(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 September 2017 (21.09.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/160965 A1

(51) International Patent Classification:
B01J 31/06 (2006.01) *B01J 23/00* (2006.01)
B01J 21/10 (2006.01) *B01J 37/08* (2006.01)

(21) International Application Number:
PCT/US2017/022485

(22) International Filing Date:
15 March 2017 (15.03.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/309,645 17 March 2016 (17.03.2016) US

(71) Applicants: **SAUDI ARABIAN OIL COMPANY** [SA/SA]; Post Office Box 5000, Dhahran, 31311 (SA). **DURHAM UNIVERSITY** [GB/GB]; South Road, Durham DH1 3LE (GB).

(71) Applicant *(for AG only)*: **ARAMCO SERVICES COMPANY** [US/US]; 9009 West Loop South, Houston, Texas 77096 (US).

(72) Inventors: **VEERABHADRAPPA, Manohara Gudiyor**; c/o Durham University, South Road, Durham DH1 3LE (GB). **GREENWELL, Hugh Christopher**; c/o Durham University, South Road, Durham DH1 3LE (GB). **ALABEDI, Gasan Selman**; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA). **HALL, John Adrian**; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA). **AL-SHAHRANI, Abdullah A.**; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA). **WHITING, Andrew**; c/o Durham University, South Road, Durham DH1 3LE (GB).

(74) Agents: **MEYER, Christopher I.** et al.; Dinsmore & Shohl LLP, One South Main Street, Fifth Third Center, Suite 1300, Dayton, Ohio 45402 (US).

(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, 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,

[Continued on next page]

(54) Title: HIGH ASPECT RATIO LAYERED DOUBLE HYDROXIDE MATERIALS AND METHODS FOR PREPARATION THEREOF

(57) Abstract: Method of producing adamantane-intercalated LDH particles (i) [preferably Ad-COOH; Mg/Al-LDH] comprising adding to an aqueous solution a first precursor, Al(OH)3, and a second precursor, a hydroxide M(OH)2 or an oxide MO [preferably M= Mg, Ca, Co, Ni, Cu, Zn], to form an initial mixture, the initial mixture having an M/ Al molar ratio of from 1 to 5, adding to the initial mixture an amount of adamantane [preferably Ad-COOH] to form a reaction mixture having an Al/adamantane molar ratio of from 0.5 to 2, and heating the reaction mixture to produce (i), having an aspect ratio, i.e. width/thickness of particles, of greater than 100.

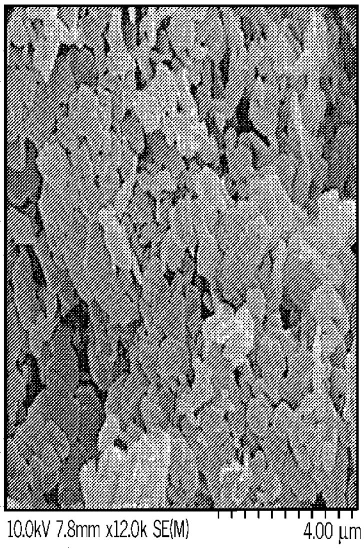

FIG. 2A

TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(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:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

HIGH ASPECT RATIO LAYERED DOUBLE HYDROXIDE MATERIALS AND METHODS FOR PREPARATION THEREOF

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims benefit to U.S. Provisional Application 62/309,645 filed March 17, 2016, which is incorporated by reference in its entirety.

BACKGROUND

Field

[0002] Embodiments of the present disclosure generally relate to layered double hydroxide materials, and specifically relate to high aspect ratio layered double hydroxide materials and methods for preparation.

Technical Background

[0003] The synthesis of supported metal or metal-oxide catalysts is of great industrial importance in heterogeneous catalysis. High activity, high selectivity, and long catalyst life are desirable characteristics of any industrial catalyst. Catalyst materials may be produced from layered double hydroxides (LDHs). LDHs, which are also known as anionic clays, are inverse charge analogues of the widely used aluminosilicate cationic clays in their structure and properties. Though a number of methods exist to prepare metal oxide particles in general, oxides obtained by decomposing LDHs have several advantages compared to oxide particles obtained by synthetic methods such as wet impregnation/solid state preparation. Specifically, LDHs may provide a simple, cost effective and environmentally suitable way to achieve a homogeneous distribution of metal ions at the atomic level. In order to make use of LDH layers for various applications, one needs to be able to exfoliate or delaminate these layers. Since carbonate LDHs are thermodynamically more stable, it is difficult to exchange it for other ions or to exfoliate LDH layers where carbonate is the charge balancing ion. As a result, these materials have limited usage. There have been attempts to prepare high aspect ratio non-carbonated LDHs starting from carbonate LDH; however, this approach has multiple steps and is cumbersome.

SUMMARY

[0004] In accordance with the background previously presented, ongoing needs exist for LDH materials having high aspect ratios.

[0005] Embodiments of the present disclosure are directed to LDHs produced with the high symmetry adamantane ion, which mediates the growth of high aspect ratio platelets. Moreover, due to its organophilic nature, adamantane can be exfoliated in organic solvents. Thus, these LDH layers can be used in various applications as previously mentioned. The embodiments of the present disclosure are directed to high aspect ratio non-carbonated LDHs, which use just one equivalent of anion salt. Moreover, these LDHs provide process improvements in that they enable "one pot" synthesis, and less washing (including no washing) at the end of the reaction due to the use of metal hydroxides as starting materials and just one equivalent of anion. The materials formed also have desirable properties once calcined.

