, the structures with MFI, FAU and LTA topologies have been phenomenal in catalysis and sorption. Nevertheless, the small micropores can impose severe mass transfer constraints and make them impractical for use in catalysis of bulkier organic moieties.

[0004] The Indian patent document IN730DEL2011A discloses a process to prepare hierarchical mesoporous zeolites with varying micro-and meso-porosities using organosilane templates. But, a controlled crystallization with an ordered mesoporous structure is not achieved. Also, the templating agent used is expensive.

[0005] The US patent document 7785563B2 relates to a method of the preparation of microporous crystalline molecular sieve possessing mesoporous frameworks. A method is provided for the synthesis of a mesoporous lithium transition metal compound,

from a lithium salt with one or more transition metal salts in the presence of a surfactant. But, a controlled crystallization with an ordered mesoporous structure is not achieved and selectivity towards 4-t-butylphenol and/or 2, 4-di-t-butylphenol is very low.

[0006] The US patent document 20160137517A1 discloses zeolites with hierarchical porosity. The US patent application 20160193586A1 discloses a zeolite material based on mesoporous zeolite. The US patent application 20160176720A1 discloses hierarchically porous zeolites. A method to prepare Y-type FAU zeolites with hierarchical porosity is disclosed. The Chinese patent CN102530980B discloses a hierarchical pore zeolite, preparation and application thereof. But, a controlled crystallization with an ordered mesoporous structure is not achieved. Also, a cost effective templating agent is not utilized.

[0007] The publication “Synthesis, characterization of hierarchical ZSM-5 zeolite catalyst and its catalytic performance for phenol tert-butylation reaction”, Xu et al (2008) discusses the preparation of a ZSM-5 zeolite under hydrothermal conditions through polystyrene (PS) colloidal spheres and tetrapropylammonium hydroxide (TPAOH) dual templates method. But, the zeolite does not show the presence of ordered mesoporous. Further the use of a polymer as a template contributes to an increased production cost.

[0008] There remains a need to develop a zeolite with ordered mesoporous structure with enhanced phenol conversion. Further, there exists a need for synthesizing cost effective catalyst which displays enhanced selectivity towards conversion of phenol.

SUMMARY OF THE INVENTION

[0009] The disclosure relates to a catalyst and a method of preparation of a zeolite crystal and in particular to catalytic conversion of phenol by the zeolite crystal.

[0010] In various embodiments is provided a hierarchically porous MFI-type zeolite crystal. The crystal has the following characteristics. The Si/Al mole ratio of the crystal is at least 15. The crystal has a microstructure and has an ordered mesoporous

structure comprising micropores and mesopores. The mesopores are elongated along the $\langle 100 \rangle$ plane or direction of the longitudinal axes of the orthorhombic crystals. The size of micropores is in the range of 0.3 to 0.7 nm and the size of mesopores is in the range of 2.8 to 3.2 nm.

[0011] In some embodiments, the zeolite has acidity in the range of 0.83 to 0.87 mmol g⁻¹. The mesopore structure lattice constant is in the range of 4.5 to 4.9 nm. The surface area of the mesopores and micropores are in the range of 140- 145 m²g⁻¹ and 475 - 480 m²g⁻¹. The mesopore wall thickness is in the range of 1.5 to 1.9 nm. The pore volume of the micropores and the mesopores in the range of 0.05 to 0.09 cm³g⁻¹ and 0.62 to 0.66 cm³g⁻¹.

[0012] In one embodiment, the zeolite has an X-ray diffraction(XRD) pattern which may exhibit 100% intensity peaks at 5 or more of the following 2θ values: 7.996°, 8.85°, 14.88°, 17.75°, 20.06°, 23.242°, 24.146°, 26.77°, and 26.02°. In many embodiments, the zeolite shows at least 40% selective for 2, 4-di-tertiary-butylphenol.

[0013] In various embodiments is provided, a hierarchically porous FAU-type zeolite crystal. The crystal has the following characteristics. The Si/Al mole ratio less than 5. The crystal exhibits a cubic morphology. The crystal has an ordered mesoporous structure comprising micropores and mesopores. The mesopores are elongated along the $\langle 100 \rangle$ direction or plane of the zeolite crystals. The size of micropores is in the range of 0.5 to 0.9 nm and the size of mesopores is in the range of 4.3 to 4.9 nm.

[0014] In some embodiments, acidity of the zeolite is in the range of 1.35 to 1.78 mmol g⁻¹. The mesopore structure lattice constant in the range of 8.7 to 11.8 nm. The surface area of the micropores and mesopores are in the range of 370 to 374 m² g⁻¹ and 152 to 264 m² g⁻¹. The mesopore-wall-thickness in the range of 4.0 to 7.3 nm. The pore volume of micropore and meosopore in the range of 0.17 to 0.22 cm³ g⁻¹ and 0.15 to 0.25 cm³ g⁻¹.

[0015] In one embodiment, the zeolite crystal has a X-ray diffraction pattern with at least 3 peaks of intensity in % corresponding to 2θ values may be selected from 6.21°

(99%), 11.90° (37%), 12.44° (12%), 15.67° (48%), 18.70° (54%), 21.63° (12%), 27.06° (100%), and 31.42° (63%), or selected from 6.13° (97%), 10.01° (97%), 11.75° (97%), 15.46° (97%), 18.45° (98%), 20.10° (98%), 27.41° (100%), and 30.99 (100%). In many embodiments, the zeolite is selective for 4 -tertiary-butylphenol by at least 75%.

[0016] In various embodiments is provided, a hierarchically porous LTA- type zeolite crystal. The zeolite crystal has the following characteristics. The Si/Al mole ratio less than 5. The zeolite crystal has a radially oriented wormhole microstructure having a cubic morphology. The crystal has a dis-ordered mesoporous structure comprising mesopores and micropores, The mesopores have complex 3-dimensional shape and are randially oriented The size of micropores is in the range of 0.2 to 0.9 and the size of mesopores is in the range of 4.3 to 6.6.

[0017] In some embodiments, the acidity of the zeolite is in the range of 1.61 to 1.65 mmol g⁻¹. The surface area of the micropores and mesopores are in the range of 2 to 6 m² g⁻¹ and 89 to 93 m² g⁻¹. The pore volume of micropore and meosopore in the range of 0.01 to 0.03 cm³ g⁻¹ and 0.19 to 0.24 cm³ g⁻¹.

[0018] In one embodiment, the zeolite crystal has a X-ray diffraction pattern with at least three of the most intense XRD peaks with intensity in % corresponding to 2θ values may be selected from 7.19° (56%), 10.16° (61%), 12.43° (40%), 16.10° (81%), 21.68° (61%), and 23.99° (100%). In many embodiments, the zeolite has at least 15% selectivity towards 2 -tertiary-butylphenol. In various embodiments, life time of the zeolite as a catalyst is at least 20h.

[0019] In various embodiments is provided, a method of preparing hierarchical MFI-type zeolite. In the first step, a first solution including alumina and a second solution including silica and an organosilane is provided. In a second step, adding the first solution to the second solution to obtain a first product comprising constituents at a ratio of 0.8-1.2 Al₂O₃: 10.2-10.4 Na₂O: 3.83-3.86 (TPA)₂O; 34.4-34.8 TEOS: 2.1 to 2.5 organosilane: 6406.8 to 6407.2 H₂O. In a third step, treating the first product hydrothermally to obtain a second product. In a fourth step, purifying and drying the

obtained second product. Finally, calcining the second product at a temperature in the range of 540 – 560 °C in the presence of air for a time period in the range of 4h to 8h at a heating rate in the range of 0.8 to 1.2 °C min⁻¹ to obtain MFI- type zeolite.

[0020] In various embodiments, the first solution is obtained by mixing NaOH, de-ionized water, tetrapropylammonium bromide (TPABr) and sodium aluminate.

[0021] In some embodiments, the second solution is obtained by mixing the organosilane and tetraethyl orthosilicate (TEOS). In various embodiments, the organosilane is dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (DOAC). In various embodiments, the first product is treated hydrothermally at a temperature in the range of 120 to 140 °C for at least 10 days.

[0022] In various embodiments is provided a method of preparing hierarchical FAU-type or LTA-type zeolite. In a first step, forming a first solution comprising colloidal silica and a second solution comprising aluminum. In a second step, mixing the second solution with first solution under constant stirring to obtain a third solution. In a third step, adding at least 1.0 g of organosilane to the third solution under stirring to obtain a first product comprising constituents at a ratio of 0.8-1.2 Al₂O₃: 1-12 SiO₂: 3.2-9.4 Na₂O: 0.10-0.38 organosilane: 138-422 H₂O. In a fourth step, aging the first product for a first time period. In a fifth step, treating the first product hydrothermally to obtain a second product. Finally purifying and drying the second product and calcining in air at a temperature in the range of 540 to 560 °C for a time period in the range of 4 to 6 h to obtain the zeolite.

[0023] In various embodiments, the organosilane is Dimethyl octadecyl [3-(trimethoxy silyl) propyl]ammonium chloride (DOAC). In some embodiments, forming a first solution comprises adding colloidal silica to a solution of NaOH in H₂O.

[0024] In some embodiments the second solution is formed by adding The Al(OH)₃ or aluminum powder to a solution of NaOH in H₂O. In various embodiments, the first product is hydrothermally treated at 48 to 52 °C for 23 to 25 h followed by 95 to 105 °C for 23 to 25 h to obtain ZH-Y. The first product is treated at 45 to 55 °C for 23 to

25 h followed by 70 to 80 °C for 46 to 50h to obtain ZH-X. The first product is treated at 45 to 55°C for 23 to 25h followed by 70 to 80°C for 10 to 14h to obtain ZH-A. In various embodiments, the first time period is at least 24 h.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] The invention has other advantages and features which will be more readily apparent from the following detailed description of the invention and the appended claims, when taken in conjunction with the accompanying drawings, in which:

- [0026] FIG. 1A depicts a MFI- type zeolite.
- [0027] FIG. 1B depicts a FAU-type zeolite.
- [0028] FIG. 1C depicts a LTA-type zeolite.
- [0029] FIG. 2A depicts a method of preparation of MFI-type zeolite.
- [0030] FIG. 2B illustrates a reaction flow to obtain ZH-5.
- [0031] FIG. 3A depicts a method of preparation of FAU or LTA-type zeolite.
- [0032] FIG. 3B illustrates a reaction flow to obtain LTA and FAU- type zeolites.
- [0033] FIG. 4A depicts low angle XRD pattern of (a) ZH-5.
- [0034] FIG. 4B depicts low angle XRD pattern of ZH-Y.
- [0035] FIG. 4C depicts low angle XRD pattern of ZH-X.
- [0036] FIG. 4A depicts low angle XRD pattern of ZH-A.
- [0037] FIG. 5A depicts high angle XRD patterns of ZH-5.
- [0038] FIG. 5B depicts high angle XRD patterns of ZH-Y.
- [0039] FIG. 5C depicts high angle XRD patterns of ZH-X.
- [0040] FIG. 5D depicts high angle XRD patterns of ZH-A.
- [0041] FIG. 6A depicts N₂ sorption isotherm of (a) ZH-5; (b) ZH-Y; (c) ZH-X; (d) ZH-A.
- [0042] FIG. 6B depicts PSD of (a) ZH-5; (b) ZH-Y; (c) ZH-X; (d) ZH-A.
- [0043] FIG. 7A shows NMR spectra of (a) ZH-5; (b) ZH-Y; (c) ZH-X; (d) ZH-A.

- [0044] FIG. 7B shows NH₃-TPD spectra of (a) ZH-5; (b) ZH-Y; (c) ZH-X; (d) ZH-A.
- [0045] FIG. 8A depicts a SEM image of ZH-5.
- [0046] FIG. 8B depicts a SEM image of ZH-Y.
- [0047] FIG. 8C depicts a SEM image of ZH-X.
- [0048] FIG. 8D depicts a SEM image of ZH-A.
- [0049] FIG. 9A depicts a TEM image of ZH-5.
- [0050] FIG. 9B depicts a TEM image of ZH-Y.
- [0051] FIG. 9C depicts a TEM image of ZH-X.
- [0052] FIG. 9D depicts a TEM image of ZH-A.
- [0053] FIG. 10A depicts a SAED image of ZH-5.
- [0054] FIG. 10B depicts a SAED image of ZH-Y.
- [0055] FIG. 10C depicts a SAED image of ZH-X.
- [0056] FIG. 10D depicts a SAED image of ZH-A.
- [0057] FIG. 11A depicts a Si MAS NMR spectra of: ZH-5.
- [0058] FIG. 11B depicts a Si MAS NMR spectra of: ZH-Y.
- [0059] FIG. 11C depicts a Si MAS NMR spectra of: ZH-X.
- [0060] FIG. 11D depicts a Si MAS NMR spectra of: ZH-A.

DETAILED DESCRIPTION

[0061] While the invention has been disclosed with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention. In addition, many modifications may be made to adapt to a particular situation or material to the teachings of the invention without departing from its scope.

[0062] Throughout the specification and claims, the following terms take the meanings explicitly associated herein unless the context clearly dictates otherwise. The

meaning of "a", "an", and "the" include plural references. The meaning of "in" includes "in" and "on." Referring to the drawings, like numbers indicate like parts throughout the views. Additionally, a reference to the singular includes a reference to the plural unless otherwise stated or inconsistent with the disclosure herein.

