

MODIFICATION OF LAYERED DOUBLE HYDROXIDES

The present invention relates to a process for modifying layered double hydroxides (LDHs) and the modified layered double hydroxides prepared thereby.

Layered double hydroxides (LDHs) are a class of compounds which comprise two metal cations and have a layered structure. A review of LDHs is provided in *Structure and Bonding*; Vol 119, 2005 *Layered Double Hydroxides* ed. X Duan and D.G. Evans. The hydrotalcites, perhaps the most well-known examples of LDHs, have been studied for many years. LDHs can intercalate anions between the layers of the structure. WO 99/24139 discloses use of LDHs to separate anions including aromatic and aliphatic anions.

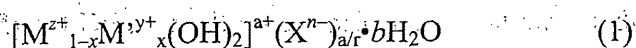
Owing to the relatively high surface charge and hydrophilic properties of LDHs, the particles or crystallites of conventionally synthesised LDHs are generally highly aggregated. The result of this is that, when produced, LDHs aggregate to form "stone-like", non-porous bodies with large particle sizes of up to several hundred microns and low specific surface area of generally 5 to 15 m²/g (as disclosed for example in Wang et al *Catal. Today* 2011, **164**, 198). Reports by e.g. Adachi-Pagano et al (*Chem Commun.* 2000, 91) of relatively high surface area LDHs have specific surface areas no higher than 5 to 120 m²/g.

In certain applications (for example adsorbents or catalyst supports) it would be advantageous to provide LDHs with higher surface areas than currently known. Relatively high surface areas would lead to a greater number of active sites and facilitate mass transport from the surface to bulk.

It is an object of the present invention to provide a process for modifying layered double hydroxides and to provide layered double hydroxides overcoming the disadvantages of the prior art. Especially LDHs shall be provided having reduced aggregation of LDH crystallines/particles, having high surface area, large pore volume and/or low particle density and/or apparent or tap density.

The present invention accordingly provides, in a first aspect, a process for modifying a layered double hydroxide (LDH), the process comprising,

- a. providing a water-wet layered double hydroxide of formula:



wherein M and M' are metal cations, $z = 1$ or 2 ; $y = 3$ or 4 , x is 0.1 to 1 , preferably $x < 1$, more preferably $x = 0.1 - 0.9$, b is 0 to 10 , X is an anion, r is 1 to 3 , n is the charge on the anion X and a is determined by x , y and z , preferably $a = z(1-x)+xy-2$;

- b. maintaining the layered double hydroxide as water-wet, and
- c. contacting the water-wet layered double hydroxide with at least one solvent, the solvent being miscible with water and preferably having a solvent polarity (P') in the range 3.8 to 9 .

This process is greatly advantageous because despite being such a simple process it, surprisingly, results in highly porous and highly dispersed LDHs, preferably having low particle density. For instance, for a conventionally synthesized Zn_2Al -borate LDH, its specific surface area (N_2) and total pore volume are only $13.4 \text{ m}^2/\text{g}$ and 0.08 cc/g , respectively. However, the inventors have discovered that LDH modified according to the invention has a specific surface area and total pore volume increased to $301 \text{ m}^2/\text{g}$ and 2.15 cc/g , respectively. In addition, the modified LDH has a very uniform particle size of about $5 \text{ }\mu\text{m}$. This method of the invention can be applied to all LDHs. In addition this method is simple and can be easily scaled up for commercial production.

Solvent polarity (P') is defined based on experimental solubility data reported by Snyder and Kirkland (Snyder, L. R.; Kirkland, J. J. In *Introduction to modern liquid chromatography*, 2nd ed.; John Wiley and Sons: New York, 1979; pp 248 - 250,) and as described in the table in the Examples section, below.

Preferably, aggregation of particles/crystallites of the LDH is reduced. Also preferred, in step a., as stated above, a substance comprising a water-wet layered double hydroxide of formula (1) may be provided

In a most preferred embodiment, the at least one solvent is not water.

The water-wet LDH should not dry before contacting the solvent and is preferably a water slurry of LDH particles. The preferred method of contacting the water-wet LDH with the solvent is dispersing the water-wet LDH in the solvent.

M may be a single metal cation or a mixture of different metal cations for example Mg, Zn, Fe for a MgFeZn/Al LDH. Preferred M are Mg, Zn, Fe, Ca or a mixture of two or more of these.

M' may be a single metal cation or a mixture of different metal cations, for example Al, Ga, Fe. The preferred M' is Al. The preferred value of y is 3.

Preferably, z is 2 and M is Ca or Mg or Zn or Fe.

Preferably, M is Zn, Mg or Ca, and M' is Al.

Preferred values of x are 0.2 to 0.5, preferably 0.22 to 0.4, more preferably 0.23 to 0.35.

Overall, as is clear for a skilled artisan, the LDH according to formula (1) must be neutral, so that the value of a is determined by the number of positive charges and the charge of the anion.

The anion in the LDH may be any appropriate anion, organic or inorganic, for example halide (e.g. chloride), inorganic oxyanions (e.g. $X_mO_n(OH)_p^{q-}$; $m = 1 - 5$; $n = 2 - 10$; $p = 0 - 4$, $q = 1 - 5$; $X = B, C, N, S, P$; e.g. carbonate, bicarbonate, hydrogenphosphate, dihydrogenphosphate, nitrite, borate, nitrate, phosphate, sulphate), anionic surfactants (such as sodium dodecyl sulfate, fatty acid salts or sodium stearate), anionic chromophores, and/or an anionic UV absorbers for example 4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (HMBA), 4-hydroxy-3-methoxy-cinnamic acid, p-aminobenzoic acid and/or urocanic acid.

Preferably, the particles of the LDH have a size in the range 1 nm to 200 microns, more preferably 2 nm to 30 microns and preferably 2 nm - 20 micron, most preferably 2 nm to 10 microns.

Preferably, the aspect ratio of the LDH particles will be in the range 30 nm to 1500 nm (determined as platelet area/platelet thickness) preferably 80 to 500 nm and more preferably 100 nm to 350 nm.

Generally, any suitable organic solvent, preferably anhydrous, may be used but the preferred solvent is selected from one or more of acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, dioxane, ethanol, methanol, n-propanol, iso-propanol, 2-propanol or tetrahydrofuran. The preferred solvent is acetone. Other preferred solvents are alkanols e.g. methanol or ethanol.

The role of the organic solvent is to strip the surface bound water from the water wet LDH particles. The dryer the solvent, the more water can be removed and thus the LDH dispersion be improved. More preferably, the organic solvent contains less than 2 weight percent water.