[0006] According to one embodiment, a method for preparing adamantane-intercalated layered double-hydroxide (LDH) particles is provided. The method comprises adding to an aqueous solution a first precursor and a second precursor to form an initial mixture, where the first precursor is $Al(OH)_3$ or Al_2O_3, and the second precursor is a hydroxide $M(OH)_2$ or an oxide MO, where M is a metal of oxidation state +2. The initial mixture has a M/Al molar ratio of from 1 to 5 or a solid loading of less than 10 weight % solids, based on a total weight of the initial mixture. The method further comprises adding to the initial mixture an amount of adamantane to form a reaction mixture having an Al/adamantane molar ratio of from 0.5 to 2, and heating the reaction mixture to produce the adamantane-intercalated LDH particles, where the adamantane-intercalated LDH particles have aspect ratios greater than 100. The aspect ratio is defined by the width of adamantane-intercalated LDH particles divided by the thickness of the adamantane-intercalated LDH particles.

[0007] According to another embodiment, an adamantane-intercalated layered double-hydroxide (LDH) material in the form of adamantane-intercalated LDH particles is provided. The adamantane-intercalated LDH particles comprise a general formula defined by $[M_{1-x}Al_x(OH)_2](A)_x{\cdot}mH_2O$, where x is from 0.14 to 0.33, m is from 0.33 to 0.50, M is chosen from Mg, Ca, Co, Ni, Cu, or Zn, and A is adamantane carboxylate. The adamantane-intercalated LDH particles further comprise an aspect ratio greater than 100. The aspect ratio is defined by the width of an adamantane-intercalated LDH particle divided by the thickness of the adamantane-intercalated LDH particle.

[0008] Additional features and advantages of the described embodiments will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the described embodiments, including the detailed description which follows, the claims, as well as the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1A is a Scanning Electron Microscopy (SEM) image of an Mg/Al-CO_3 LDH produced via anion exchange;

[0010] FIG. 1B is an SEM image of an Mg/Al-CO_3 LDH produced via co-precipitation;

[0011] FIGS. 2A and 2B are SEM images of different magnifications of an Mg/Al-adamantoate LDH produced in accordance with one or more embodiments of the present disclosure;

[0012] FIG. 3 is a Powder X-Ray Diffraction (PXRD) graph of a Mg/Al-adamantoate LDH in accordance with one or more embodiments of the present disclosure;

[0013] FIG. 4 is an Infrared (IR) Spectroscopy graph of a Mg/Al-adamantoate LDH in accordance with one or more embodiments of the present disclosure;

[0014] FIG. 5 is a graph of the ^1H solid-state Nuclear Magnetic Resonance (NMR) spectra of a Mg/Al-adamantoate LDH in accordance with one or more embodiments of the present disclosure; and

[0015] FIG. 6 is a graph of the ^{13}C solid-state NMR spectra of a Mg/Al-adamantoate LDH in accordance with one or more embodiments of the present disclosure.

DETAILED DESCRIPTION

[0016] The dispersion of active reduced metal or metal-oxide particles on a stable support is a complex and laborious process. To achieve this, one needs to consider various parameters such as the synthesis conditions, nature of the support and appropriate ways of dispersing/distributing active catalyst on the support. Among the metal/metal oxide supported catalysts, the $Cu/ZnO/Al_2O_3$ system and metal/metal oxide (Pt, Pd, Rh and Au) systems supported on various supports (alumina, silica, and carbon) have great industrial importance. These catalytic systems are known to have potential for catalyzing industrially important reactions such as synthesis of methanol, water gas shift reaction, desulfurization of petrochemical streams, photochemical/electrochemical splitting of water, and photochemical/electrochemical reduction of carbon dioxide into useful chemicals, for example.

[0017] Reference will now be made in detail to embodiments of adamantane-intercalated layered double-hydroxide (LDH) particles with high aspect ratios and the methods of producing them. Specifically, the adamantane-intercalated LDH particles have aspect ratios greater than 100. As defined, the aspect ratio is defined by the width of the LDH particle divided by the thickness of the LDH particle. As defined, an aspect ratio below 10 is considered low, an aspect ratio less than 100 is considered medium, and an aspect ratio of 100 or greater is considered a high aspect ratio. The LDH particles may be calculated from the SEM images. For example, referring to the embodiment of FIG. 2B, it is clear that the layered particles have large surface area, but lack thickness, thereby resulting in a high aspect ratio. Additionally, Atomic Force Microscopy (AFM) may be utilized to measure the width and thickness of the LDH particles and determine an aspect ratio.

[0018] Methods for preparing adamantane-intercalated LDH particles may include the step of adding to an aqueous solution a first precursor and a second precursor to form an initial mixture. In one embodiment, the aqueous solution may consist essentially of water. The first precursor may comprise $Al(OH)_3$ or Al_2O_3. The second precursor may include a metal containing compound, for example, a hydroxide $M(OH)_2$ or an oxide MO, where M is a metal of oxidation state of +2. While various other metals are also contemplated, the M may be chosen from Mg, Ca, Co, Ni, Cu, Zn, or combinations thereof. In one or more embodiments, the second precursor may include $Mg(OH)_2$, $Ca(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, or combinations thereof. In further embodiments, the second precursor is $Mg(OH)_2$ or MgO. In one example, the second precursor is $Mg(OH)_2$ and the first precursor is $Al(OH)_3$.