[0063] The invention in its various embodiments discloses novel forms of zeolite and a method of preparation thereof. Use of the zeolite as a catalyst for butylation of phenol is also disclosed. The zeolite is fabricated, by varying the reactants, composition of the reactants and reaction conditions to form MFI- type zeolite named ZH-5 henceforth, FAU Y- type zeolite or FAU X- type zeolite named ZH-Y or ZH-X henceforth, or LTA-type zeolite crystal named ZH-A henceforth.

[0064] In various embodiments, provided herein is a hierarchically porous MFI-type or ZH-5 zeolite **100**. In some embodiments, the zeolite **100** is characterized by an ordered porous structure made of micropores **101** and mesopores **103** as shown in FIG. 1A. The MFI-type zeolite **100** may include any suitable aluminosilicate. In one embodiment, the crystal is an aluminosilicate of one of a sodium, potassium, calcium, or barium. In some embodiments, the MFI-type zeolite **100** has a higher silicon content relative to the aluminium content. In some embodiments, Si/Al ratio is at least 15. In some embodiments, Si/Al ratio is 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, or greater, or any number therebetween. In some embodiments, the zeolite **100** includes a serrated super-ellipsoid microstructure which is contributed by a plurality of MFI/MEL intergrowths. In some embodiments, the mesopores are elongated along <100> plane or direction of the longitudinal axes of the orthorhombic crystals. In some embodiments, the mesopores are stacked parallel to adjacent pores in the <110> direction.

[0065] In some embodiments, the size of micropores **101** is in the range of 0.3 to 0.7 nm and the size of mesopores **103** is in the range of 2.8 to 3.2 nm. The size of the pores may be determined by a suitable technique known in the art such as Horváth-Kawazoe (HK) using N₂ adsorption or Barrett-Joyner-Halenda (BJH) analysis using N₂

desorption. In some embodiments, the acidity of the zeolite is in the range of 0.83 to 0.87 mmol g⁻¹. In various embodiments, the mesopore structure lattice constant is in the range of 4.5 to 4.9 nm. The mesopore structure lattice constant may be calculated from the formula $1/d^2 = 4/3 (h^2 + hk + k^2/a^2)$. In some embodiments, the surface area of the mesopores and micropores are in the range of 140- 145 m²g⁻¹ and 475 - 480 m²g⁻¹, respectively. In some embodiments, the mesopore wall thickness is in the range of 1.5 to 1.9 nm. In some embodiments, the pore volume of the micropores and the mesopores are in the range of 0.05 to 0.09 cm³g⁻¹ and 0.62 to 0.66 cm³g⁻¹ respectively.

[0066] In one embodiment, the zeolite has an X-ray diffraction(XRD) pattern as in Table 1. The X-ray diffraction pattern may exhibit 100% intensity peaks at 5 or more of the following 2θ values: 7.996°, 8.85°, 14.88°, 17.75°, 20.06°, 23.242°, 24.146°, 26.77°, and 26.02°.

[0067] In various embodiments, provided herein is a hierarchically porous FAU-type zeolite **110**. In some embodiments, the zeolite **110** is characterized by an ordered porous structure made of micropores **111** and mesopores **113** as shown in FIG. 1B. In some embodiments, the zeolite crystal exhibits a low Si/Al ratio due to presence of a high Al content. In some embodiments, the Si/Al ratio is less than 5. In some embodiments, the Si/Al ratio is 5, 4, 3, 2, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, or lower, or any number therebetween. In some embodiments, the zeolite crystals are characterized by a cubic morphology. The mesopores are elongated along the <100> plane or direction of the zeolite crystals. In some embodiments, the mesopores are stacked parallel to adjacent pores in the <110> direction.

[0068] In some embodiments, acidity of the zeolite is in the range of 1.35 to 1.78 mmol g⁻¹ due to a high amount of aluminum. In some embodiments, the size of the micropores are in the range of 0.5 to 0.9 nm and the size of mesopores are in the range of 4.3 to 4.9 nm. The size of the pores may be determined by a suitable technique known in

the art such as HK and BJH methods. The mesopore structure lattice constant may be calculated from $1/d^2 = 4/3 (h^2 + hk + k^2/a^2)$. In some embodiments, mesopore structure lattice constant is in the range of 8.7 to 11.8 nm. In some embodiments, surface area of the micropores and mesopores are in the range of 370 to 374 m²g⁻¹ and 152 to 264 m²g⁻¹, respectively. In some embodiments, mesopore-wall-thickness in the range of 4.0 to 7.3 nm. In some embodiments, pore volume of micropore and mesopore in the range of 0.17 to 0.22 cm³ g⁻¹ and 0.15 to 0.25 cm³ g⁻¹, respectively.

[0069] In one embodiment, the zeolite crystal has a X-ray diffraction pattern as in Table 2 or 3. In some embodiments, the zeolite crystal has a XRD pattern with at least 3 peaks of high intensity in % corresponding to 2θ values may be selected from 6.21° (99%), 11.90° (37%), 12.44° (12%), 15.67° (48%), 18.70° (54%), 21.63° (12%), 27.06° (100%), and 31.42° (63%), or selected from 6.13° (97%), 10.01° (97%), 11.75° (97%), 15.46° (97%), 18.45° (98%), 20.10° (98%), 27.41° (100%), and 30.99 (100%).

[0070] In various embodiments, provided herein is a hierarchically porous LTA-type or ZH-A- type zeolite **120**. In some embodiments, zeolite **120** is characterized by a radially oriented wormhole microstructure as shown in FIG. 1C. In some embodiments, the zeolite **120** includes a disordered mesoporous structure comprising micropores **121** and mesopores **123**. In some embodiments, the zeolite has a Si/Al ratio of less than 2. In some embodiments, the zeolite has a Si/Al ratio of 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, or lower, or any number therebetween. In some embodiments, the zeolite crystals are three dimensional and radially oriented.

[0071] In some embodiments, the size of micropores is in the range of 0.2 to 0.9 and the size of mesopores is in the range of 4.3 to 6.6. The size of the pores may be determined by any suitable method known in the art such as HK and BJH methods. In some embodiments, acidity of the zeolite is in the range of 1.61 to 1.65 mmol g⁻¹. The increased selectivity of 2-tertiary-butylphenol in case of ZH-A due to the presence of high amount of aluminium decreasing the acidity. The weak acid sites thereby increasing

selectivity towards 2 tertiary -butylphenl isomer. In some embodiments, surface area of the micropores and mesopores are in the range of 2 to 6 m²g⁻¹ and 89 to 93 m²g⁻¹, respectively. In some embodiments, pore volume of micropore and meosopore are in the range of 0.01 to 0.03 cm³g⁻¹ and 0.19 to 0.24 cm³g⁻¹, respectively.

[0072] In one embodiment, the zeolite crystal has a X-ray diffraction pattern as in Table 4. In one embodiments, the XRD pattern has at least three of the most intense XRD peaks with intensity in % corresponding to 2θ values may be selected from 7.19° (56%), 10.16° (61%), 12.43° (40%), 16.10° (81%), 21.68° (61%), and 23.99° (100%).

[0073] In various embodiments, the zeolite **100, 110, 120** shows a high catalytic efficiency and enables a long life time. In some embodiments, the zeolite **100, 110, 120** as a catalyst shows a lifetime of 0.1, 4, 8, 12, 16, 20, 24h, or any number therebetween, or greater than 24h. The zeolite crystals can be re-used without deterioration in catalytic properties.

[0074] In various embodiments, provided herein is a method **200** of preparing a hierarchical MFI-type zeolite as shown in FIG. 2A. In step **201**, a first solution and a second solution is provided. The first solution includes at least a metal hydroxide in deionized water, a first templating agent such as tetrapropylammoniumbromide (TPABr) and an aluminum containing compound. The second solution includes at least a second templating agent such as organosilane and a silica containing compound such as TEOS. In step **203**, a second solution is added in a dropwise manner to the first solution to obtain a third solution. The resulting solution is stirred to form a gel upon condensation and nucleation. The crystallization conditions are controlled to form homogeneous nuclei. In step **205**, the gel is hydrothermally treated at a temperature in the range of 120-140°C for up to 200-280h under static conditions to obtain a second product. In step **207**, the second product is purified and dried. In step **209**, the second product is calcined at a temperature in the range of 400 to 600 °C for a time period in the

range of 0 to 96h. The final calcined product is then purified and dried to obtain a MFI-type zeolite crystal.

[0075] Without being bound to any particular theory it is suggested herein that the reaction flow with various products and byproducts formed to obtain ZH-5 is provided as shown in FIG. 2B. The raw materials **202** are combined as in step **201**. The resulting solution is stirred to form a first gel intermediate **204** upon condensation and nucleation. The first gel intermediate is then micellized to form a second intermediate **206** by hydrothermal treatment. The interaction of the organosilane with the zeolitic network plays a key role in stabilizing the mesostructure. Under optimized synthesis conditions, the organosilanes interact not only with covalent Si-C bond but also with the electrovalent quaternary ammonium cations and can restrict the zeolitic growth to obtain an ordered mesoporous network of product **208**. The electrovalent interactions of organosilanes may have also contributed for the formation of serrated morphologies.

[0076] In some embodiments, treating the first product hydrothermally comprises treating the product at a temperature in the range of 120 to 140 °C for at least 10 days.

[0077] In various embodiments provided herein is a method **300**, for preparing a hierarchical FAU-type or LTA-type zeolite as shown in FIG. 3A. In step **301**, providing a first solution and a second solution. The first solution includes a metal hydroxide in DI water, and silica containing compound. The second solution includes a metal hydroxide in DI water, and an aluminum containing compound. In step **303**, a second solution is added in a dropwise manner to the first solution under ice bath to obtain a third solution. In step **305**, an organosilane is added to the third solution to obtain a first product. In step **307**, the first product is aged under predetermined conditions for a first time. In step **309**, the first product hydrothermally treated. In step **311**, the second product is calcined at a temperature in the range of 540 – 560 °C for a time period in the range of 0 to 96h. The calcined product is purified and dried to obtain a LTA- type and FAU- type zeolite.

[0078] Without being bound to any particular theory it is suggested herein that the reaction flow with various products and byproducts formed to obtain ZH-X, ZH- Y and ZH- A is provided as shown in FIG. 3B. The raw materials **302** are utilized for form the first intermediate gel **304** upon condensation and nucleation. The prolonged hydrothermal treatment results in micellization and zeolitization to obtain a second zeolite product **308** with a micellar aggregate **306** formed as an intermediate. The organosilicane acts as a nucleation promoting template by enabling bonding of the reactants. The interaction of surfactant with the zeolitic network plays a key role in stabilizing the mesostructure. Under the preferred synthesis conditions, the organosilanes interact not only with covalent Si-C bond but also with the electrovalent quaternary ammonium cations and restricts the zeolitic growth to obtain an ordered mesoporous network.

[0079] In some embodiments, to obtain a ZH-Y type zeolite the raw materials are varied between 0.8 to 1.2 Al_2O_3 : 8 to 12 SiO_2 : 7.8 to 8.2 Na_2O : 0.34 to 0.38 organosilane: 418 to 422 H_2O to obtain the first product. The obtained product is hydrothermally treated at a temperature in the range of 48 to 52 °C for 23- 25 h and 95 to 105 °C for 23- 25 h each to obtain a second product.

[0080] In some embodiments, to obtain a ZH-X type zeolite the raw materials are varied between 0.8 to 1.2 Al_2O_3 : 8.8 to 9.2 SiO_2 : 0.34 to 0.38 Na_2O : 0.34 to 0.38 DOAC: 378 to 382 H_2O . The obtained product is hydrothermally treated at a temperature in the range of 45-55 °C for at least 23 to 25h and at 70 to 80 °C for 46 to 50h to obtain a second product.

[0081] In some embodiments, to obtain a ZH-A type zeolite the raw materials are varied between 0.8 to 1.2 Al_2O_3 : 1.8 to 2.2 SiO_2 : 3.2 to 9.2 Na_2O : 0.10 to 0.14 DOAC: 138 to 142 H_2O to obtain the first product. The obtained product is hydrothermally treated at a temperature in the range of 45 to 55°C for a period in the range of 23 to 25 and 70 to 80°C for a period in the range of 10- 14 h to obtain a second product.

[0082] In some embodiments, the aluminum containing compound is selected from one of an aluminate, aluminum hydroxide $\text{Al}(\text{OH})_3$, Al powder, alumina, AlCl_3 or $\text{Al}_2(\text{SO}_4)_3$. The silica containing compound is one of but, not restricted to a colloidal silica, or tetraethyl orthosilicate (TEOS) or sodium silicate. In some embodiments, the organosilane for the preparation of the zeolite crystal is selected from one of a dimethyl octa decyl [3-(trimethoxy silyl) propyl] ammonium chloride) DOAC. The reaction mixture may contain a one or more active source of alkali metal oxide. The source may include one of oxides, hydroxides, nitrates, sulfates, halogenides, oxalates, citrates or acetates of sodium, potassium calcium or barium. In some embodiments, a micropore-templating agent is employed to obtain ZH-5. In one embodiment, the micropore-templating agent is a Tetrapropylammoniumbromide (TPABr).