Preferably, the modified layered double hydroxide obtained has a specific surface area (N_2) in the range $155 \text{ m}^2/\text{g}$ to $850 \text{ m}^2/\text{g}$, preferably $170 \text{ m}^2/\text{g}$ to $700 \text{ m}^2/\text{g}$, more preferably $250 \text{ m}^2/\text{g}$ to $650 \text{ m}^2/\text{g}$. Preferably, the modified layered double hydroxide has a BET pore volume (N_2) greater than $0.1 \text{ cm}^3/\text{g}$. Preferably, the inventive modified layered double hydroxide has a BET pore volume (N_2) in the range $0.1 \text{ cm}^3/\text{g}$ to $4 \text{ cm}^3/\text{g}$, preferably $0.5 \text{ cm}^3/\text{g}$ to $3.5 \text{ cm}^3/\text{g}$, more preferably 1 to $3 \text{ cm}^3/\text{g}$.

Further steps in the process may comprise drying the LDH obtained in step c and/or subjecting the LDH to a thermal treatment. The thermal treatment may comprise heat treatment at temperature ranges from room temperature to about 150°C , and/or about 150°C to 400°C and/or about 400°C to 1000°C . Thermal treatment may comprise calcining the LDH (e.g. at a temperature in the range 110°C to 950°C).

The inventive process can be called an aqueous miscible organic solvent treatment (AMOST) process. The inventive process can be either a continuous or a batch process.

According to the second object, a layered double hydroxide is provided, prepared according to the inventive process.

Preferably the layered double hydroxide has a BET pore volume (N_2) greater than $0.1 \text{ cm}^3/\text{g}$.

Preferably, the process results in a LDH having a de-aggregation ratio greater than 2, preferably greater than 5, more preferably in the range 5 to 200. De-aggregation ratio is the ratio of the BET surface of the inventive material compared to the material treated in a comparative way. The comparison is based on an identical LDH synthesis in which the water wet LDH is just dried and not been treated with a water miscible solvent. The de-aggregation ratio is closely related to the % decrease in particle densities.

The modified LDHs prepared according to the present invention could be called aqueous miscible organic-LDHs (AMO-LDHs).

The modified LDHs of the present invention have preferably a loose bulk density of 0.1 - 0.25 g/mL , have preferably a tap density between 0.1 - 0.35 g/mL , have preferably a GyoPyc tap density of 0.2 - 0.4 g/mL . The Carr index of an inventive LDH is preferably increased by 0 - 45% compared to conventionally prepared LDH. Further, the surface area of an inventive LDH is preferably increased by 34 - $11,000\%$ compared to conventionally prepared LDH, while the pore volume of an inventive LDH may be increased by 11 - $150,000\%$ compared to a conventionally prepared LDH. Application of the inventive method imparts new thermal

characteristics to an inventive LDH compared to a conventionally prepared LDH, as shown by thermogravimetric analysis (TGA).

Preferably, the process results in a LDH having an apparent density of less than 0.8 g/cm^3 , preferably less than 0.5 g/cm^3 , more preferably less than 0.4 g/cm^3 . Apparent density may be determined by the following procedure. The LDH as a free-flowing powder was filled into a 2 mL disposable pipette tip, and the solid was packed as tight as possible by tapping manually for 2 min. The weight of the pipette tip was measured before and after the packing to determine the mass of the LDH. Then the apparent density of LDH was calculated using the following equation:

$$\text{Apparent density} = \text{LDH weight (g)}/\text{LDH volume (2 mL)}$$

The LDHs according to the invention are particularly suitable to be used for a large variety of applications.

Applications of these LDHs include use as catalyst supports and in many other applications.

The preferred and optional features of the first and second aspects of the invention are as discussed in relation to the other aspects and as specified in the claims.

Further advantages and features of the subject-matter of the present invention can be taken from the following detailed description taking the drawing into consideration, in which:

Figure 1. The LDH synthesis procedure including the inventive acetone treatment.

Figure 2. XRD patterns of Zn_2Al -borate LDH (a) slurry after washing with water, (b) dried powder after washing with water, (c) slurry after washing with acetone, and (d) dried powder after washing with acetone. ($\blacktriangledown$) reflections from sample holder.

Figure 3. XRD patterns of acetone washed Zn_2Al -borate LDH slurry, (a) run 1, (b) run 2, (c) run 3, and (d) run 4.

Figure 4. TEM image of Zn_2Al -borate LDH washed with acetone.

Figure 5. High resolution TEM image of Zn_2Al -borate LDH washed with acetone.

Figure 6. SEM of Zn_2Al -borate LDH washed with acetone.

Figure 7. Nitrogen absorption isotherm of Zn_2Al -borate LDHs washed with (a) water, and (b) acetone in BET analysis.

Figure 8. XRD patterns of acetone washed Zn_2Al -borate LDH (a) dried powder, (b) exposed to air for 4 days, (c) re-contacted with H_2O , and (d) re-contact with Na_2CO_3 solution.

Figure 9. TEM image of acetone washed Zn_2Al -borate LDH after re-contacting with (a) H_2O and (b) Na_2CO_3 aqueous solution.

Figure 10. The LDH particle growth steps during acetone washing.

Figure 11. XRD patterns of Mg_3Al -borate LDH washed with (a) water and (b) acetone.

Figure 12. TEM images of Mg_3Al -borate LDH washed with (a) water and (b) acetone.

Figure 13. XRD patterns of $\text{Mg}_3\text{Al-NO}_3$ LDH washed with (a) water and (b) acetone.

Figure 14. TEM image of $\text{Mg}_3\text{Al-NO}_3$ LDH washed with (a) water and (b) acetone.

Figure 15. XRD patterns of $\text{Mg}_3\text{Al-Cl}$ LDH washed with (a) water and (b) acetone.

Figure 16. TEM images of $\text{Mg}_3\text{Al-Cl}$ LDH washed with (a) water and (b) acetone.

Figure 17. XRD patterns of $\text{Mg}_3\text{Al-SO}_4$ LDH washed with (a) water and (b) acetone.

Figure 18. TEM images of $\text{Mg}_3\text{Al-SO}_4$ LDH washed with (a) water and (b) acetone.

Figure 19. XRD patterns of $\text{Zn}_3\text{Al-NO}_3$ LDH washed with (a) water and (b) acetone.

Figure 20. TEM image of $\text{Zn}_3\text{Al-NO}_3$ LDH washed with (a) water and (b) acetone.

Figure 21. XRD patterns of $\text{Ca}_2\text{Al-NO}_3$ LDH washed with (a) water and (b) acetone.

Figure 22. SEM images of $\text{Ca}_2\text{Al-NO}_3$ LDH washed with (a) water and (b) acetone.

Figure 23. TEM images of $\text{Ca}_2\text{Al-NO}_3$ LDH washed with (a) water and (b) acetone.

Figure 24. TGA analysis of $\text{Mg}_3\text{Al-NO}_3$ LDH washed with water and acetone.

Figure 25. XRD patterns of Zn_2Al -borate LDHs washed with acetone, ethanol and methanol.