[0019] Moreover, in further embodiments, the initial mixture may have a M/Al molar ratio of 1 to 5, or 1 to 3. Furthermore, the initial mixture may have a solid loading of less than 10 weight % solids, based on a total weight of the initial mixture, or a solids loading or less than 5 weight % solids.

[0020] Subsequently, the method includes adding to the initial mixture an amount of adamantane to form a reaction mixture having an Al/adamantane molar ratio of from 0.5 to 2. In one or more additional embodiments, the Al/adamantane molar ratio may be from 0.8 to 1.2, or may be 1 to 1. Various adamantane sources are contemplated. In one embodiment, the adamantane may be added in the form of a carboxylic acid. Optionally, the reaction may be stirred.

[0021] Generally, LDHs for conversion to mixed metal oxide catalysts are prepared with inorganic guest anions, which may be easily removed under thermal treatment. When using an organic anion, such as carboxylic acid functionalized adamantane, improved properties for LDHs may be achieved. Adamantane has a structure characterized by high symmetry (T_d), is free from intra-molecular strain and, as a result, is extremely thermodynamically stable. At the same time, adamantane can be chemically functionalized. Adamantane has a melting point of 270 °C and it slowly sublimes even at room temperature. Adamantane is poorly soluble in water, but readily soluble in hydrocarbons.

[0022] Without being bound by theory, the use of thermally stable adamantane is as a structure directing agent, which allows for preferential growth of the LDH in the *a* and *b* crystallographic directions over the *c* crystallographic axes. This results in the high aspect ratio particles observed. Moreover, the use of hydrothermal synthesis and metal hydroxide precursors carefully controls the growth conditions in terms of pH and kinetics.

[0023] Next, the method includes heating the reaction mixture to produce the adamantane-intercalated LDH particles, where the adamantane-intercalated LDH particles have aspect ratios greater than 100. As defined, the adamantane-intercalated LDH particles means the adamantane is inserted into the LDH particle matrix. In further embodiments, the aspect ratio of the adamantane-intercalated LDH particles is greater than 125, or greater than 150, or greater than 200. Moreover, the adamantane-intercalated LDH particles have a particle diameter of 2 to 12 μm, or from 5 to 10 μm. The heating step may occur at a reaction temperature from 110 °C to 180 °C for a reaction time of 12 hours to 48 hours, or from 130 °C to 170 °C for a reaction time of 20 hours to 30 hours.

[0024] The largest group of the LDH family of materials includes positively charged metal hydroxide layers having the composition $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$ or $[M^{I}_{x}M^{III}_{1-x}(OH)_2]^{x+}$ (M^{I} = Li; M^{II} = Mg, Ca, Co, Ni, Zn; M^{III} = Al, Cr, Fe; $0.14 \leq x \leq 0.33$). The positive charge on the layers is balanced by anions present in the interlayer. The anions give rise to the name anionic clays. One group of anionic clays includes materials having a general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ or $[M^{I}_{x}M^{III}_{1-x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$ ($m = 0.33–0.50$), where A is an anion such as nitrate or halogen.

[0025] The adamantane-intercalated LDH particle may have a general formula $[M_{1-x}Al_x(OH)_2](A)_x\cdot mH_2O$, where x is from 0.14 to 0.33, m is from 0.33 to 0.50, M is chosen from Mg, Ca, Co, Ni, Cu, or Zn and A is adamantane carboxylate.

[0026] LDHs with high aspect ratios play a role in the development of oxygen barriers in packaging, as fillers in nanocomposite materials, and as flame-retardants, amongst others. For all these applications, high aspect ratio platelets that can be readily dispersed in a polymer matrix are desirable, but not easily attainable. Anion (charge and symmetry of the anion) plays a crucial role in nucleation and growth of LDH crystals. The carbonate ion, which is ubiquitous in nature, has D_3h symmetry matching well with interlayer symmetry of the LDH and also it has higher charge density compared to other anions. As a result, LDHs prefer carbonate ions over other ions and this mediates the ordered stacking of layers. The SEMs of FIGS 1A and 1B shown Mg/Al-carbonate LDHs produced via anion exchange and co-precipitation respectively.

[0027] In contrast to the present embodiments, LDHs are conventionally prepared by a co-precipitation technique, in which a homogeneous mixed solution of metal salts is added to another solution containing sodium hydroxide and an excess of the guest anion to be incorporated. LDHs obtained from this method always show crystallites with submicron size due to rapid multiple nucleation and crystallization events. Co-precipitated crystals may have aspect ratios of approximately 1-10 or less. This indicates that the crystals have narrow breadth and grow preferentially along the *c* axis. This is a reflection of the high supersaturation of both anion and cation and the rapid nucleation of many crystals in the mixed zone in the reactor.