[0083] In some embodiments, the phenol conversion (%) of ZH- 5 is in the range of 60% to 65%. In some embodiments, selectivity towards 2-tertiary-butylphenol is in the range of 6.5 to 8%. The selectivity of ZH- 5 towards 4- tertiary-butylphenol is in the range of 50 to 85%. The selectivity of 2,4-di- tertiary-butylphenol is in the range of 8 to 44 9%.

[0084] In some embodiments, phenol conversion (%) of ZH-Y is in the range of 50 to 60% . The selectivity of ZH-Y towards 2-tertiary-butylphenol is in the range of 3 to 4%. The selectivity of 4- tertiary-butylphenol is in the range of 80 to 90% The selectivity of 2,4-di- tertiary-butylphenol is in the range of, and 5 to 10%.

[0085] In various embodiments, the phenol conversion (%) of ZH-X is in the range of 40 to 50%. The ZH-X shows selectivity towards 2-tertiary-butylphenol in the range of 10 to 15% The ZH-X shows selectivity towards 4-tertiary-butylphenol in the range of 75 to 80% and 2, 4-ditertiary butylphenol in the range of 7 to 10%.

[0086] In some embodiments, the phenol conversion (%) of ZH-A is in the range of 5 to 6%. The ZH- A shows selectivity towards 2-tertiary-butylphenol in the range of 18 to 20%. The ZH- A shows selectivity towards 4-tertiary-butylphenol in the range of

70 to 74%. The ZH- A shows selectivity towards 2,4-di-tertiary-butylphenol in the range of 8 to 10%, respectively.

[0087] In some embodiments, ZH-5 has enhanced phenol conversion as compared to ZH- Y, ZH- X and ZH- A. In some embodiments, ZH- Y has improved selectivity towards 4-tert-butylphenol as compared to ZH- 5, ZH- X and ZH- A. In some embodiments ZH-A has an enhanced selectivity towards 2- tertiary- butyl phenol as compared to ZH- 5, ZH- Y and ZH- X. In some embodiments, ZH-X has a significantly large surface area as compared to ZH- 5, ZH- Y and ZH- A.

[0088] Without being bound to any particular theory, it is considered that the aging and controlled nucleation promotes the orientation of the synthesis towards the desired zeolite with the ordered mesoporous microstructure. Without being bound to any particular theory, it is suggested herein that the strong organosilane interactions and slow rate of zeolitization at low-temperatures assists the formation of short range ordered mesostructures of MFI-frameworks. For, low-silica zeolites such as ZH-Y, ZH-X and ZH-A- type zeolites, a low-temperature oligomerization process followed by two-step crystallization process, facilitates the homogenous nucleation and slow rate of crystallization for the formation of durable mesostructure.

[0089] While the invention has been disclosed with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention. In addition, many modifications may be made to adapt to a particular situation or material the teachings of the invention without departing from its scope. Further, the examples to follow are not to be construed as limiting the scope of the invention which will be as delineated in the claims appended hereto.

EXAMPLES

[0090] Example 1 – Synthesis of hierarchical MFI-type zeolite, ZH-5

[0091] In a typical synthesis, two solutions A and B were prepared separately and then mixed to form a gel. Sol A was prepared by dissolving 1.0 g NaOH in 150 mL of de-ionized water followed by the addition of 3.0 g of TPABr. The mixture was stirred for 15 min and then a prescribed amount of sodium aluminate [Si/Al =20 (194 mg)] was added. The obtained solution was stirred vigorously for 10 min. On the other hand, sol B was prepared by mixing 2.5 g of surfactant DOAC with 9.5 g TEOS to form a solution constituting 1.0 Al₂O₃: 10.4 Na₂O: 3.85 (TPA)₂O: 34.6 TEOS: 2.3 ODAC: 6407.0 H₂O). The resultant solution was stirred for 15 min. Then, sol B was added dropwise to sol A under vigorous stirring and the resulting white solution was stirred for 2 h. Thus gel obtained was hydrothermally treated at 130°C for 10 days under static conditions. The obtained solids were filtered, washed and dried at 100°C followed by calcination at 550°C in the flow of air for 6 h at a heating rate of 1°C min⁻¹. Thus obtained samples are designated as ZH-5 (20) for 12 h.

[0093] Example 2- Synthesis of hierarchical FAU-type zeolite, ZH-Y:

[0094] In a typical synthesis, sol-A was prepared by mixing 1.0 g of NaOH in 16.0 g of H₂O, followed by the addition of 5.0 g of colloidal silica. Sol-B was prepared by dissolving 1.14 g of NaOH in 6.0 g of H₂O, followed by the careful addition of 0.52 g of Al(OH)₃. Both the precursor solutions, sol-A and sol-B were stirred for 15 min and then, the sol-B was added drop wise to the sol-A on the ice bath (0-4°C) under vigorous stirring (800 rpm). The stirring was continued for 1 h, followed by the addition of 1.0 g of organosilane, DOAC (dimethyloctadecyl [3- (trimethoxysilyl) propyl] ammonium chloride) under stirring (500 rpm). The mixture with final composition 1Al₂O₃: 10SiO₂: 8.0Na₂O: 0.36DOAC: 420H₂O was further stirred for 2 h and aged at room temperature for 24 h. The aged gel was crystallized by hydrothermal treatment at 50°C and 100°C for 24 h each. The resulting solids were washed with distilled water, filtered and dried at 100°C, followed by the calcinations in air at 550°C for 6 h to obtain highly crystalline zeolite mesostructure, ZH-Y.

[0095] Example 3- Synthesis of hierarchical FAU-type zeolite, ZH-X:

[0096] Hierarchical zeolite, ZH-X was obtained by using the similar procedure as that of ZH-Y except for the change in the synthesis composition and crystallization temperature. The initial gels with synthesis composition $1.0\text{Al}_2\text{O}_3$: 9.0SiO_2 : $9.0\text{Na}_2\text{O}$: 0.36DOAC : $380\text{H}_2\text{O}$ were aged at room temperature for 24 h and hydrothermally treated at 50°C for 24 h and 75°C for 48 h. The finally obtained solids were washed with distilled water, filtered and dried at 100°C , followed by the calcinations in air at 550°C for 6 h to obtain highly crystalline zeolite mesostructure, ZH-X.

[0097] Example 4- Synthesis of hierarchical ZH-A -type zeolite:

[0098] Sodium silicate solution is prepared separately by dissolving 1.0 g of NaOH in 11.2 g of H_2O , followed by the addition of 3.0 g of colloidal silica. The solution was stirred vigorously for 15 min. Meanwhile, sodium aluminate solution was prepared by dissolving 1.72 g of NaOH in 11.0 g of H_2O , followed by careful addition of 0.54 g of Al metal powder. Both the precursor solutions were stirred for 15 min and then mixed to each other on an ice bath under vigorous stirring. The stirring was continued for 1 h, followed by the addition of 1.0 g of organosilane (DOAC). The mixture with final composition $1\text{Al}_2\text{O}_3$: 2SiO_2 : $3.4\text{Na}_2\text{O}$: 0.12DOAC : $140\text{H}_2\text{O}$ was further stirred for 2 h and aged at room temperature for 24 h. The aged gel was crystallized by hydrothermal treatment at 50°C for 24 h and 75°C for 12 h. The resulting solids were washed with distilled water, filtered and dried at 100°C , followed by the calcinations in air at 550°C for 6 h to obtain highly crystalline zeolite mesostructure, ZH-A.

[0099] Example 5- Characterization

[00100] The prepared samples were analyzed by various characterization techniques such as XRD, N_2 sorption, SEM and TEM, to systematically investigate the physicochemical properties. FIGs 4A - 4D depicts the low angle and FIGs 5A - 5D depicts high angle XRD patterns of the prepared samples. The samples, ZH-5, ZH-Y and ZH-X had shown characteristic Bragg's reflections in the low-angle typical of 2D-hexagonal structure (MCM-41). Whereas, ZH-A had not shown any significant pattern corresponding to ordered mesoporous structure, however, there was a broad reflection in

the low-angle region indicating the nature of disordered wormhole like mesopores. The high-angle pattern is distinctive of orthorhombic (MFI) and cubic (FAU and LTA) crystal symmetry respectively.

Table 1: hkl Phase – 1 Lebail Method - ZH-5

h	k	l	m	d	2 Θ	I
1	0	1	4	11.05	7.996	1.01
2	0	0	2	9.98	8.85	1.01
3	0	1	4	5.949	14.88	1.01
4	0	0	2	4.992	17.75	1.01
2	4	0	4	4.424	20.06	1.01
5	0	1	4	3.82	23.242	1.01
3	0	3	4	3.683	24.146	1.01
6	0	0	2	3.33	26.77	1.01
5	0	2	4	3.42	26.02	1.01

Table 2: hkl Phase - 2 Lebail Method for ZH-Y

h	k	l	m	d	2	I
1	1	1	8	14.22	6.21	1.71
3	1	1	24	7.23	11.90	0.64
2	2	2	8	7.11	12.44	0.20
3	3	1	24	5.65	15.67	0.82
3	3	3	8	4.74	18.70	0.93
5	1	1	24	4.74	18.70	0.93
4	4	2	24	4.11	21.63	0.21
6	4	2	48	3.29	27.06	1.72
7	5	1	48	2.84	31.42	1.09

Table 3: hkl Phase – 1 Lebail Method ZH-X

h	k	l	m	d	2 Θ	I
1	1	1	8	14.42	6.13	1.08
0	2	2	12	8.83	10.01	1.08
3	1	1	24	7.53	11.75	1.08
3	3	1	24	5.728	15.46	1.08
5	1	1	24	4.81	18.45	1.09
0	4	4	12	4.41	20.10	1.09
5	5	3	24	3.25	27.41	1.11
7	5	1	48	2.88	30.99	1.11

Table 4: hkl Phase – 1 Le bail Method ZH- A

h	k	l	m	d	2 Θ	I
2	0	0	24	3.93	7.19	1.13
2	2	0	8	3.41	10.16	1.24
2	2	2	48	2.57	12.43	0.82
4	2	0	24	1.97	16.10	1.65
4	4	2	24	1.78	21.68	1.24
6	2	2	48	1.58	23.99	2.03

[00101] FIG. 6A depicts the nitrogen sorption isotherms and FIG. 6B depicts pore size distributions of the samples which show a combination of type-I and type-IV isotherms, indicating the co-existence of mesopores along with the micropores. The steep rise in the isotherm at 0.1 P/P₀ could be attributed to the adsorption in the micropores whereas the narrow H1 hysteresis indicates the presence of uniform mesopores. The structural and textural properties of the samples are listed in Table 1. FIG. 7A depicts ²⁷Al MAS NMR spectra of the prepared zeolites which show single resonance around 55-60 ppm corresponding to the presence of aluminum atom in the tetrahedral coordination inside the zeolitic framework. On the other hand, the absence of significant

resonance around '0 ppm' indicates the lack of non-framework aluminum species. The quantitative examination of acidity was determined by NH₃-TPD (FIG. 7B) and the obtained values are reported in table 1. FIGs 8A- 8D depict the SEM images of the prepared zeolites which exhibit interesting morphologies. Hierarchical ZSM-5 has shown serrated super-ellipsoid morphologies owing to the MFI/MEL intergrowths as shown in FIG. 8A. On the other hand, SEM of ZH-X, ZH-Y and ZH-A has shown octahedral and cubic morphologies characteristic of FAU and LTA structures respectively as shown in FIGs. 8B, 8C and 8D. FIGs. 9A- 9D depict the TEM images of the prepared zeolites which show the co-existence of zeolitic micropores along with the uniform mesopores in a hierarchical organization. It is clearly evident from the TEM images of ZH-A that the mesopores are disordered and are radially arranged as branch-like structures within the crystal domain as shown in FIG. 9A.

Table 5: Structural, Textural and Acidic Properties of Various Aluminosilicates

Sample	Si/Al	a _o (nm)	SBET (m ² g ⁻¹)		D (nm)		V _p (cm ³ g ⁻¹)		h _w (nm)	Acidity (mmol g ⁻¹)
			Micro	Total	Micro	Meso	Micro	Total		
ZH-5	20.0	4.7	143	620	0.5	3.0	0.07	0.64	1.7	0.85
ZH-Y	2.1	8.9	372	634	0.7	4.7	0.20	0.43	4.2	1.76
ZH-X	1.4	11.6	367	521	0.7	4.5	0.19	0.36	7.1	1.37
ZH-A	1.0	-	4	95	0.4	6.4	0.01	0.22	-	1.63

[00102] Example 5- Catalyst testing

[00103] Vapor phase tertiary butylation of phenol was carried out in a fixed-bed down flow reactor using 500 mg of zeolite sample. The reactor set-up was pre-heated to 350°C in the flow of air for 2 h followed by cooling to desired reaction temperature using nitrogen flow of 30 mL h⁻¹ for 1 h. Nitrogen was used as carrier gas and liquid injection pump (Miclins) was used to feed the mixture of reactants. The transformed gaseous products are condensed in an ice bath and the resulting liquids were collected

every hour. The products viz., ortho- (2-tetra-butylphenol), para- (4-tetra-butylphenol) and 2,4-di-tert-butyl phenols (2,4-di-tetra-butylphenol) were analyzed using Perkin-Elmer gas chromatograph with a ZB-1 capillary column.