Figure 26. TGA and DTG analysis of $\text{Mg}_3\text{Al-NO}_3$ -10 LDHs (a) in the range of 30-600 °C and (b) in the range of 30-230 °C. $\text{Mg}_3\text{Al-NO}_3$ -10-W was prepared by a conventional coprecipitation method in water at pH 10, while $\text{Mg}_3\text{Al-NO}_3$ -10-A was prepared under identical conditions in water at pH 10 according to the method of the present invention using acetone as the solvent.

The invention is further illustrated by the following Examples.

Examples

1. Synthesis methods for LDH

1.1 Conventional co-precipitation method – a metal precursor solution is added dropwise into an anion solution, and the pH of precipitation solution is adjusted to a predetermined value using a NaOH solution in water. The precipitant is aged at a predetermined temperature for about 12 h. LDH is collected by filtration and washing with water, followed by drying at 65 °C.

Further, it is well known in the art that other synthesis methods for LDHs are known, such as use of controlled hydrolysis of urea or a related organic compound, hydrothermal synthesis, or sol-gel methods.

1.2 Inventive method with solvent treatment – the inventive method is designed based on the coprecipitation method as described above, but the water washed “wet cake” is redispersed in acetone. After stirring for about 1 - 2 h, the sample is filtered and washed with acetone. The final LDH product is dried at 65 °C. Comparing to the coprecipitation method, a simple solvent/acetone treatment step is added before the LDH “wet cake” is dried. Such a simple step surprisingly results in a very different LDHs product with much higher surface area. The synthesis procedure is illustrated in Figure 1.

2. Characterization methods

X-ray diffraction (XRD) – XRD patterns were recorded on a PANalytical X'Pert Pro instrument in reflection mode with Cu K α radiation. The accelerating voltage was set at 40 kV with 40 mA current ($\lambda = 1.542 \text{ \AA}$) at 0.01 °/s from 1° to 70° with a slit size of 1/4 degree.

Fourier Transform Infrared Spectroscopy (FT-IR) – FT-IR spectra were recorded on a Bio-Rad FTS 6000-FTIR Spectrometer equipped with a DuraSamplIR II diamond accessory in attenuated total reflectance (ATR) mode in the range of 400-4000 cm^{-1} ; 100 scans at 4 cm^{-1} resolution were collected. The strong absorption in the range 2500 - 1667 cm^{-1} was from the DuraSamplIR II diamond surface.

Transmission Electron Microscopy (TEM) – TEM analysis was performed on JEOL 2100 microscope with an accelerating voltage of 400 kV. Samples were dispersed in ethanol with sonication and then cast onto copper TEM grids coated with lacey carbon film.

Scanning Electron Microscopy (SEM) and Energy dispersive X-ray Spectrometry (EDS) – SEM and SEM-EDS analyses were performed on a JEOL JSM 6100 scanning microscope with an accelerating voltage of 20 kV. Powder samples were spread on carbon tape adhered to an SEM stage. Before observation, the samples were sputter coated with a thin Platinum layer to prevent charging and to improve the image quality.

BET specific surface areas – BET specific surface areas were measured from the N₂ adsorption and desorption isotherms at 77 K, collected from a Quantachrome Autosorb-6B surface area and pore size analyzer. Before each measurement, LDH samples were first degassed overnight at 110 °C.

Thermal gravimetric analysis (TGA) – The thermal stability of LDHs was studied by TGA (Netzsch) analysis, which was carried out with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and an air flow rate of 50 mL min^{-1} from 25 to $700\text{ }^{\circ}\text{C}$.

The apparent density was determined using the following procedure. The LDH as a free-flowing powder was filled into a 2 mL disposable pipette tip, and the solid was packed as tight as possible by tapping manually for 2 minutes. The weight of the pipette tip was measured before and after the packing to determine the mass of the LDH. Then the apparent density of LDH was calculated using the following equation:

Apparent density = LDH weight (g)/LDH volume (2 mL).

Loose bulk density – The Loose Bulk Density was determined by the following procedure: The freely flowing powder was poured into a graduated cylinder (10 mL) using the solid addition funnel. The cylinder containing the powder was tapped once and the volume measured. The Loose Bulk Density was determined using Equation (1).

$$\text{Loose Bulk Density} = \frac{m}{V_0} \quad (1)$$

Where m is the mass of the powder in the graduated cylinder, V_0 is the powder volume in the cylinder after one tap.

3. Synthesis of Zn_2Al -borate and Mg_3Al -borate LDHs

Synthesis of Zn_2Al -borate LDH (Chemical Formulas)

$\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{B}_4\text{O}_5(\text{OH})_4)_{0.125} \cdot 0.34(\text{H}_2\text{O}) \cdot 0.11(\text{acetone})$ Zn_2Al -borate LDH was prepared by adding 100 mL $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.075 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.0375 mol) solution drop-wise into a 100 mL H_3BO_3 (0.187 mol) solution. The pH of the precipitation solution was controlled at about 8.3 using a NaOH (1 M) solution. During the whole synthesis, the system was protected with N_2 gas to prevent the contamination by atmosphere CO_2 . The mixture was aged at $65\text{ }^{\circ}\text{C}$ for overnight. The LDH product was first filtered and washed with water to give a "water-wet cake". Then the "water-wet cake" was redispersed in acetone solution. After stirring for about 1–2 h, the sample was filtered and washed with acetone. The final LDH product was dried at $65\text{ }^{\circ}\text{C}$.

Synthesis of Mg_3Al -borate LDH (Chemical Formula)

$\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{B}_4\text{O}_5(\text{OH})_4)_{0.125} \cdot 0.53(\text{H}_2\text{O}) \cdot 0.21(\text{acetone})$ was prepared by adding 100 mL $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.075 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.025 mol) solution drop-wise into a 100 mL H_3BO_3 (0.187 mol) solution. The pH of the precipitation solution was controlled at about 9 using

a NaOH (1 M) solution. During the whole synthesis, the system was protected with N_2 gas to prevent the contamination by atmosphere CO_2 . The mixture was aged at $65^\circ C$ overnight. The LDH product was first filtered and washed to give a "water-wet cake". Then the "water-wet cake" was redispersed in acetone solution again. After an adequate stirring for about 1 - 2 h, the sample was filtered and washed with acetone. The final LDH product was dried at $65^\circ C$.

The XRD patterns of Zn_2Al -borate LDH synthesized by the conventional co-precipitation method (LDH was washed with water until pH close to 7 and dried at $65^\circ C$ in oven) shows five characteristic peaks of Zn_2Al -borate LDH observed at 8.3° , 16.5° , 24.1° , 34.3° , and 60.8° , which can be index to the reflections of (003), (006), (009), (100), and (110/113) planes, respectively. According to the Bragg equation, the d-spacing was calculated as 1.05 nm, which is consistent with the previous reported values. Subtracting 0.46 nm, the thickness of one brucite layer, gives the interlayer spacing of 0.59 nm, indicating that the borate species is intercalated into the inter-layers. The morphology and the particle size distribution were characterized using SEM and TEM and indicates that nanoplatelets conventionally produced aggregate severely after being dried, forming particles with an average size of 10's of micrometers. It is thought that freshly prepared LDH nanoplatelets washed with water, have a surface surrounded by water molecules due to its high surface charge density. During the drying process nanoplatelets recombine together and grow to big particles. Such Zn_2Al -borate LDHs are generally nonporous, with a very low surface area less than $15\text{ m}^2/\text{g}$.