[0028] For illustration, SEM images of Mg/Al-CO_3 LDH samples prepared by co-precipitation and anion exchange method are provided in FIGS. 1A and 1B. As shown, these particles are irregular thick agglomerates. As a result of this thickness, the aspect ratio is low for the Mg/Al-CO_3 LDH samples. In contrast, the SEM micrographs of Mg/Al-adamantoate LDH produced as shown in FIGS. 2A and 2B depict sheet like layers having much less thickness than the Mg/Al-CO_3. In light of these low thicknesses, these Mg/Al-adamantoate LDH particles have a high aspect ratio.

EXAMPLES

[0029] The described embodiments will be further clarified by the following example.

Example 1

Preparation of Layered Double Hydroxide

[0030] In one typical preparation, a 5 weight % solution of $Mg(OH)_2$ was prepared by dissolving 5 grams (g) of $Mg(OH)_2$ in 95 g of de-ionized water. To this 3.36 g of $Al(OH)_3$ was added to give a Mg/Al molar ratio of 2. Then, 9.31 g of adamantane carboxylic acid was added to the same solution (Al/adamantane molar ratio = 1) and the resultant reaction mixture was stirred vigorously for 1 hour at room temperature. After this, the solution was transferred to a Teflon lined autoclave and heated at 150 °C for 24 hours (h). The pH of the initial reaction mixture and final filtrate was measure and was found to be 9.5 and 8.6 respectively. In another set of experiments, the above procedure was repeated by taking Mg/Al molar ratio of 5. After the reaction was over, the products were washed thoroughly with water and dried at 65 °C.

[0031] For comparison, an Mg/Al-NO_3 LDH (Mg/Al molar ratio= 2) was synthesized by a more conventional ammonia precipitation method starting from metal nitrates.

[0032] The PXRD pattern of the as-synthesized LDH is given in FIG. 3, and shows that the basal reflection (*001*) at 20.84 Å corresponds to a bilayer arrangement of adamantane ions in the interlayer. The submultiples of (*001*) are seen at higher 2θ values. Intercalation of adamantoic acid was further characterized with IR spectra as shown in FIG. 4. The vibrations at 1517 cm^{-1} and 1395 cm^{-1} correspond to anti-symmetric and symmetric stretching vibrations of the COO^- group. The vibrations at 2901 cm^{-1} and 2847 cm^{-1} are for the C-H vibrations. The 4302 cm^{-1} vibration is due to hydrogen bonding of layer metal hydroxide groups with intercalated water molecules in the interlayer.

[0033] The ^1H and ^{13}C solid-state NMR spectra of Mg/Al-adamantoate LDH were recorded and are given in FIGS. 5 and 6, respectively. The 4 sharp peaks in the ^1H spectra of FIG. 5 at lower ppm values are due to the hydrogens present in the adamantane ring. The peaks at 3.8 ppm and 4.8 ppm are due to the hydrogens of the intercalated water and metal hydroxide respectively. Referring to FIG. 6, the ^{13}C NMR spectra of Mg/Al-adamantoate shows 4 peaks at 29.5 ppm, 37.3 ppm, 40.6 ppm and 42.8 ppm, which are due to 4 different carbons present in the adamantane molecule. The peak at 186.98 ppm is due to the carbon of the carboxylate group. Scanning Electron Microscope (SEM) images of as-synthesized LDH show platelet morphology typical of layered materials (FIGS. 2A and 2B).

[0034] It will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments described herein without departing from the spirit and scope of the claimed subject matter. Thus it is intended that the specification cover the modifications and variations of the various embodiments described herein, provided such modification and variations come within the scope of the appended claims and their equivalents.

CLAIMS

1. A method for preparing adamantane-intercalated layered double-hydroxide (LDH) particles, the method comprising:

adding to an aqueous solution a first precursor and a second precursor to form an initial mixture, where:

the first precursor is $Al(OH)_3$ or Al_2O_3;

the second precursor is a hydroxide $M(OH)_2$ or an oxide MO, where M is a metal of oxidation state +2; and

the initial mixture has a M/Al molar ratio from 1 to 5;

the initial mixture has a solid loading of less than 10 weight % solids, based on a total weight of the initial solution;

adding to the initial mixture an amount of adamantane to form a reaction mixture having an Al/adamantane molar ratio from 0.5 to 2; and

heating the reaction mixture to produce the adamantane-intercalated LDH particles, where the adamantane-intercalated LDH particles have an aspect ratio greater than 100, the aspect ratio defined by a width of an adamantane-intercalated LDH particle divided by a thickness of the adamantane-intercalated LDH particle.

2. The method of claim 1 further comprising stirring the reaction mixture.

3. The method of claim 1 where the adamantane is added as a carboxylic acid.

4. The method of claim 1 where the heating step occurs at a reaction temperature from 110 °C to 180 °C for a reaction time of 12 hours to 48 hours.

5. The method of claim 1 where M is chosen from Mg, Ca, Co, Ni, Cu, or Zn.

6. The method of claim 1 where the second precursor is $Mg(OH)_2$, $Ca(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Cu(OH)_2$, or $Zn(OH)_2$.

7. The method of claim 1 where the second precursor is $Mg(OH)_2$ or MgO.

8. The method of claim 1 where the second precursor is $Mg(OH)_2$ and the first precursor is $Al(OH)_3$.

9. The method of claim 1 where the Al/adamantane molar ratio is from 0.8 to 1.2.

10. The method of claim 1 where the adamantane-intercalated LDH particles have a general formula $[M_{1-x}Al_x(OH)_2](A)_x \cdot mH_2O$, where x is from 0.14 to 0.33, m is from 0.33 to 0.50, M is chosen from Mg, Ca, Co, Ni, Cu, or Zn, and A is adamantane carboxylate.