[00104] The catalytic activities of the synthesized zeolites have been evaluated for vapor phase tertiary butylation of phenol and the obtained values are enlisted in table 2. The hierarchical zeolite, ZH-5, ZH-Y and ZH-X have shown excellent catalytic activities with enhanced selectivity towards mono-alkylated product, 4-t-BP. More importantly, ZH-5 has shown remarkable selectivity of 42% towards 2,4-di-t-BP by tuning the reaction conditions (condition-II). This high selectivity towards the dialkylations in case of ZH-5 may be attributed to the presence of strong bronsted acid sites. The reaction was carried out for a period of 24 h to study the life time of the catalysts. The catalysts had shown good activity for prolonged periods without notable change in the efficiency. Although LTA shows relatively lower conversion as compared to the other zeolites, it has wide range of applications in industries for example for use in adsorption, separation and ion-exchange processes. It accounts for greater than 60% of the total zeolite consumption. The increased selectivity of 2-t-BP selectivity in case of ZH-A can be attributed to the increased aluminum content which can increase the structural Lewis acid sites originating from the geometric defects.

Table 6: Activity of Various Hierarchical Zeolites

Catalyst	n_{Si}/n_{Al}	t-BuOH / Phenol	Phenol Conversion (%)	Selectivity		
				2-t-BP	4-t-BP	2,4-di-t-BP
ZH-5	19.0	2	61.3	7.3	83.0	9.7
		4	50.6	6.8	51.0	42.1
ZH-Y	2.1	2	57.5	3.5	88.0	8.4
ZH-X	1.4	2	40.5	12.5	79.5	7.9

ZH-A	1.0	2	5.2	19.2	72.0	8.8
------	-----	---	-----	------	------	-----

[00105] FIG. 6A depicts the nitrogen sorption isotherms and FIG. 6B depicts the pore size distributions (PSD) of the samples which show a combination of type-I and type- IV isotherms, indicating the co-existence of mesopores along with the micropores. The steep rise in the isotherm at 0.1 P/P_o could be attributed to the adsorption in the micropores whereas the narrow H1 hysteresis indicates the presence of uniform mesopores. The structural and textural properties of the samples are listed in Table 5.

[00106] FIG. 7A depicts ²⁷Al MAS NMR spectra of the prepared zeolites which show single resonance around 55-60 ppm corresponding to the presence of aluminum atom in the tetrahedral coordination inside the zeolitic framework. On the other hand, the absence of significant resonance around '0 ppm' indicated the lack of non-framework aluminum species. The quantitative examination of acidity was determined by NH₃-TPD as shown in FIG. 7B and the obtained values are reported in table VI. FIGs. 8A- 8D depict the SEM images of the prepared zeolites which exhibit interesting morphologies. Hierarchical ZSM-5 had shown serrated super-ellipsoid morphologies owing to the MFI/MEL intergrowths. On the other hand, SEM of ZH-X, ZH-Y and ZH-A had shown octahedral and cubic morphologies characteristic of FAU and LTA structures respectively. FIGs. 9A- 9D depict the TEM images of the prepared zeolites which show the co-existence of zeolitic microspores along with the uniform mesopores in a hierarchical organization. FIGs. 10A- 10D depict the SAED patterns of ZH-5, ZH-X, ZH-Y and ZH-A. Table VII: denotes Al/Si coordination peaks of FIG. 11A- 11D.

Table 7: Al/Si Coordination Peaks Corresponding to FIG. 11A-11D

Peak	'Si' coordination
(i)	4Si(0Al)
(ii)	3Si(1Al)
(iii)	2Si(2Al)
(iv)	1Si(3Al)
(v)	0Si(4Al)

We claim,

1. A hierarchically porous MFI-type zeolite (100) crystals, having at least the following characteristics:

Si/Al mole ratio of at least 15;

a microstructure having an orthorhombic morphology; and

an ordered mesoporous structure comprising micropores and mesopores,

wherein the size of micropores is in the range of 0.3 to 0.7 nm and the size of mesopores is in the range of 2.8 to 3.2 nm, and the mesopores are elongated along <100> plane of the longitudinal axes of the orthorhombic crystals.

2. The zeolite of claim 1, wherein:

acidity of the zeolite is in the range of 0.83 to 0.87 mmol g⁻¹;

mesopore structure lattice constant is in the range of 4.5 to 4.9 nm;

surface area of the mesopores and micropores are in the range of 140- 145 m² g⁻¹ and 475 - 480 m² g⁻¹, respectively;

mesopore wall thickness is in the range of 1.5 to 1.9 nm; or

pore volume of the micropores and the mesopores in the range of 0.05 to 0.09 cm³ g⁻¹ and 0.62 to 0.66 cm³ g⁻¹, respectively.

3. The zeolite of claim 1, having an X-ray diffraction pattern exhibiting 100% intensity peaks at 5 or more of the following 2θ values: 7.996°, 8.85°, 14.88°, 17.75°, 20.06°, 23.242°, 24.146°, 26.77°, and 26.02°.

4. The zeolite of claim 1, wherein the zeolite is selective for 2, 4-di-tertiary-butylphenol by at least 40%.

5. A hierarchically porous FAU-type zeolite (110) crystals, having at least the following characteristics:

a Si/Al mole ratio less than 5;

crystals exhibiting a cubic morphology; and

an ordered mesoporous structure comprising micropores and mesopores, wherein the size of micropores is in the range of 0.5 to 0.9 nm and the size of mesopores is in the range of 4.3 to 4.9 nm, and the mesopores are elongated along the <100> plane of the zeolite crystals.

6. The zeolite of claim 5, wherein;

acidity of the zeolite is in the range of 1.35 to 1.78 mmol g⁻¹;

mesopore structure lattice constant in the range of 8.7 to 11.8 nm;

surface area of the micropores and mesopores are in the range of 370 to 374 m² g⁻¹ and 152 to 264 m² g⁻¹;

mesopore-wall-thickness in the range of 4.0 to 7.3 nm; or

pore volume of micropore and mesopore in the range of 0.17 to 0.22 cm³ g⁻¹ and 0.15 to 0.25 cm³ g⁻¹.

7. The zeolite of claim 5, having a X-ray diffraction pattern with at least 3 of the most intense peaks with intensity in % corresponding to 2θ values selected from 6.21° (99%), 11.90° (37%), 12.44° (12%), 15.67° (48%), 18.70° (54%), 21.63° (12%), 27.06° (100%), and 31.42° (63%), or with at least 3 of the most intense peaks with intensity in % corresponding to 2θ values selected from 6.13° (97%), 10.01° (97%), 11.75° (97%), 15.46° (97%), 18.45° (98%), 20.10° (98%), 27.41° (100%), and 30.99 (100%).

8. The zeolite of claim 5, wherein the zeolite is selective for 4 -tertiary-butylphenol by at least 75%.

9. A hierarchically porous LTA- type zeolite (120) crystals, having at least the following characteristics:

a Si/Al mole ratio less than 5;
a radially oriented wormhole microstructure having a cubic morphology; and
a dis-ordered mesoporous structure comprising mesopores and micropores,
wherein the size of micropores is in the range of 0.2 to 0.9 and the size of mesopores is
in the range of 4.3 to 6.6, and the mesopores have complex 3-dimensional shape and are
radially oriented.

10. The zeolite of claim 9, wherein;
acidity of the zeolite is in the range of 1.61 to 1.65 mmol g⁻¹;
surface area of the micropores and mesopores are in the range of 2 to 6 m² g⁻¹ and
89 to 93 m² g⁻¹; and
pore volume of micropore and meosopore in the range of 0.01 to 0.03 cm³ g⁻¹ and
0.19 to 0.24 cm³ g⁻¹.

11. The zeolite of claim 9, having a X-ray diffraction pattern with at least 3 of the
most intense peaks with intensity in % corresponding to 2θ values selected from 7.19°
(56%), 10.16° (61%), 12.43° (40%), 16.10° (81%), 21.68° (61%), and 23.99° (100%).

12. The zeolite of claim 9, wherein the zeolite is selective for 2 -tertiary-butylphenol
by at least 15%.

13 The zeolite of any one of claims 1-12, wherein life time of the zeolite as a
catalyst is at least 20h.

14. A method of preparing hierarchical MFI-type zeolite crystals, comprising:
providing a first solution comprising alumina and a second solution
comprising silica and an organosilane;

adding the first solution to the second solution to obtain a first product comprising constituents at a ratio of 0.8-1.2 Al_2O_3 : 10.2-10.4 Na_2O : 3.83-3.86 $(\text{TPA})_2\text{O}$; 34.4-34.8 TEOS: 2.1 to 2.5 organosilane: 6406.8 to 6407.2 H_2O ;

treating the first product hydrothermally to obtain a second product;

purifying and drying the obtained second product; and

calcining the second product at a temperature in the range of 540 – 560 °C in the presence of air for a time period in the range of 4h to 8h at a heating rate in the range of 0.8 to 1.2 °C min^{-1} to obtain MFI- type zeolite.

15. The method of claim 14, wherein the first solution is obtained by mixing NaOH, de-ionized water, tetra propyl ammonium bromide (TPABr) and sodium aluminate.

16. The method of claim 14, wherein the second solution is obtained by mixing the organosilane and Tetraethyl orthosilicate (TEOS).

17. The method of claim 14, wherein the organosilane is dimethyl octadecyl [3-(trimethoxysilyl) propyl] ammonium chloride) (DOAC).

18. The method of claim 14, wherein treating the first product hydrothermally comprises treating the product at a temperature in the range of 120 to 140 °C for at least 10 days.

19. A method of preparing hierarchical FAU-type or LTA-type zeolite crystals, comprising:

forming a first solution comprising colloidal silica and a second solution comprising aluminum;

mixing the second solution with first solution under constant stirring to obtain a third solution;

adding at least 1.0 g of organosilane to the third solution under stirring to obtain a first product comprising constituents at a ratio of 0.8-1.2 Al_2O_3 : 1-12 SiO_2 : 3.2-9.4 Na_2O : 0.10-0.38 organosilane: 138-422 H_2O ;

aging the first product for a first time period;

treating the first product hydrothermally to obtain a second product; and

purifying and drying the second product and calcining in air at a temperature in the range of 540 to 560 °C for a time period in the range of 4 to 6 h to obtain the zeolite.

20. The method of claim 19, wherein the organosilane is di-methyl octa decyl [3-(tri methoxysilyl) propyl] ammonium chloride) (DOAC).

21. The method of claim 19, wherein forming a first solution comprises adding colloidal silica to a solution of NaOH in H_2O .

22. The method of claim 19, wherein forming a second solution comprises adding $\text{Al}(\text{OH})_3$ or aluminum powder to a solution of NaOH in H_2O .

23. The method of claim 19, wherein the first product is hydrothermally treated at:
48 to 52 °C for 23 to 25 h followed by 95 to 105 °C for 23 to 25 h;
45 to 55°C for 23 to 25 h followed by 70 to 80 °C for 46 to 50h; or
45 to 55°C for 23 to 25h followed by 70 to 80°C for 10 to 14h.