In the inventive process it was noticed that dispersing in acetone has a great effect on the properties of the final LDH samples. Therefore, after being washed with water to pH = 7, the water-wet Zn_2Al -borate LDH slurry is re-dispersed in acetone and washed with acetone thoroughly, followed by drying at $65^\circ C$. The structural changes during each step were monitored using XRD, as shown in Figure 2. For the water washed sample, the 001 reflections were observed for both the slurry and dried powder, and they had a very similar XRD pattern. However, with a further washing with acetone, a lower 003 reflection was seen with the slurry, which may be due to the replacement of the interlayer water molecules by acetone molecules. More interestingly, when the acetone washed slurry was dried, the 001 reflections disappeared while the 100 and 110/113 reflections remained, suggesting that the LDH was exfoliated. In addition, the acetone washed samples became so fine and light that the X-ray can pass through the samples, with the Nickel sample holder was detected at 43.4° and 50.4° . It was also confirmed that these two impurity peaks can be avoided with a deeper sample holder.

In order to further confirm that the exfoliation of Zn_2Al -borate LDH is purely due to the loss of acetone molecules, another experiment was conducted, as shown in Figure 3. Acetone washed slurry was put in a deep XRD sample holder, and its XRD pattern was recorded immediately (Figure 3(a)). After that, three more runs were carried out with the same sample (Figure 3(a-d)), and each run was fixed to 30 min. It was noticed that for the first run, when the acetone molecules were still in the LDH sample, the $00l$ reflections can be detected. However, only after 30 min in air, the sample lost its $00l$ reflections. Further exposure to air did not change its XRD patterns. This result clearly demonstrated that the evaporation (loss) of acetone molecules can result in an exfoliated Zn_2Al -borate LDH.

The exfoliation of Zn_2Al -borate LDH was further examined by TEM analysis, as shown in Figure 4 and Figure 5. After being washed with acetone, highly porous, sponge-like particles were obtained. This morphology is very much different from the water washed sample. The exfoliated Zn_2Al -borate LDH single layer can be clearly seen in HRTEM images (see Figure 5). It can also be seen that the exfoliated single layers were curved and irregular compared with the ordered, layered structure of the water washed sample. It is believed that the curving of the single layers led to the disordering of LDH along the z -axis direction, explaining why the $00l$ reflections disappeared with this sample. The SEM image in Figure 6 indicates that the acetone washed sample has a dramatic different morphology and particle size compared with the water washed samples. Washing with water produced large particles with an uneven, aggregated morphology. Acetone washed Zn_2Al -borate LDH has a significantly smaller particle size with a more uniform, spherical morphology.

According to the fact that the acetone washed Zn_2Al -borate LDH is exfoliated into single layers and curved, inventors expect it should have an extremely high specific surface area and high pore volume.

Figure 7 shows the N_2 adsorption/desorption isotherm curves for water washed and acetone washed Zn_2Al -borate LDHs. Both of them showed a H3 type hysteresis loop, which does not exhibit any limiting adsorption at the high P/P_0 . It indicates that these LDHs are aggregates of plate-like particles giving rise to slit-shaped pores. This is consistent with the SEM and TEM analyses. For acetone washed sample, the N_2 adsorption/desorption behaviour mainly occurred at the higher P/P_0 region, suggesting that it possesses larger pores than water washed sample. After being washed with acetone, both the specific surface area (from 13.4 to 301.0 m^2/g) and the total pore volume (from 0.08 to 2.15 cc/g) were significantly increased, see Table 1. The BET analysis is consistent with other characterizations and further confirms that the Zn_2Al -

borate LDH was de-aggregated by acetone washing and drying. The BET analysis also suggests that the acetone washed Zn_2Al -borate LDH has superior advantages as catalyst/support, adsorbent, nanocomposite filler, and so on.

Table 1. Specific surface area and total pore volume of Zn_2Al -borate washed with water or acetone.

Samples	Specific surface area (m^2/g)	Total pore volume (cc/g)
Zn_2Al -borate, water wash	13.4	0.08
Zn_2Al -borate, acetone wash	301.0	2.15

Memory effect is a characteristic of LDH, in which the destroyed layered structures can be reconstructed under certain circumstances. Different conditions were examined, (1) exposing to atmosphere for 4 days, (2) re-contact with H_2O , and (3) re-contact with Na_2CO_3 solution. The final products were checked using XRD analysis, as shown in Figure 8. After being exposed to air for 4 days, a very weak 003 reflection was observed for the acetone washed LDH dry powder, which indicates that the exfoliated LDH single layers started to recombined and the regular layered structure is partially reconstructed. This structure change is believed to be driven by the adsorption of water molecules from atmosphere. The reconstruction process is so slow that the structure change is not significant. However, if the acetone washed LDH sample is immersed in water for 2 h, a very strong 003 peak was observed. And the XRD pattern is similar to that of the water washed LDH sample, indicating that the exfoliated LDH single layers recombined in the presence of water and completely reconstructed into its original regular layered structure, Figure 9(a). When the acetone-washed sample was immersed in a Na_2CO_3 solution, highly crystallized $\text{Zn}_2\text{Al}(\text{CO}_3)_2$ LDH was obtained. This is reasonable because CO_3^{2-} has higher negative charge and is preferably intercalated into the LDH gallery than $\text{B}_3\text{O}_3(\text{OH})_4^-$, Figure 9(b). This result shows that the exfoliated Zn_2Al -borate LDH still possesses the memory effect property.

A possible mechanism for the effects of the invention is illustrated in Figure 10. For water washing, due to its high surface charge and hydrophilic property, the LDH nanoplates will be surrounded by water molecules. During the drying step, LDH plates will combine together and grow to bigger particles. In other words, the drying step acts as another aging step for the water washed LDH slurry. However, for the acetone washed LDH sample, the water molecules on LDH surface will be washed off and replaced by acetone molecules. Then during the drying

step, acetone molecules will be easily evaporated, leading to the formation of highly dispersed and highly porous LDHs.

Similar phenomena were observed with Mg_3Al -borate LDH. Figure 11 shows that after being washed with acetone, the Bragg diffractions disappeared, indicating that the LDH was exfoliated by the acetone treatment. SEM images clearly shows that the water washed sample consists of very big and chunky nonporous LDH particles, while the acetone washed sample becomes highly porous and is composed of very small and uniform LDH particles. TEM images in Figure 12 reveals that the water washed LDH is plate-like particles which aggregated severally, while the acetone washed LDH becomes flower-like particles. Such big difference in the structure and morphology of these two samples is solely due to a simple acetone treatment and will lead to significantly different performance in many fields such as catalysts, catalyst supports, adsorbents, etc.