11. The method of claim 1 where M is Mg.

12. The method of claim 1 where the initial mixture has less than 5 weight % solids, based on the total weight of the initial mixture.

13. The method of claim 1 where the aspect ratio is greater than 125.

14. The method of claim 1 where the adamantane-intercalated LDH particle have a particle diameter of 5 to 10 μm.

15. An adamantane-intercalated layered double-hydroxide (LDH) material in a form of adamantane-intercalated LDH particles, where the adamantane-intercalated LDH particles comprise:

a general formula defined by $[M_{1-x}Al_x(OH)_2](A)_x \cdot mH_2O$, where x is from 0.14 to 0.33, m is from 0.33 to 0.50, M is chosen from Mg, Ca, Co, Ni, Cu, or Zn, and A is adamantane carboxylate; and

an aspect ratio greater than 100, the aspect ratio defined by a width of an adamantane-intercalated LDH particle divided by a thickness of the adamantane-intercalated LDH particle.

16. The adamantane-intercalated LDH material of claim 15 where M is Mg.

17. The adamantane-intercalated LDH material of claim 15 where the aspect ratio is greater than 125.

18. The adamantane-intercalated LDH material of claim 15 where the adamantane-intercalated LDH particles have a particle diameter of 5 to 10 μm.

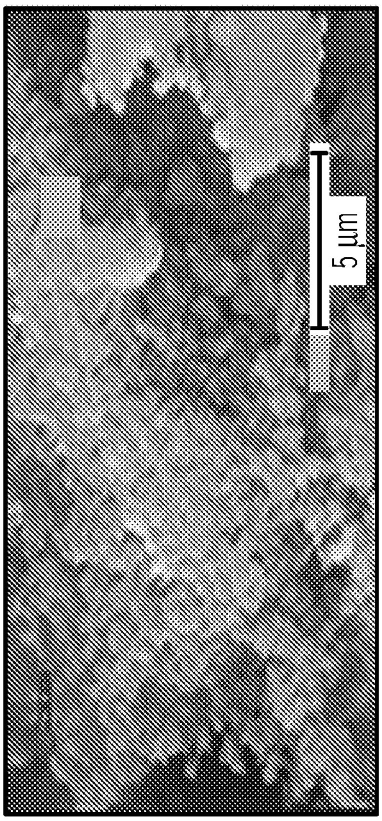

FIG. 1A

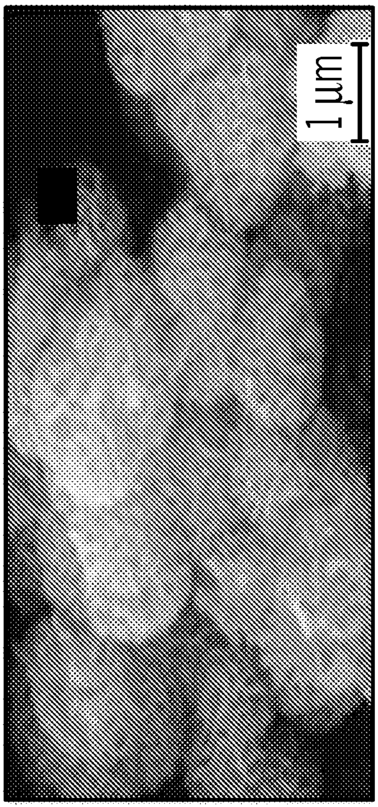

FIG. 1B

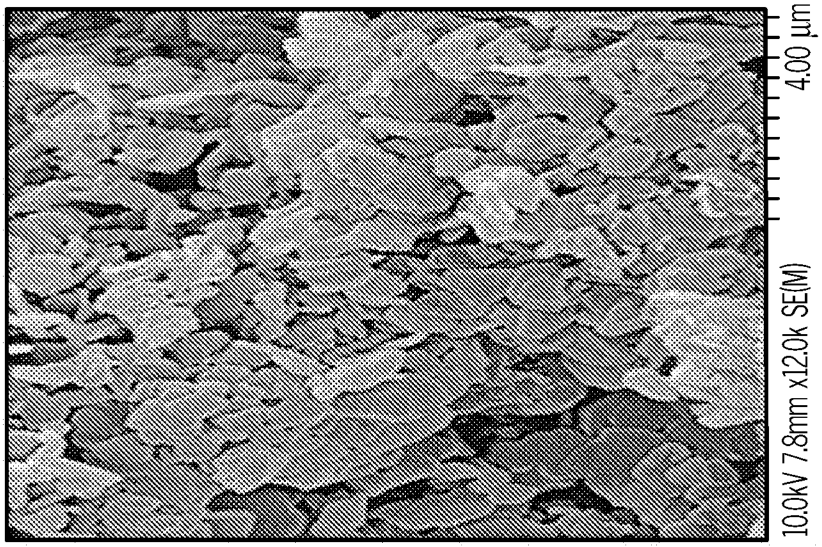

FIG. 2A

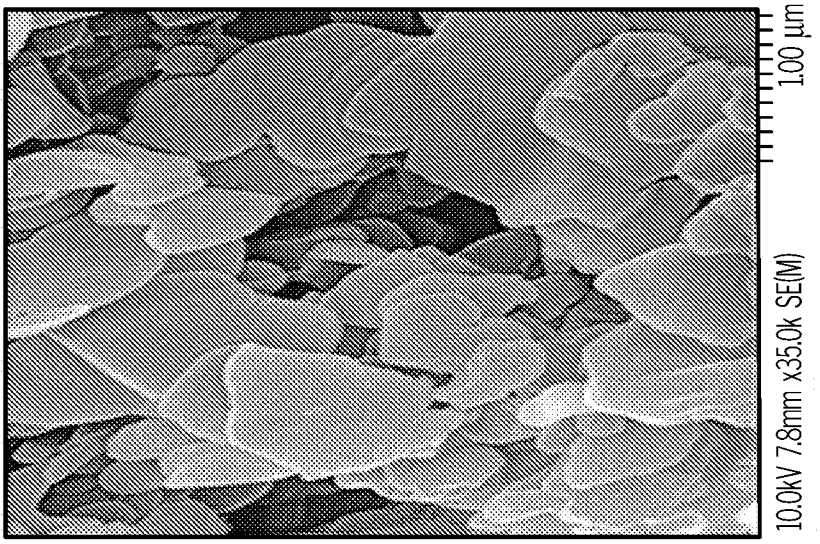

FIG. 2B

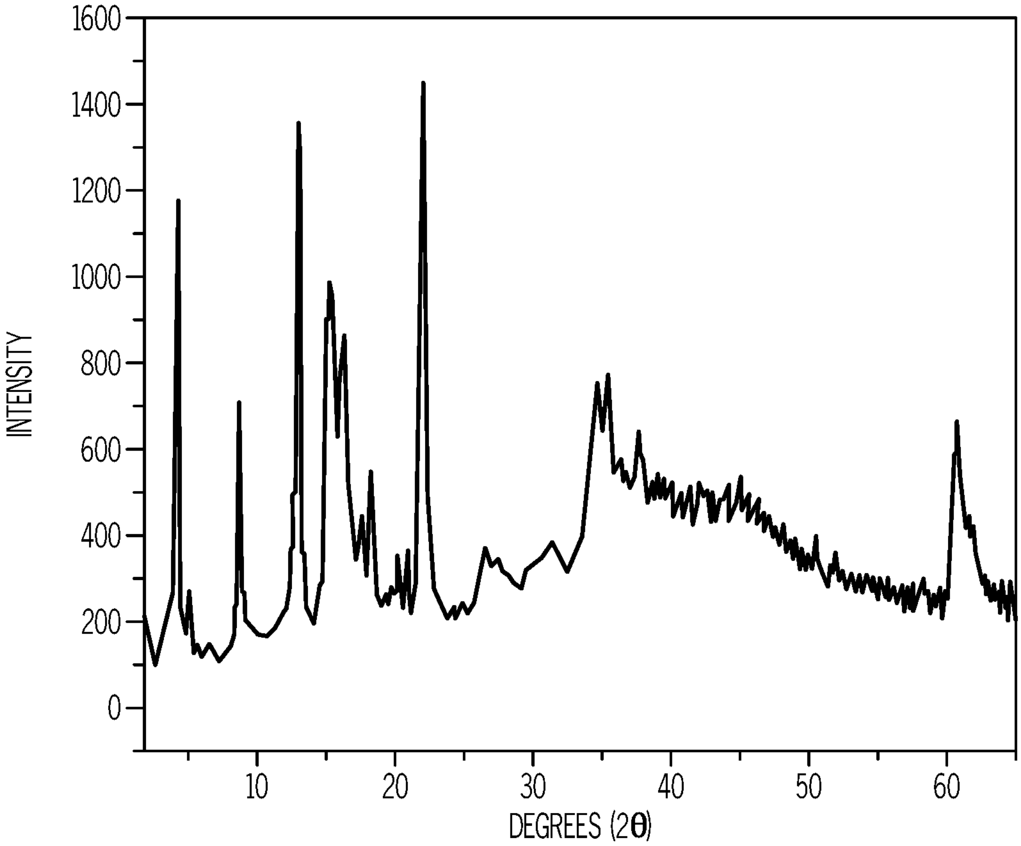
INTENSITY
1600
1400
1200
1000
800
600
400
200
0
10
20
30
40
50
60
DEGREES (2θ)