24. The method of claims 19, wherein the first time period is at least 24 h.

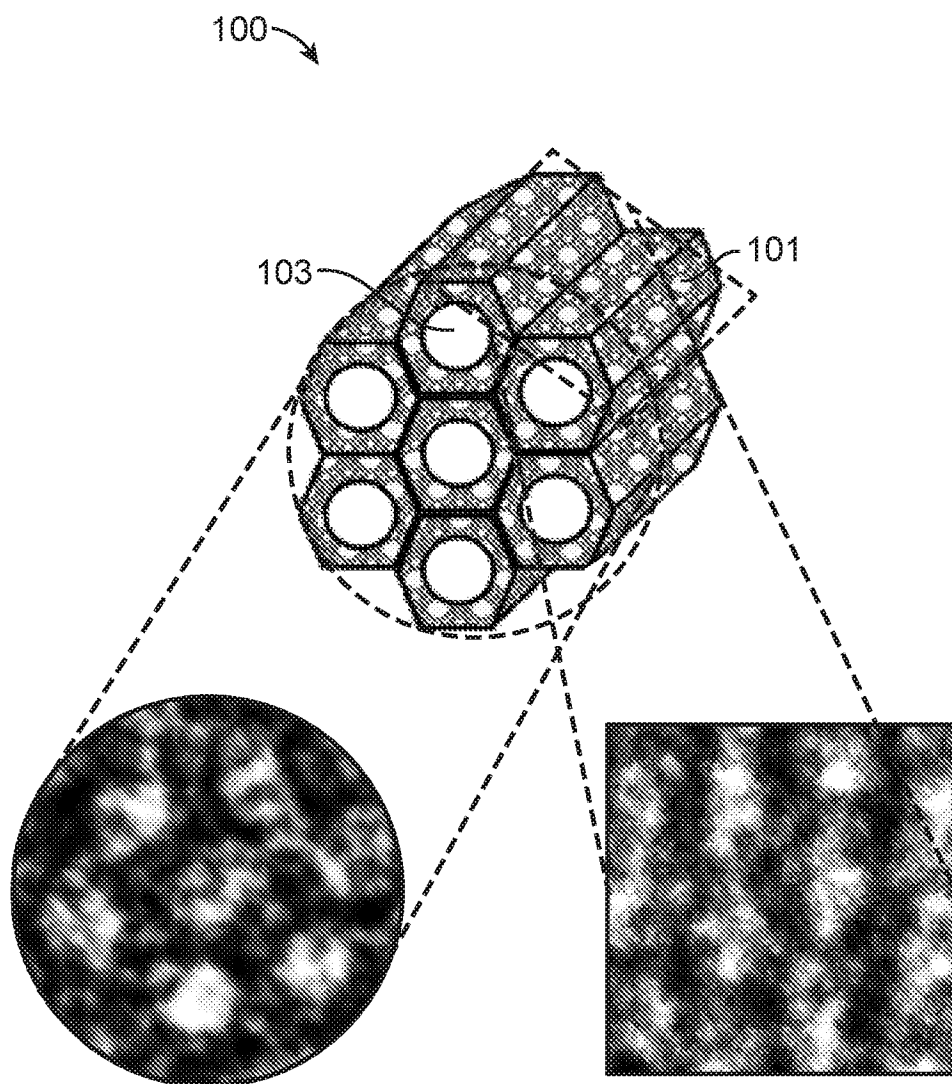


FIG. 1A

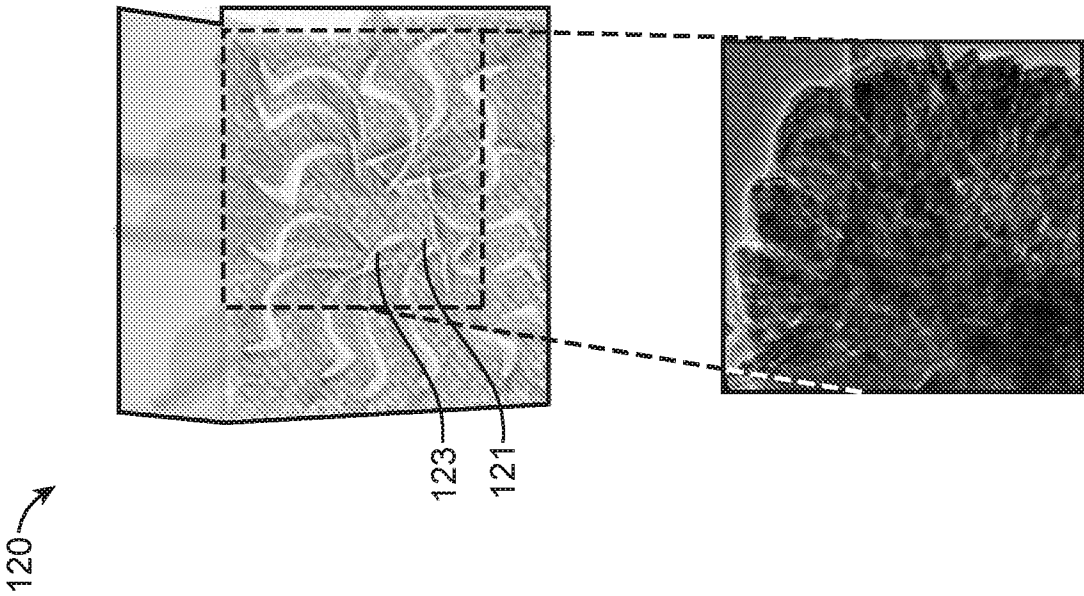


FIG. 1C

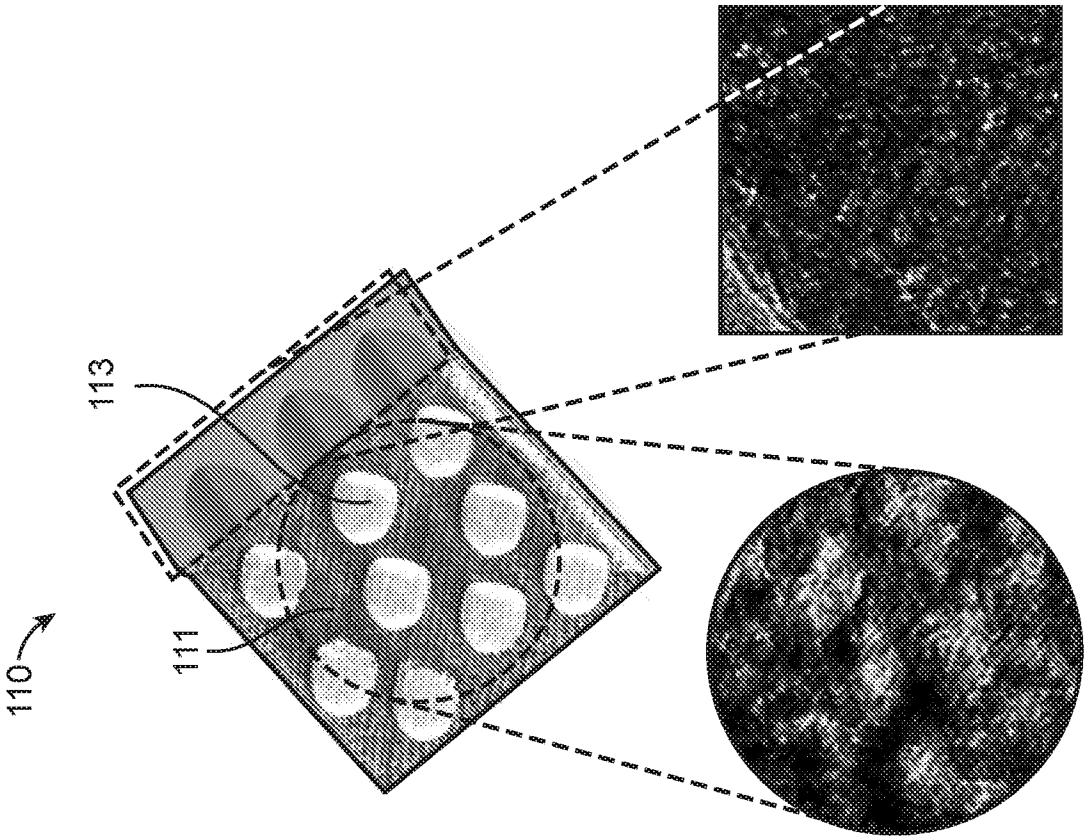


FIG. 1B

3 / 14

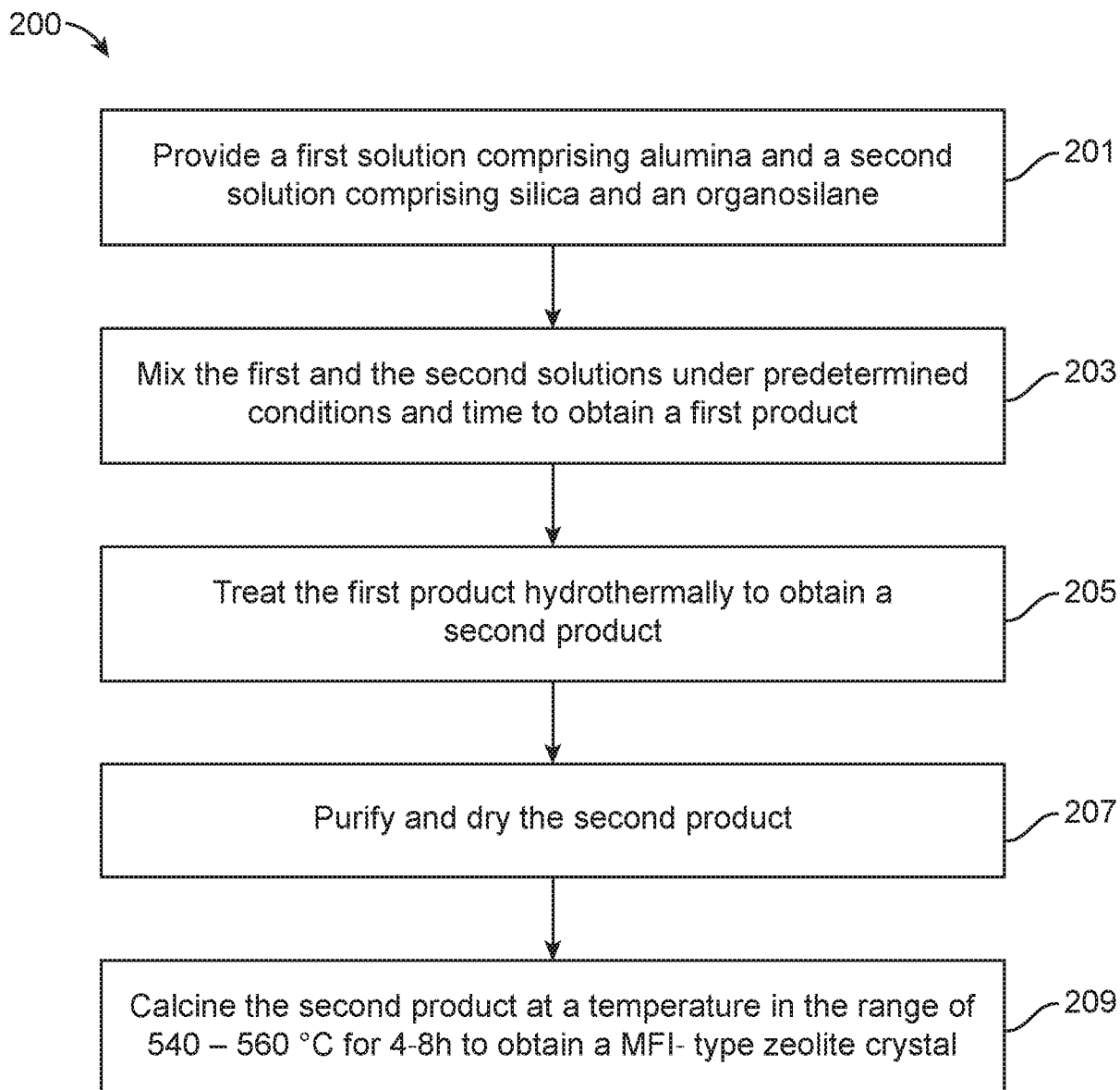


FIG. 2A

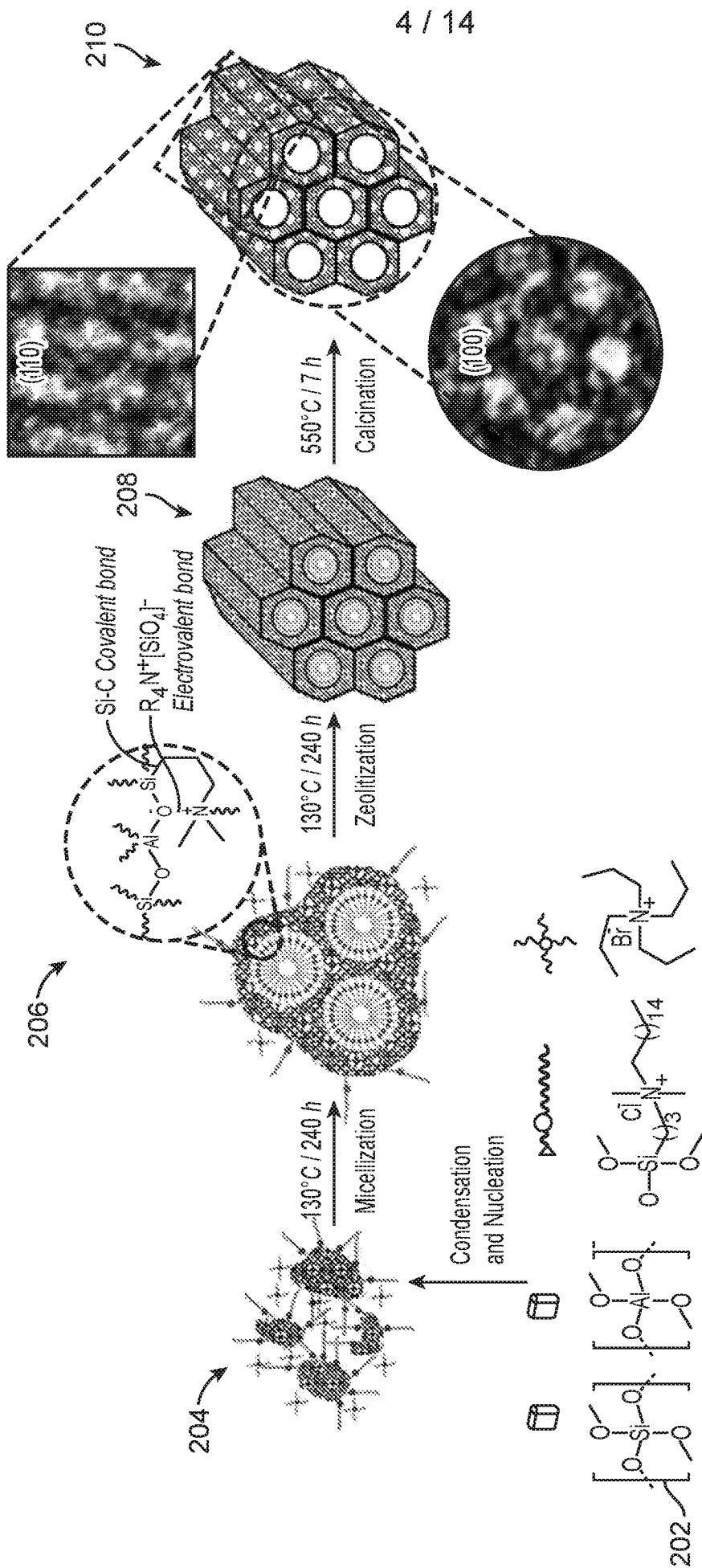


FIG. 2B

5 / 14

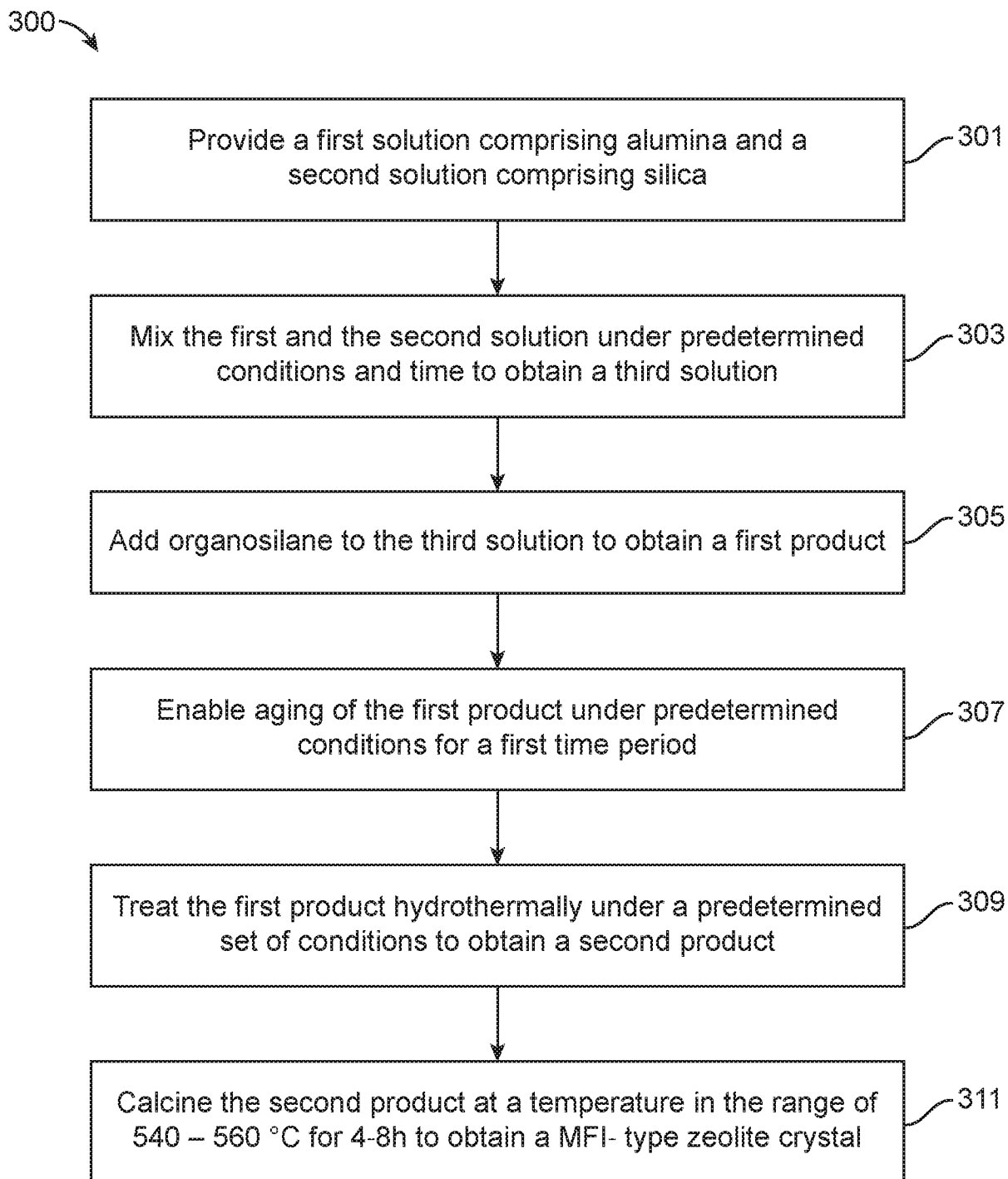


FIG. 3A

6 / 14

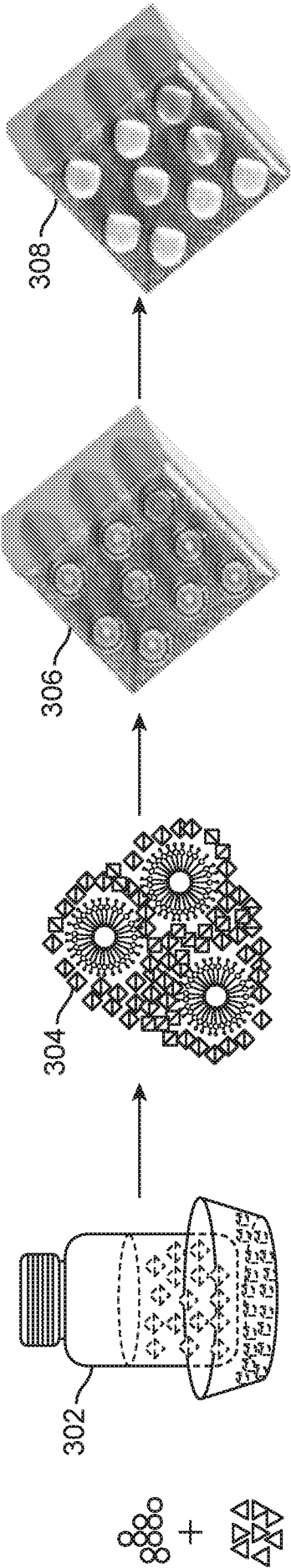


FIG. 3B

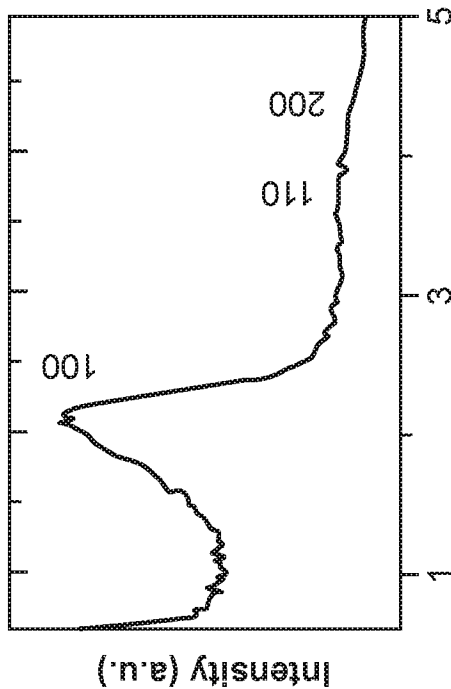


FIG. 4B

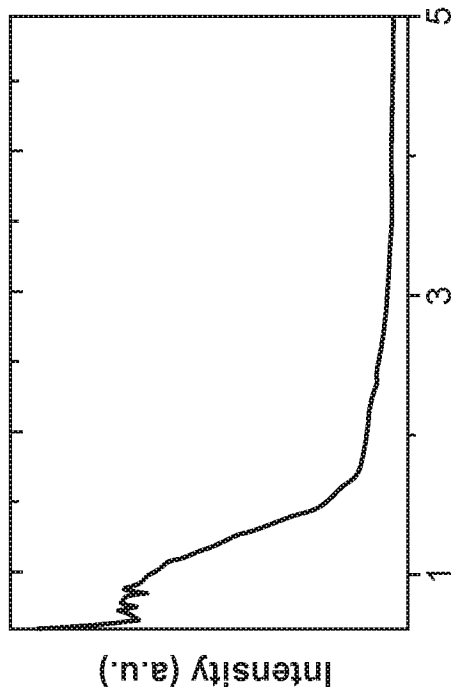


FIG. 4D

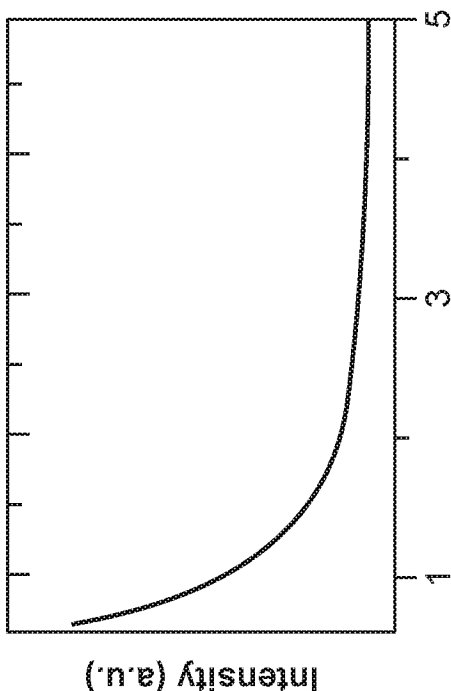


FIG. 4A

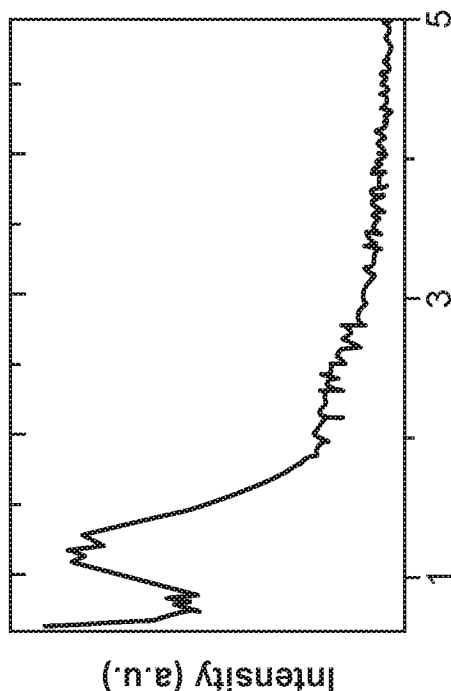


FIG. 4C

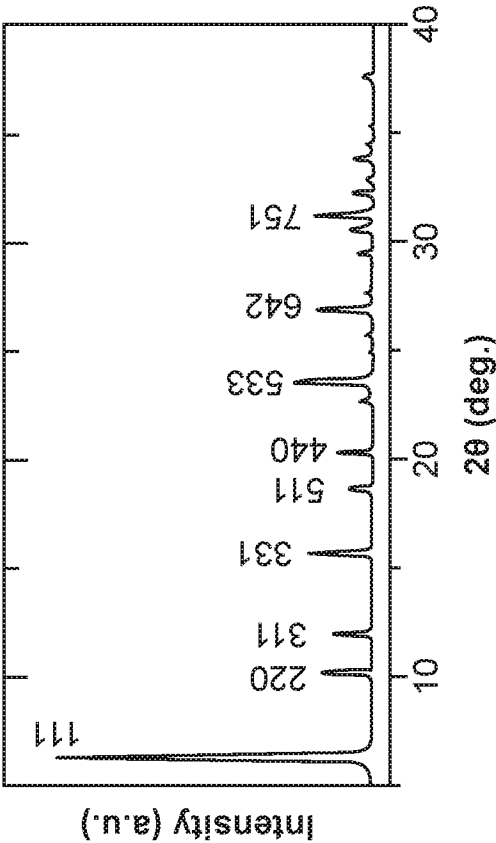


FIG. 5B

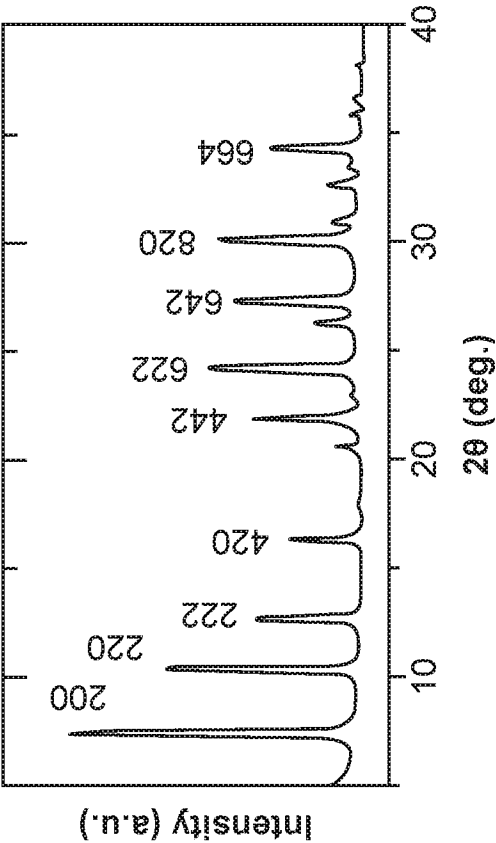


FIG. 5D

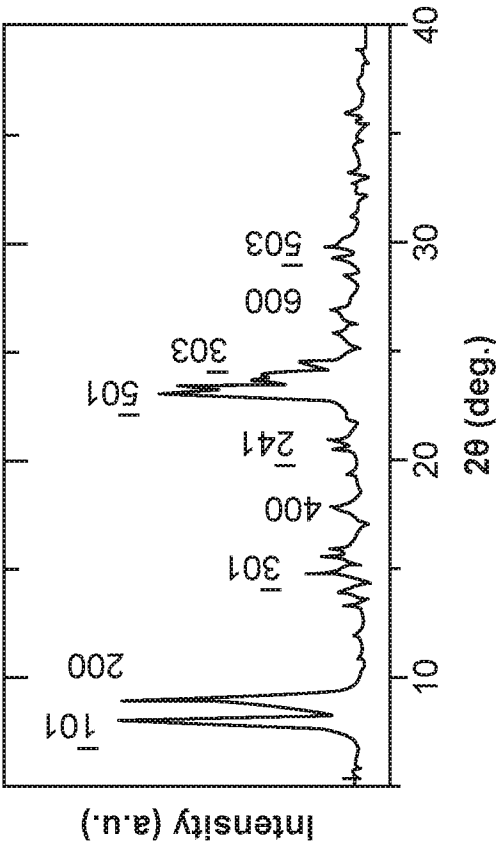