4. Synthesis of other LDHs

Synthesis of $\text{Mg}_3\text{Al-NO}_3$ LDH $\text{Mg}_3\text{Al-NO}_3$ LDH (Chemical Formula: $\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{NO}_3)_{0.25} \cdot 0.38(\text{H}_2\text{O}) \cdot 0.12(\text{acetone})$) was synthesized by adding 50 mL $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0375 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.0125 mol) solution drop-wise into a 50 mL NaNO_3 (0.025 mol) solution. The pH of the precipitation solution was controlled at about 10 using a NaOH solution (4 M). The obtained LDHs were filtered and washed with H_2O until pH =

7. In order to show a direct comparison, half of the "water-wet cake" was dried conventionally at 65 °C, and the other half was redispersed in acetone solution again. After an adequate stirring for about 1-2 h, the sample was filtered and washed with acetone, followed by a drying step at 65 °C.

Synthesis of $\text{Mg}_3\text{Al-Cl}$ LDH $\text{Mg}_3\text{Al-Cl}$ LDH (Chemical Formula: $\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{Cl})_{0.25} \cdot 0.48(\text{H}_2\text{O}) \cdot 0.04(\text{acetone})$) was synthesized by adding 50 mL $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0375 mol) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0125 mol) solution drop-wise into a 50 mL NaCl (0.025 mol) solution. The pH of the precipitation solution was controlled at about 10 using a NaOH solution (4 M). The obtained LDHs were filtered and washed with H_2O until pH = 7. In order to show a direct comparison, half of the "water-wet cake" was dried conventionally at 65 °C, and the other half was redispersed in acetone solution again. After an adequate stirring for about 1-2 h, the sample was filtered and washed with acetone, followed by a drying step at 65 °C.

Synthesis of $\text{Mg}_3\text{Al-SO}_4$ LDH $\text{Mg}_3\text{Al-SO}_4$ LDH (Chemical Formula:

Mg(NO₃)₂·6H₂O (0.0375 mol) and Al₂(SO₄)₃·16H₂O (0.0125 mol) solution drop-wise into a 50 mL Na₂SO₄ (0.025 mol) solution. The pH of the precipitation solution was controlled at about 10 using a NaOH solution (4 M). The obtained LDHs were filtered and washed with H₂O until pH = 7. Half of the "water-wet cake" was dried at 65 °C, and the other half was redispersed in acetone solution again. After an adequate stirring for about 1 - 2 h, the sample was filtered and washed with acetone, followed by a drying step at 65 °C.

Synthesis of Zn₃Al-NO₃ LDH – Zn₃Al-NO₃ LDH (Chemical Formula: Zn_{0.75}Al_{0.25}(OH)₂(NO₃)_{0.25}·0.34(H₂O)·0.1(acetone)) was synthesized by adding 50 mL Zn(NO₃)₂·6H₂O (0.0375 mol) and Al(NO₃)₃·9H₂O (0.0125 mol) solution drop-wise into a 50 mL NaNO₃ (0.025 mol) solution. The pH of the precipitation solution was controlled at about 10 using a NaOH solution (4 M). The obtained LDHs were filtered and washed with H₂O until pH = 7. Half of the "water-wet cake" was dried at 65 °C, and the other half was redispersed in acetone solution again. After an adequate stirring for about 1 - 2 h, the sample was filtered and washed with acetone, followed by a drying step at 65 °C.

Synthesis of Ca₂Al-NO₃ LDH – Ca₂Al-NO₃ LDH (Chemical Formula: Ca_{0.67}Al_{0.33}(OH)₂(NO₃)_{0.125}·0.52(H₂O)·0.16(acetone)) was synthesized by adding 50 mL Ca(NO₃)₂·4H₂O (0.0375 mol) and Al(NO₃)₃·9H₂O (0.0125 mol) solution drop-wise into a 50 mL NaNO₃ (0.025 mol) solution. The pH of the precipitation solution was controlled at about 11 using a NaOH solution (4 M). The obtained LDHs were filtered and washed with H₂O until pH = 7. Half of the "water-wet cake" was dried at 65 °C, and the other half was redispersed in acetone solution again. After an adequate stirring for about 1 - 2 h, the sample was filtered and washed with acetone, followed by a drying step at 65 °C.

Other LDHs with either different cations or different anions were synthesized using the same method. The studied LDHs include Mg₃Al-NO₃, Mg₃Al-Cl, Mg₃Al-SO₄, Zn₃Al-NO₃, and Ca₂Al-NO₃, etc. With all the studied LDHs, it was observed that acetone treatment highly increases their surface area and leads to the formation of highly dispersed and much smaller LDH particles. For the water washed samples, most of the dried powders are very dense and hard to be crushed into fine powders. For the acetone washed samples, all of them are very "fluffy". These powders are so fine and so highly-dispersed that a further grinding is actually not needed. The samples were characterized using XRD, SEM, TEM, TGA, etc, see Figure 13 - 25. SEM images show that all water washed samples are composed of very big and nonporous chunky particles. The particle size is in the range of 20 - 200 μm. While after acetone treatment, all samples become very porous and are composed of very small and uniform particles. And the

particle size becomes around 1 - 5 μm . TEM images show the similar phenomenon with borate-intercalated LDHs. The water washed LDHs are all plate-like particles which aggregated severally, while the acetone washed LDHs become flower-like particles. This is the reason why acetone washed LDHs have much higher surface area comparing to the water washed samples. The TGA analysis in Figure 24 shows that the acetone washed $\text{Mg}_3\text{Al-NO}_3$ LDH has a higher thermal decomposition kinetics than the water washed sample. For instance, both the inter-layer water desorption temperature and the dehydration and inter-layer anion desorption temperature become much lower after being treated with acetone washing. This result is a further evidence that the acetone washed $\text{Mg}_3\text{Al-NO}_3$ LDH has a much smaller particle size.

For a number of sample LDHs the results for surface area, pore volume and deaggregation factor are given in Table 2 below. In column 1 defining the LDH, the last digits after the anion are the pH of the synthesis solution. For example, in line 1 of Table 2, $\text{Mg}_3\text{Al-CO}_3\text{-10}$ means that the synthesis solution had a pH = 10.

5. BET surface area (N_2) after calcination and apparent density

Also shown are values of BET surface area after calcination for $\text{Mg}_3\text{Al-borate}$ showing a dramatic increase (to $290 \text{ m}^2/\text{g}$) resulting from the process of the invention in Table 2a. The apparent density of the samples is shown in Table 2b.