FIG. 3

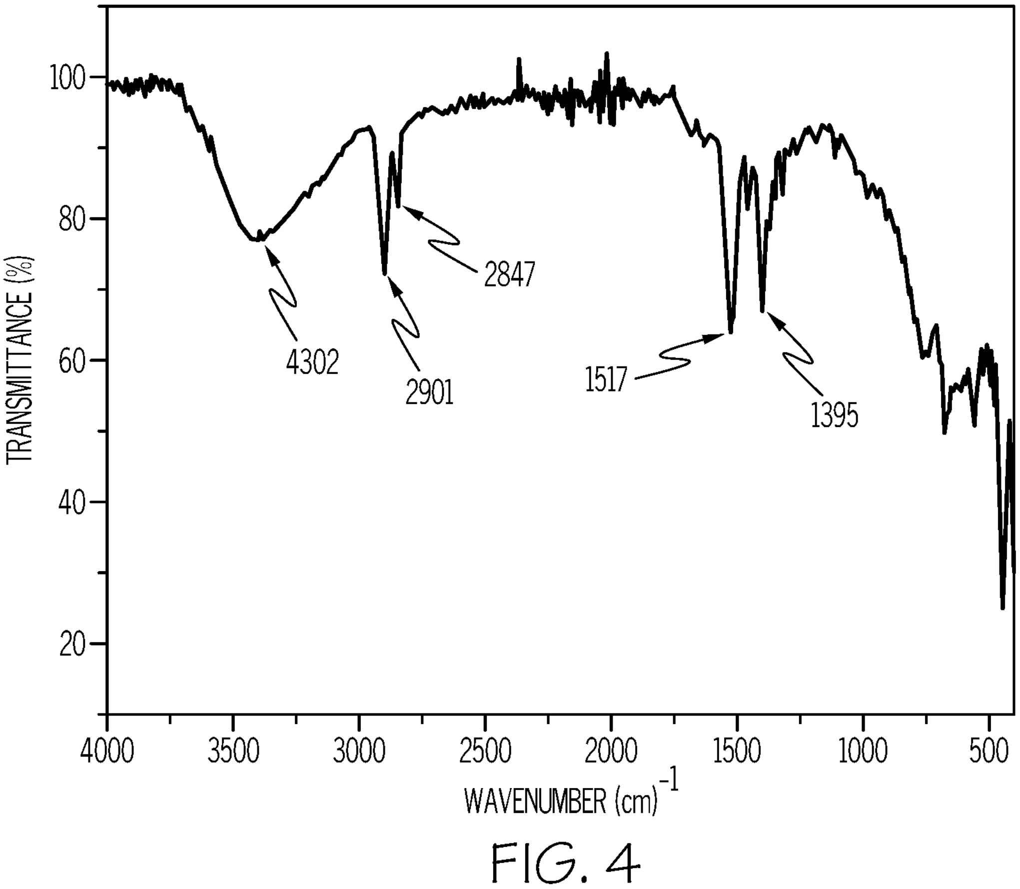
TRANSMITTANCE (%)
100
80
60
40
20
4302
2901
2847
1517
1395
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER (cm)-1

FIG. 4

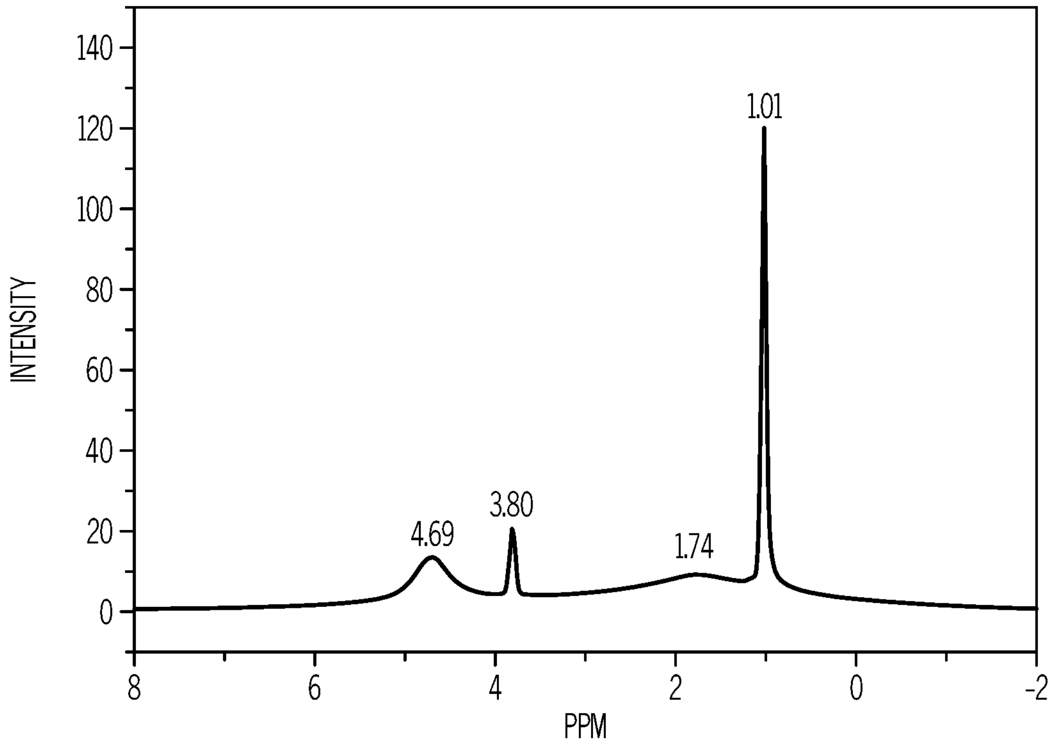
INTENSITY
140
120
100
80
60
40
20
0
8
6
4
2
0
-2
PPM
4.69
3.80
1.74
1.01