FIG. 5A

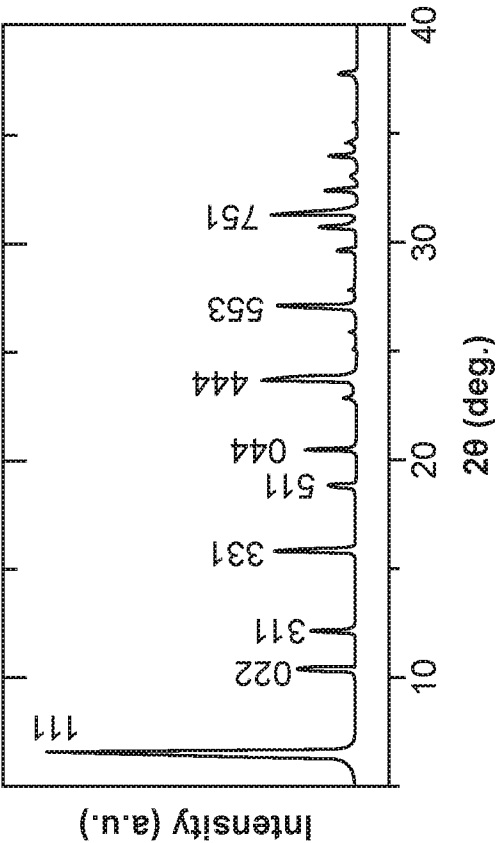


FIG. 5C

9 / 14

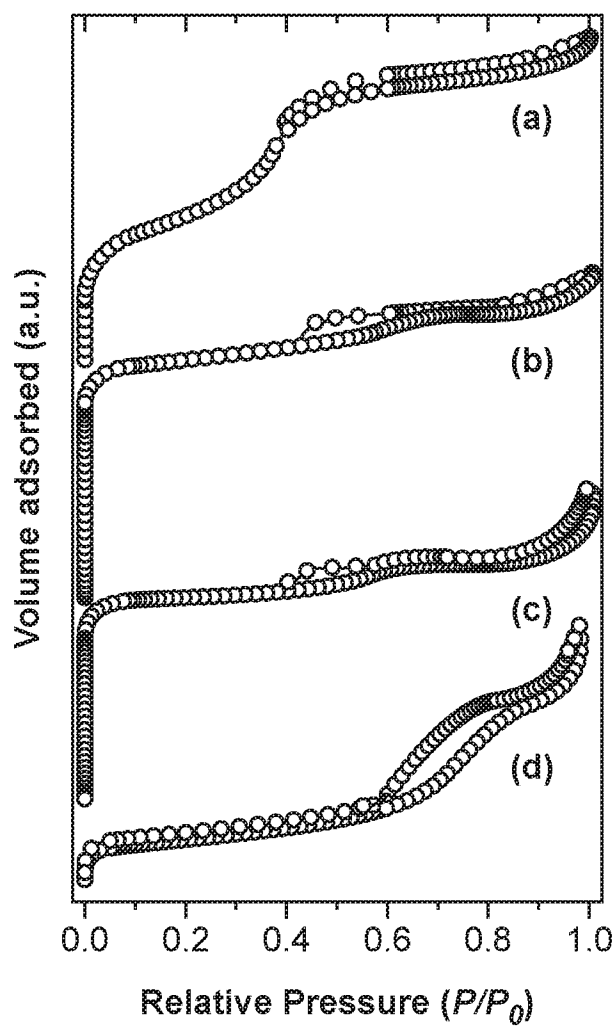


FIG. 6A

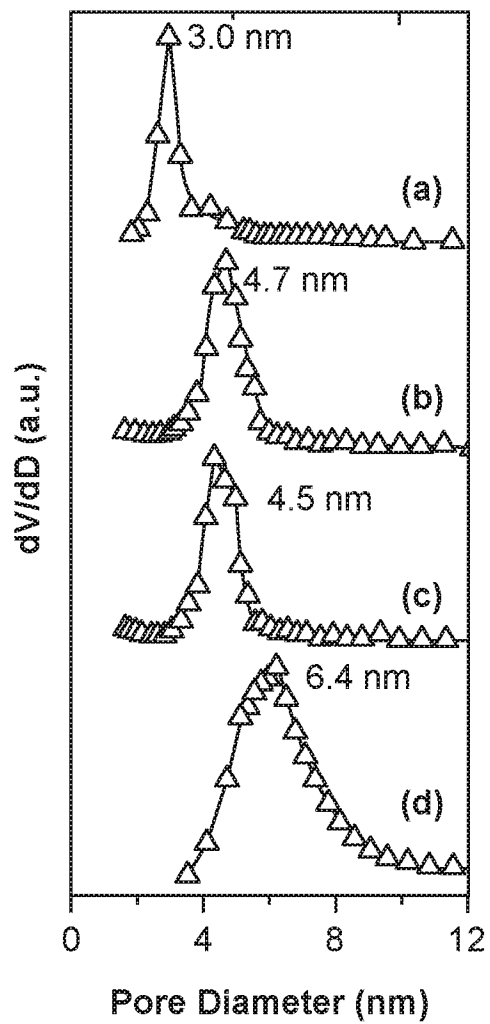


FIG. 6B

10 / 14

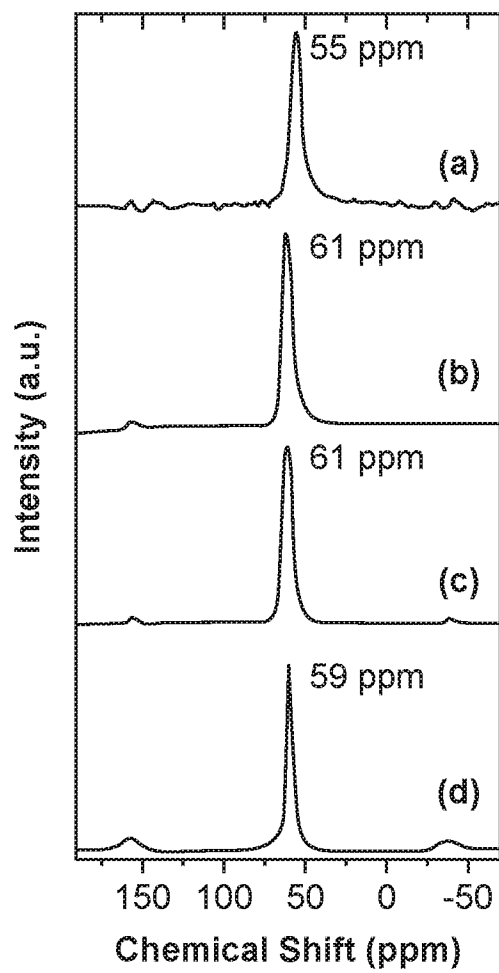


FIG. 7A

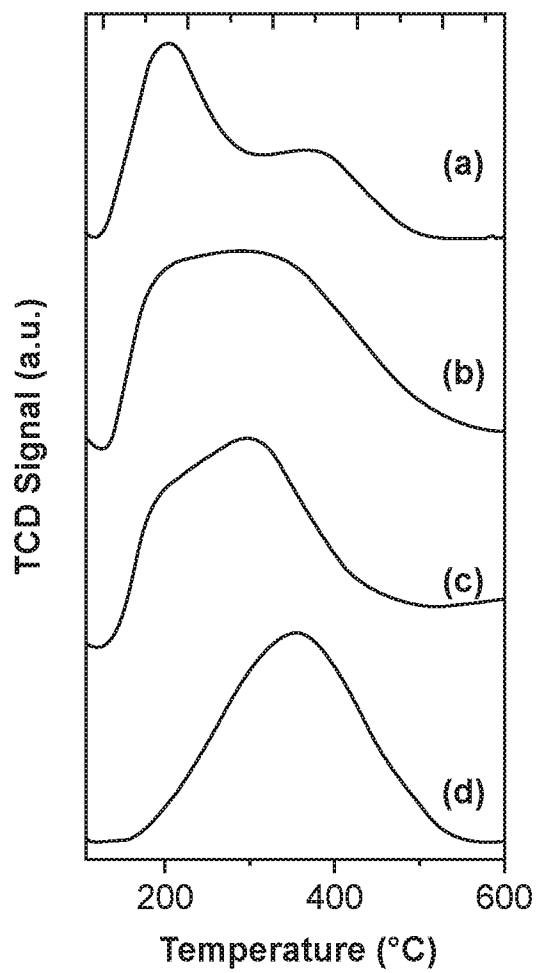


FIG. 7B

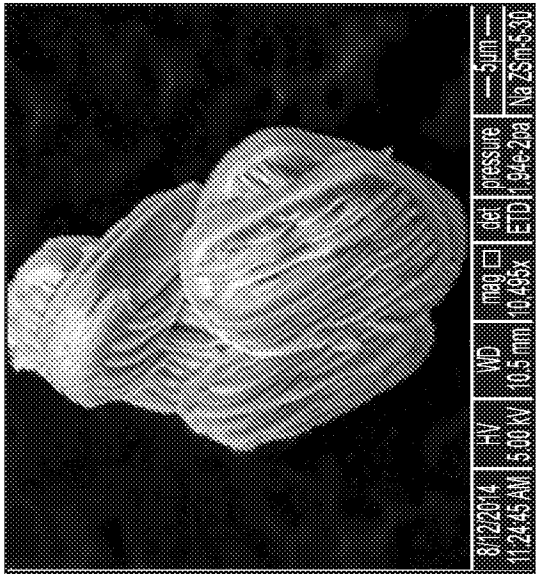


FIG. 8A

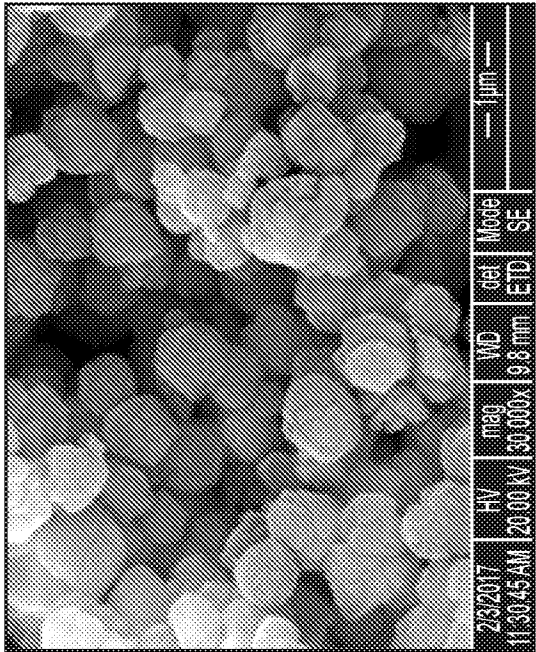


FIG. 8B

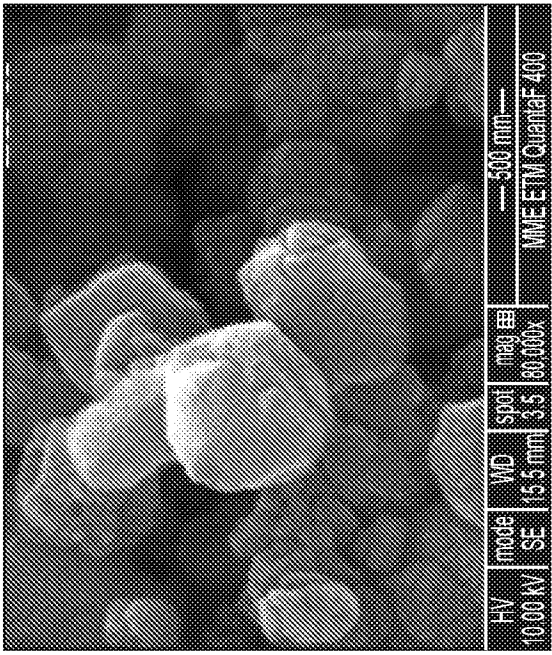


FIG. 8C

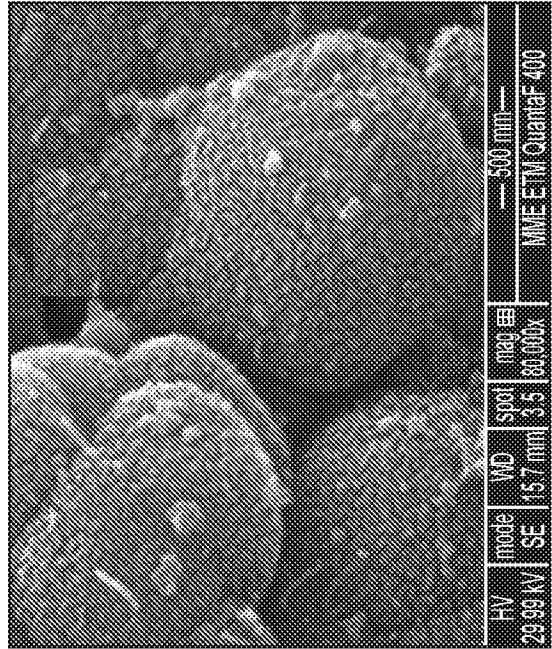


FIG. 8D

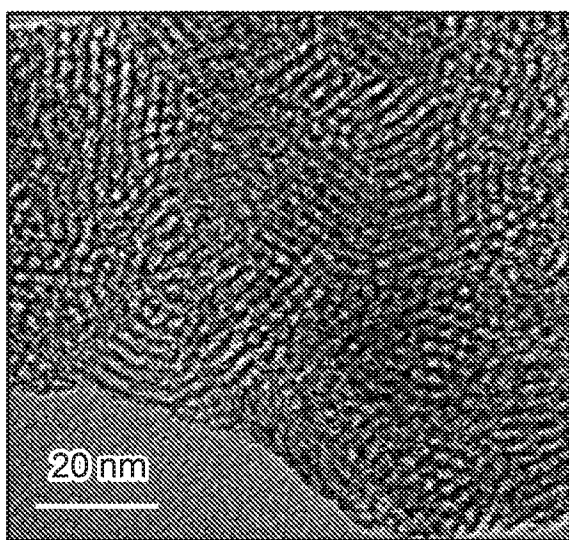


FIG. 9A

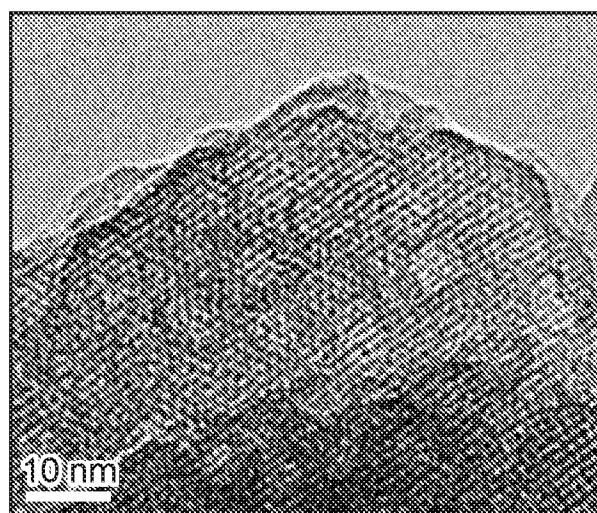


FIG. 9B

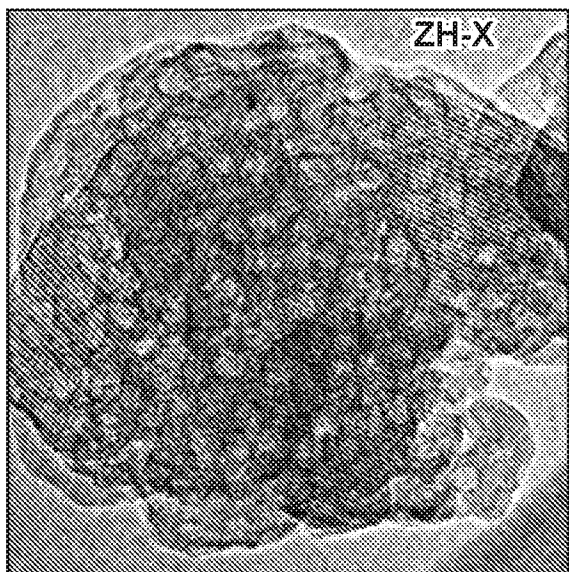


FIG. 9C

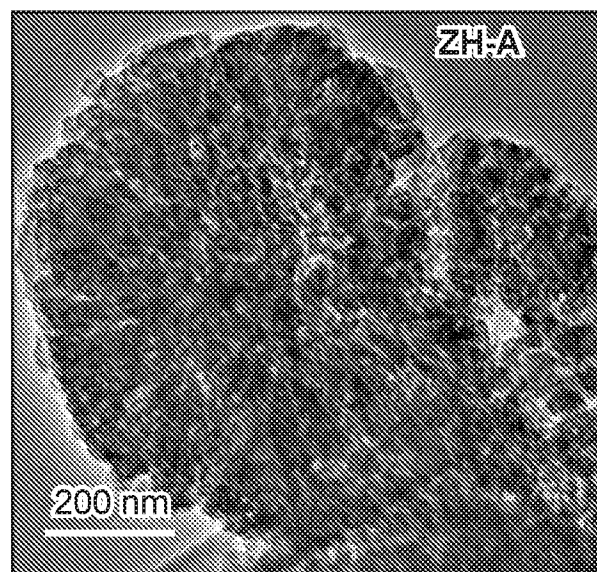


FIG. 9D

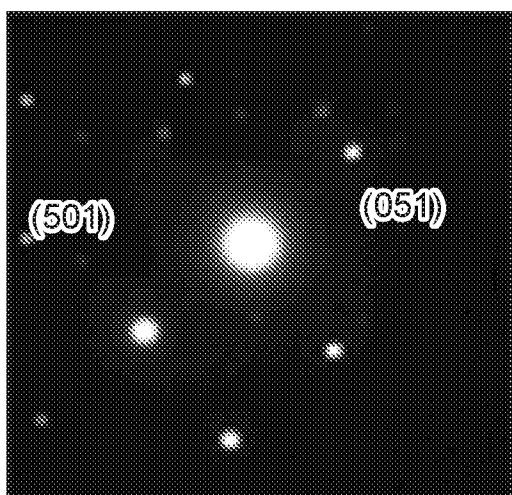


FIG. 10A

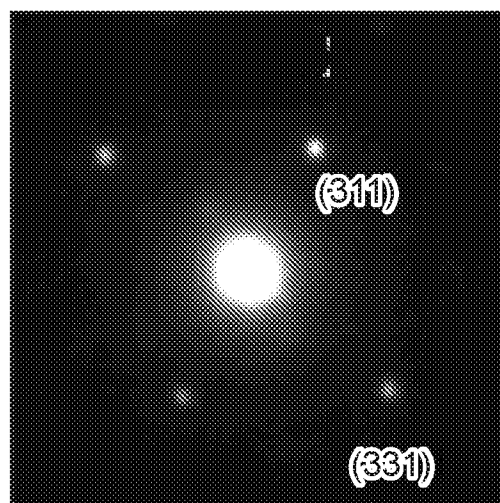


FIG. 10B