Table 2. The Surface Properties of AMO-LDHs and C-LDHs

LDH ¹	Surface Area (m^2/g)		Deaggregation Factor	Pore Volume (cc/g)			Formula of AMO-LDH-A	Formula of C-LDH
	AMO-LDH ² A ¹	C-LDH ² LDH ²		AMO-LDH ² A ¹	C-LDH ² LDH ²	% Change		
$\text{Mg}_3\text{Al-CO}_3\text{-10}$	277	43	6.4	0.63	0.11	472	$\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{CO}_3)_{0.125} \cdot 1.36\text{H}_2\text{O} \cdot 0.17(\text{Acetone})$	$\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{CO}_3)_{0.125} \cdot 1.67\text{H}_2\text{O}$
$\text{Mg}_2\text{Al-CO}_3\text{-10}$	199	148	1.3	1	0.9	11	$\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.125} \cdot 0.52(\text{H}_2\text{O}) \cdot 0.16(\text{acetone})$	$\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.125} \cdot 0.92(\text{H}_2\text{O})$
$\text{Mg}_3\text{Al-CO}_3\text{-12}$	148	41	3.6	0.405	0.13	222	$\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{CO}_3)_{0.125} \cdot 1.76\text{H}_2\text{O} \cdot 0.45(\text{Acetone})$	$\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{CO}_3)_{0.125} \cdot 2.83\text{H}_2\text{O}$

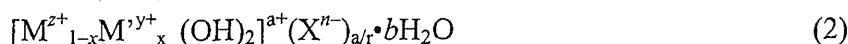
Mg ₃ Al _{0.5} Fe _{0.5} - NO ₃ -10	128	91	1.4	1.1	0.68	62	Mg _{0.75} Al _{0.125} Fe _{0.125} (OH) ₂ (CO ₃) _{0.125} • 0.56(H ₂ O)• 0.07(acetone)	Mg _{0.75} Al _{0.125} Fe _{0.125} (OH) ₂ (CO ₃) _{0.125} • 0.74(H ₂ O)
Zn ₂ Al- Borate- 8.3	301	13	23	2.15	0.0816	2534	Zn _{0.67} Al _{0.33} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.34(H ₂ O)• 0.11(acetone)	Zn _{0.67} Al _{0.33} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.65(H ₂ O)
Mg ₃ Al- Borate-9 Fe _{0.5} -	263	1	263	0.516	0.0003 5	147329	Mg _{0.75} Al _{0.25} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.53(H ₂ O)• 0.21(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.59(H ₂ O)
Mg ₃ Al- SO ₄ -10 Borate-	101	14	7.2	0.305	0.012	2442	Mg _{0.75} Al _{0.25} (OH) ₂ (SO ₄) _{0.125} • 0.55(H ₂ O) •0.13(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (SO ₄) _{0.125} • 0.6(H ₂ O)
Mg ₃ Al- NO ₃ -10 Borate-9	169	1.5	112	0.639	0.0066 5	9581	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} • 0.38(H ₂ O) •0.12(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} • 0.57(H ₂ O)
Mg ₃ Al- Cl-10 Borate-9	64	1	64	0.319	0.0031	10190	Mg _{0.75} Al _{0.25} (OH) ₂ (Cl) _{0.25} • 0.48(H ₂ O) •0.04(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (Cl) _{0.25} • 0.61(H ₂ O)
Zn ₃ Al- NO ₃ -8.3 NO ₃ -10	61	1	61	0.37	0.016	2212	Zn _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} •0.32(H ₂ O). 0.1(acetone)	Zn _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} • 0.61(H ₂ O)
LDH	AMO-LDH-M ¹	C-LDH ²	³ Deaggregation Factor	AMO-LDH-M ¹	C-LDH ²	% Change	Formula of AMO-LDH-M	Formula of C-LDH
Mg ₃ Al- CO ₃ -12	157	43	3.65	0.94	0.11	755	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} • 0.44(H ₂ O)• 0.11(methanol)	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •1.67H ₂ O

¹AMO-LDH-A and AMO-LDH-M are an LDH of formula

$$[M^{z+}_{1-x}M'^{y+}_x(OH)_2]^{a+}(X^{n-})_{a/r} \cdot bH_2O \cdot c(AMO-solvent) \quad (1)$$

wherein M and M' are metal cations; z = 1 or 2; y = 3 or 4, 0 < x < 1, b = 0-10, c = 0-10, X is an anion, r is 1 to 3 and a = z(1-x) + xy - 2. AMO-solvent (A=Acetone, M=Methanol)

²**C-LDH** is an LDH of formula



wherein M and M' are metal cations, $z = 1$ or 2 ; $y = 3$ or 4 , $0 < x < 1$, $b = 0-10$, $c = 0-10$, X is an anion, r is 1 to 3 and $a = z(1-x) + xy - 2$.

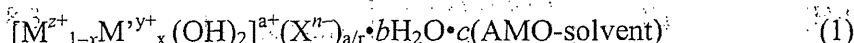
³**Deaggregation Factor** is defined as the ratio of the BET surface area of acetone washed sample to the water washed sample.

Table 2a.

LDH	BET Surface Area (m^2/g^{-1})		Formula of AMO-LDH-A (before calcination)	Formula of C-LDH (before calcination)
	C-LDH ² (calcined) ^s	AMO-LDH-A ¹ (calcined) ^s		
Mg ₃ Al-NO ₃ -10		310	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} •0.38(H ₂ O)•0.12(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} •0.57(H ₂ O)
Mg ₃ Al-Borate-9	5	290	Mg _{0.75} Al _{0.25} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} •0.53(H ₂ O)•0.21(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} •0.59(H ₂ O)
Zn ₂ Al-Borate-8.3		221	Zn _{0.67} Al _{0.33} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} •0.34(H ₂ O)•0.11(acetone)	Zn _{0.67} Al _{0.33} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} •0.65(H ₂ O)
Mg ₃ Al-CO ₃ -10		327	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.12} •1.36H ₂ O•0.17(Acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.12} •1.67H ₂ O

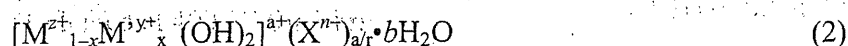
^s Calcined at 400 °C for 5 hrs.

¹**AMO-LDH-A** is an LDH of formula



wherein M and M' are metal cations, $z = 1$ or 2 ; $y = 3$ or 4 , $0 < x < 1$, $b = 0-10$, $c = 0-10$, X is an anion, r is 1 to 3 and $a = z(1-x) + xy - 2$. AMO-solvent (A=Acetone, M=Methanol)

²**C-LDH** is an LDH of formula

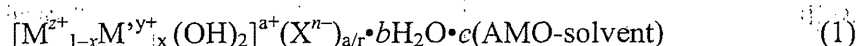


wherein M and M' are metal cations, $z = 1$ or 2 ; $y = 3$ or 4 , $0 < x < 1$, $b = 0-10$, $c = 0-10$, X is an anion, r is 1 to 3 and $a = z(1-x) + xy - 2$.