FIG. 5

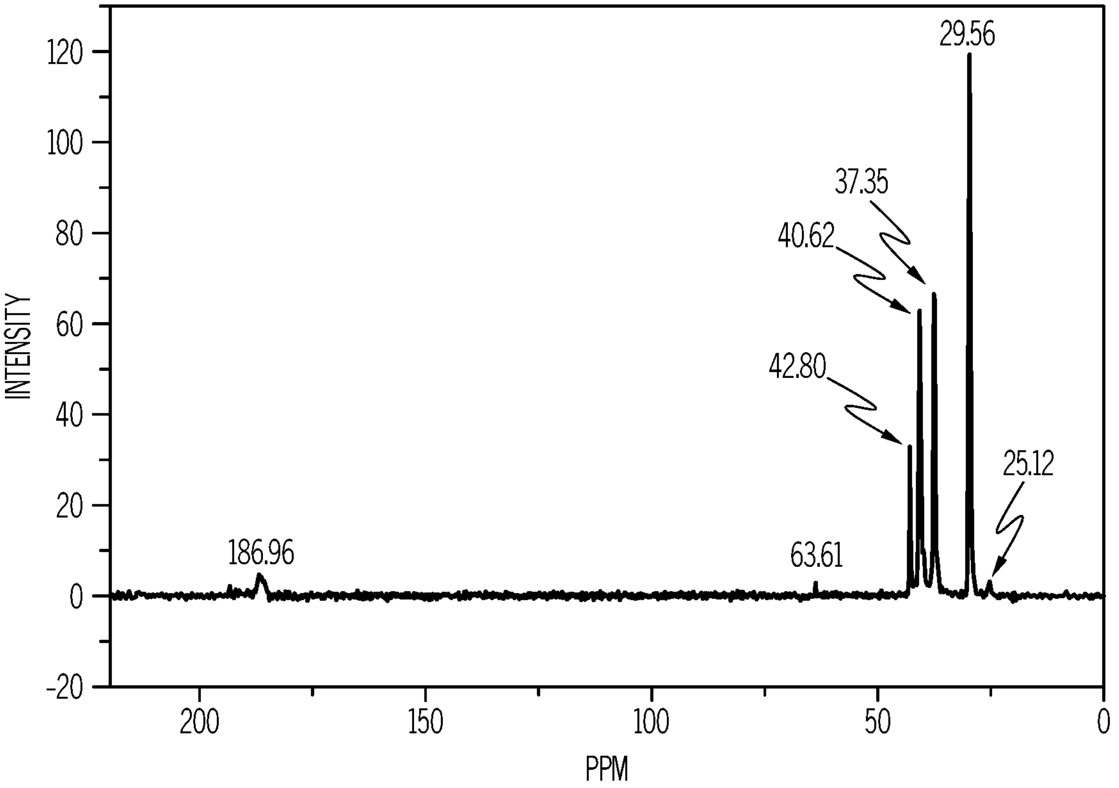
INTENSITY
120
100
80
60
40
20
0
-20
200
150
100
50
0
PPM
186.96
63.61
42.80
40.62
37.35
29.56
25.12

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/022485

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J31/06 B01J21/10 B01J23/00 B01J37/08
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)
B01J

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

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

EPO-Internal, 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	KHAN A I ET AL: "The intercalation of bicyclic and tricyclic carboxylates into layered double hydroxides", JOURNAL OF SOLID STATE CHEMISTRY, ORLANDO, FL, US, vol. 183, no. 12, 1 December 2010 (2010-12-01), pages 2877-2885, XP027553691, ISSN: 0022-4596 [retrieved on 2010-10-01]	15-18
Y	abstract Section 3.6.; page 2882 - page 2883; figure 7; tables 1,2 page 2878 ----- -/--	1-14

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 June 2017

Date of mailing of the international search report

13/07/2017

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

Goebel, Matthias

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	U. COSTANTINO ET AL: "Preparation and characterisation of hydrotalcite/carboxyadamantane intercalation compounds as fillers of polymeric nanocomposites", JOURNAL OF MATERIALS CHEMISTRY, vol. 17, no. 11, 22 December 2006 (2006-12-22), pages 1079-1086, XP055384240, GB ISSN: 0959-9428, DOI: 10.1039/B613842J	15-18
Y	page 1080; figures 1,5,6; table 1 -----	1-14
Y	GOH ET AL: "Application of layered double hydroxides for removal of oxyanions: A review", WATER RESEARCH, ELSEVIER, vol. 42, no. 6-7, 7 November 2007 (2007-11-07), pages 1343-1368, XP022523680, ISSN: 0043-1354, DOI: 10.1016/J.WATRES.2007.10.043	1-14
A	page 1346, right-hand column, paragraph 2-4 -----	15-18
A	US 5 399 329 A (SCHUTZ ALAIN A [US] ET AL) 21 March 1995 (1995-03-21) column 4, lines 53-68; claims 1,4,5,12; example 2; table 2 -----	1-18
A	US 5 326 891 A (BREUER WOLFGANG [DE] ET AL) 5 July 1994 (1994-07-05) column 3, lines 44-66; claims 1,3; examples 1-9,11,12 -----	1-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/022485

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5399329 A	21-03-1995	NONE	
US 5326891 A	05-07-1994	DE 4034305 A1	30-04-1992
		EP 0555246 A1	18-08-1993
		ES 2073176 T3	01-08-1995
		JP H06502139 A	10-03-1994
		US 5326891 A	05-07-1994
		WO 9207795 A1	14-05-1992