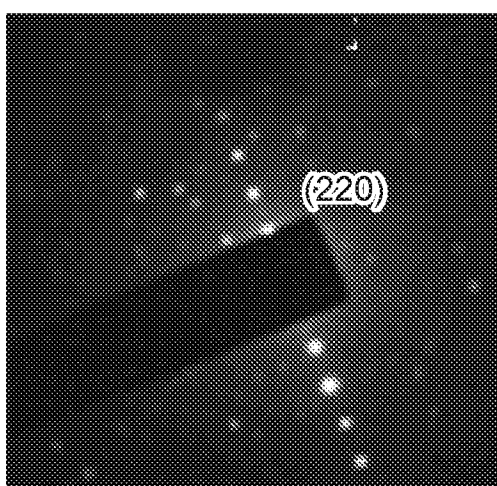


FIG. 10C

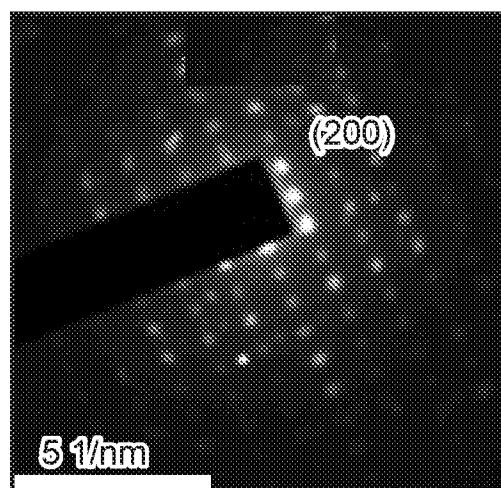


FIG. 10D

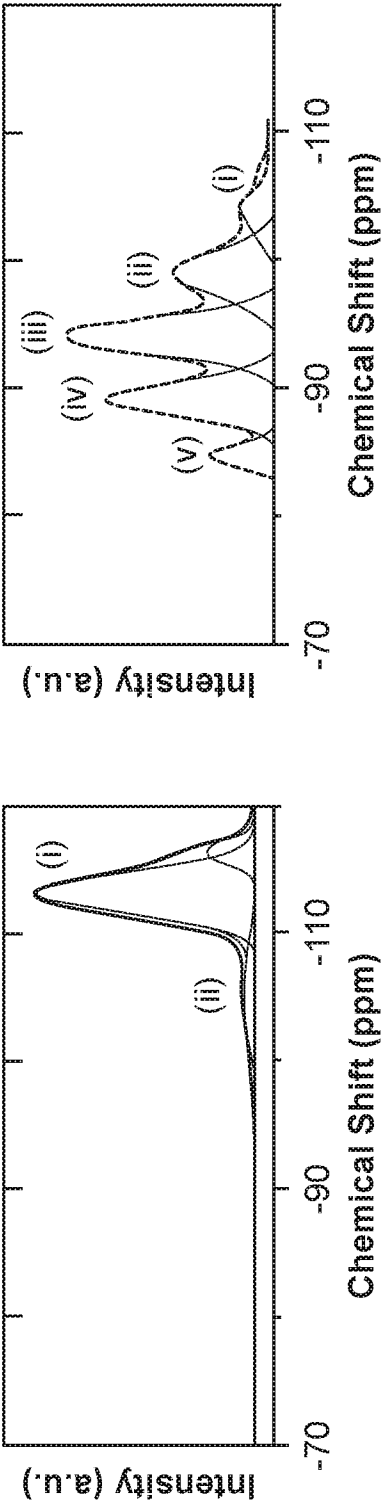


FIG. 11A

FIG. 11B

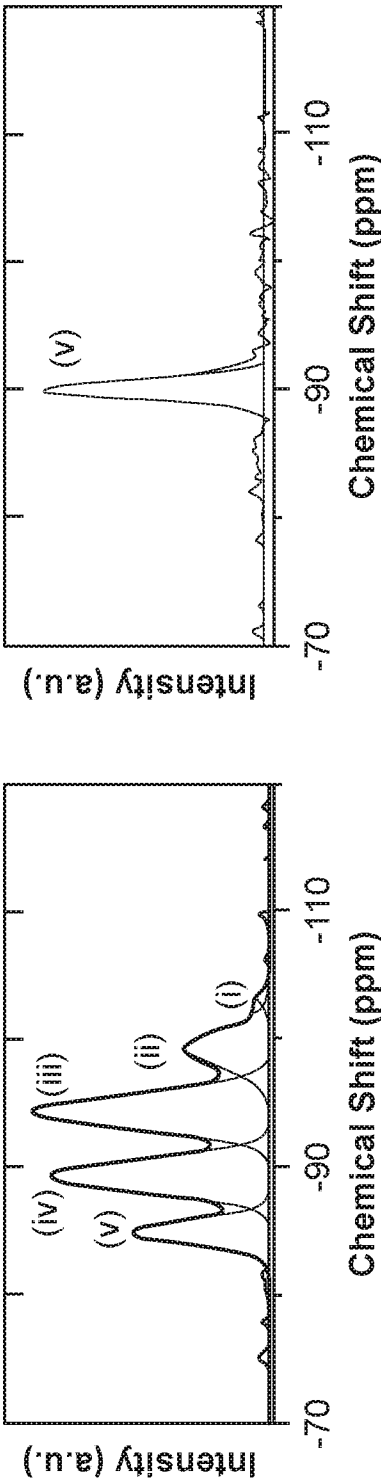


FIG. 11C

FIG. 11D

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2019/050202

A. CLASSIFICATION OF SUBJECT MATTER
C01B39/14, C01B39/22 Version=2019.01

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US2016137517 A1 (CECA SA [FR]) 19 May 2016 (19-05-2016) para[0028]- para[0031]	1-24
A	CN103979570 A (UNIV WUHAN TECH [CN]) 13 August 2014 (13-08-2014) abstract	1-24
A	US2016176720 A1 (CECA SA[FR]) 23 June 2016 (23-06-2016) para[0035]- para[0040]	1-24
A	Cho H S Et Al: 'Synthesis of ordered mesoporous MFI zeolite using CMK carbon templates', Microporous and Mesoporous Materials, 151, (2012), 107-112 whole document	1-24
A	Groen J C Et Al: 'Desilication: on the controlled generation of mesoporosity in MFI zeolites', J. Mater. Chem., 2006,16, 2121-2131 whole document	1-24

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

26-06-2019

Date of mailing of the international search report

26-06-2019

Name and mailing address of the ISA/

Indian Patent Office
Plot No.32, Sector 14, Dwarka, New Delhi-110075
Facsimile No.

Authorized officer

Parameswar Sau

Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2019/050202

Citation	Pub.Date	Family	Pub.Date
US 2016137517 A1	19-05-2016	WO 2015019013 A2	12-02-2015
		KR 20160003076 A	08-01-2016
		EP 3030521 A2	15-06-2016
		JP 2016522156 A	28-07-2016
US 2016176720 A1	23-06-2016	WO 2015028740 A1	05-03-2015
		KR 20160005054 A	13-01-2016
		CN 105431380 A	23-03-2016
		EP 3041793 A1	13-07-2016