Table 2b.

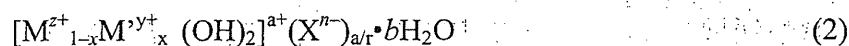
LDH	Apparent density ³ (g/mL)		Density Decrease %	Formula of AMO-LDH-A	Formula of C-LDH
	C-LDH ²	AMO-LDH-A ¹			
Mg ₃ Al-NO ₃ -10	0.91	0.12	86.8	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.2} • 0.38(H ₂ O) • 0.12(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} • 0.5 7(H ₂ O)
Mg ₃ Al-SO ₄ -10	0.99	0.13	86.8	Mg _{0.75} Al _{0.25} (OH) ₂ (SO ₄) _{0.12} • 0.55(H ₂ O) • 0.13(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (SO ₄) _{0.125} • 0.6(H ₂ O)
Mg ₃ Al-Cl-10	1.03	0.24	76.7	Mg _{0.75} Al _{0.25} (OH) ₂ (Cl) _{0.25} • 0.48(H ₂ O) • 0.04(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (Cl) _{0.25} • 0.61(H ₂ O)
Zn ₃ Al-NO ₃ -8.3	1.24	0.31	75.0	Zn _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} • 0.32(H ₂ O) • 0.1(acetone)	Zn _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} • 0.61(H ₂ O)
Mg ₃ Al-Borate-9	1.01	0.14	86.1	Mg _{0.75} Al _{0.25} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.53(H ₂ O) • 0.21(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.59(H ₂ O)
Zn ₂ Al-Borate-8.3	0.62	0.10	83.9	Zn _{0.67} Al _{0.33} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.34(H ₂ O) • 0.11(acetone)	Zn _{0.67} Al _{0.33} (OH) ₂ (B ₄ O ₅ (OH) ₄) _{0.125} • 0.65(H ₂ O)
Mg ₃ Al-CO ₃ -10	0.9	0.10	90.0	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} • 1.36H ₂ O • 0.17(Acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} • 1.67H ₂ O

5 ¹AMO-LDH-A is an LDH of formula



wherein M and M' are metal cations, $z = 1$ or 2 ; $y = 3$ or 4 , $0 < x < 1$, $b = 0-10$, $c = 0-10$, X is an anion, r is 1 to 3 and $a = z(1-x) + xy - 2$. AMO-solvent (A = Acetone, M = Methanol)

10 ²C-LDH is an LDH of formula



wherein M and M' are metal cations, $z = 1$ or 2 ; $y = 3$ or 4 , $0 < x < 1$, $b = 0-10$, $c = 0-10$, X is an anion, r is 1 to 3 and $a = z(1-x) + xy - 2$.

15 ³Apparent Density is the weight per unit volume of a LDH powder (after tapping manually for 2 min), this may be different to the weight per unit volume of individual LDH particles.

Method. Apparent density may be determined by the following procedure. The LDH as a free-flowing powder was filled into a 2 mL disposable pipette tip, and the solid was packed as tight as possible by tapping manually for 2 min. The weight of the pipette tip was measured before and after the packing to determine the mass of the LDH. Then the apparent density of LDH was calculated using the following equation:

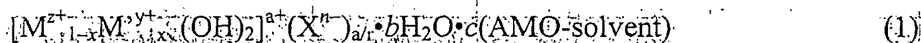
$$\text{Apparent density} = \text{LDH weight (g)}/\text{LDH volume (2 mL)}$$

Further, the water and AMO-solvent content in the LDHs of the present invention compared to conventional C-LDHs was determined by the TGA data. The results are summarized in Table 3.

Table 3. Summary of water and AMO-solvent content in the AMO-LDHs compared to conventional C-LDHs as determined by analysis of the TGA data (Figures 14, 15, and 16).

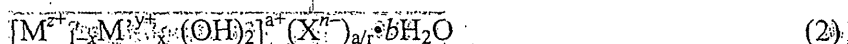
LDH	C-LDH ²		AMO-LDH-A ¹		AMO-LDH-M ¹	
	<i>b</i> ³	<i>c</i> ⁴	<i>b</i> ³	<i>c</i> ⁴	<i>b</i> ³	<i>c</i> ⁴
Mg ₃ Al-CO ₃ -10	0.42	1.0	0.34	0.04	0.44	0.11
Mg ₃ Al-CO ₃ -12	0.71	0	0.44	0.11	0.44	0.11
Mg ₃ Al-CO ₃ -10	0.92	0	0.52	0.16	--	--
Mg ₃ Al-Cl-10	0.61	0	0.48	0.04	--	--
Mg ₃ Al-SO ₄ -10	0.60	1.0	0.55	0.13	--	--
Mg ₃ Al-NO ₃ -10	0.57	0	0.38	0.12	--	--
Mg ₃ Al-Borate-10	0.59	0	0.53	0.21	--	--
Mg ₃ Al _{0.3} Fe _{0.5} -10	0.74	0	0.56	0.07	--	--
Zn ₃ Al-Borate-8.3	0.65	0	0.34	0.11	--	--
Zn ₃ Al-NO ₃ -8.3	0.61	0	0.32	0.10	0.44	0.11

¹AMO-LDH-A and AMO-LDH-M are the LDH with the formula of



wherein M and M' are metal cations, *z* = 1 or 2, *y* = 3 or 4, $0 < x < 1$, *b* = 0 - 10, *c* = 0 - 10, X is an anion, *r* is 1 to 3, and $a = z(1-x) + xy - 2$. AMO-solvent (A = Acetone, M = Methanol)

²C-LDH is an LDH of formula



wherein M and M' are metal cations, *z* = 1 or 2, *y* = 3 or 4, $0 < x < 1$, *b* = 0 - 10, *c* = 0 - 10, X is an anion, *r* is 1 to 3 and $a = z(1-x) + xy - 2$.

³ b is the water content in the formula (1) and (2).

⁴ c is the acetone content in the formula (1).

6. Other possible washing solvents

In addition to acetone, several other washing solvents were also investigated. Figure 25 shows the XRD patterns of Zn_2Al -borate LDHs washed with acetone, ethanol, and methanol, respectively. The Bragg diffraction peaks disappeared for all samples, indicating that all these washing solvents are effective for the treatment. Because the key function of the washing solvents is to wash off the surface adsorbed water molecules and prevent the further combination of LDH nanoparticles during the drying step, it is believed that all the solvents which have a 100 % miscibility with H_2O and appropriate polarity, as listed in Table 4, should be effective as washing solvent.

Table 4. Solvents that have a 100 % miscibility with H_2O and can be used as washing solvents.

Solvents	Boiling point (°C)	Viscosity (cPoise)	P [*]	Solubility in water (%w/w)
Acetone	56	0.32	5.1	100
Acetonitrile	82	0.37	15.8	100
Dimethylformamide	155	0.92	6.4	100
Dimethyl Sulfoxide	189	2	7.2	100
Dioxane	101	1.54	4.8	100
Ethanol	78	1.2	4.3	100
Methanol	65	0.6	5.1	100
n-propanol	97	2.27	4.0	100
Iso-propanol	82	2.3	3.9	100
Tetrahydrofuran	65	0.55	4.0	100

Polarity (P^{}) as defined in Snyder and Kirkland (Snyder, L. R., Kirkland, J. J. In Introduction to modern liquid chromatography, 2nd ed., John Wiley and Sons, New York, 1979; pp 248-250)

7. Further investigations

Characteristic density properties of an LDH prepared according to the invention (AMO-LDH) compared to a conventionally prepared LDH (C-LDH) were measured. Results can be taken from Table 5.

Table 5. Density Properties of AMO-LDHs, C-LDHs and Commercial LDHs.

LDH	Loose Bulk Density (g/mL)			Tap Density (g/mL)			Carr's Index			Formula of AMO-LDH-A	Formula of C-LDH
	AMO-LDH-A ¹	C-LDH ²	% Change	AMO-LDH-A ¹	C-LDH ²	% Change	AMO-LDH-A ¹	C-LDH ²	% Change		
Mg ₃ Al-SO ₄ -10	0.1	0.41	76	0.16	0.63	75	40	35	14	Mg _{0.75} Al _{0.25} (OH) ₂ (SO ₄) _{0.125} •0.55(H ₂ O)•0.13(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (SO ₄) _{0.125} •0.6(H ₂ O)
Mg ₃ Al-NO ₃ -10	0.15	0.95	84	0.22	1.2	82	32	22	45	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} •0.38(H ₂ O)•0.12(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} •0.57(H ₂ O)
Mg ₃ Al-Cl-10	0.18	0.29	38	0.26	0.44	41	35	35	0	Mg _{0.75} Al _{0.25} (OH) ₂ (Cl) _{0.2} •0.48(H ₂ O)•0.04(acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (Cl) _{0.2} •0.61(H ₂ O)
	AMO-LDH-A ¹	MG 62	% Change	AMO-LDH-A ¹	MG 62	% Change	AMO-LDH-A ¹	MG 62	% Change	Formula of AMO-LDH-A	Formula of MG 62
Mg ₃ Al-CO ₃ -10	0.14	0.46	70	0.2	0.64	68	35	29	20	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •1.36(H ₂ O)•0.17(Acetone)	NA

¹AMO-LDH-A is the LDHs with the formula of

$$[M^{z+}_{1-x}M'^{y+}_x(OH)_2]^{a+}(X^{n-})_{a/r} \cdot bH_2O \cdot c(AMO-solvent) \quad (1)$$

wherein M and M' are metal cations, z = 1 or 2; y = 3 or 4, 0 < x < 1, b = 0-10, c = 0-10, X is an anion, r is 1 to 3, a = z(1-x) + xy - 2, AMO-solvent (A=Acetone, M=Methanol)

²C-LDH is the LDHs with the formula of

$$[M^{z+}_{1-x}M'^{y+}_x(OH)_2]^{a+}(X^{n-})_{a/r} \cdot bH_2O \quad (2)$$

wherein M and M' are metal cations, z = 1 or 2; y = 3 or 4, 0 < x < 1, b = 0-10, c = 0-10, X is an anion, r is 1 to 3 and a = z(1-x) + xy - 2.

³MG 62 is the commercial hydrotalcite, PURAL MG 62 HT, from Sasol Ltd.

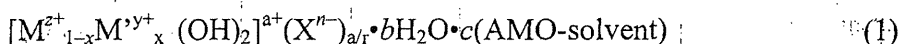
Further, thermal properties of inventive LDHs and conventional C-LDHs were measured. The results are summarized in Table 6.

Table 6. Thermal properties of AMO-LDHs and C-LDHs.

LDH	T1 (°C)			T2 (°C)			Formula of AMO-LDH-A	Formula of C-LDH
	AMO-LDH-A ¹	C-LDH ²	% Change	AMO-LDH-A ¹	C-LDH ²	% Change		
Mg ₃ Al-CO ₃ -12	187	205	-18	382	399	-17	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •1.76H ₂ O•0.45(Acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •2.83H ₂ O
Mg ₃ Al-CO ₃ -10	150	169	-19	340	424	-84	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •1.36H ₂ O•0.17(Acetone)	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •1.67H ₂ O
Mg ₂ Al-CO ₃ -10	181	187	-6	347	392	-45	Mg _{0.67} Al _{0.33} (OH) ₂ (CO ₃) _{0.125} •0.52(H ₂ O)•0.16(acetone)	Mg _{0.67} Al _{0.33} (OH) ₂ (CO ₃) _{0.125} •0.92(H ₂ O)
LDH	AMO-LDH-M ¹	C-LDH ²	% Change	AMO-LDH-M ¹	C-LDH ²	% Change	Formula of AMO-LDH-A	Formula of C-LDH
Mg ₃ Al-CO ₃ -12	191	205	-14	392	399	-7	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •0.44(H ₂ O)•0.11(methanol)	Mg _{0.75} Al _{0.25} (OH) ₂ (CO ₃) _{0.125} •1.67H ₂ O

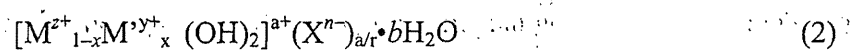
T1 and T2 are defined as the turning points in 1st derivative of the weight loss as a function of temperature {d(%Wt loss)/d(°C)} as measured by the TGA. (i.e. when 2nd derivative of the TGA is zero). These points indicate significant changes in heat flow and so mark out key changes to a material on heating.

¹AMO-LDH-A and AMO-LDH-M are the LDH with the formula of



wherein M and M' are metal cations; z = 1 or 2; y = 3 or 4, 0 < x < 1, b = 0-10, c = 0-10, X is an anion, r is 1 to 3 and a = z(1-x) + xy - 2. AMO-solvent (A=Acetone, M=Methanol)

²C-LDH is the LDH with the formula of



wherein M and M' are metal cations, z = 1 or 2; y = 3 or 4, 0 < x < 1, b = 0-10, c = 0-10, X is an anion, r is 1 to 3 and a = z(1-x) + xy - 2.

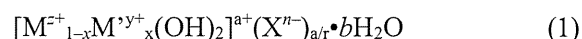
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The features disclosed in the foregoing description, in the claims and in the accompanying drawings may both separately or in any combination be material for realizing the invention in diverse forms thereof.

CLAIMS

1. A process for modifying a layered double hydroxide (LDH), the process comprising,

a. providing a water-wet layered double hydroxide of formula:



wherein M and M' are metal cations, $z = 1$ or 2 ; $y = 3$ or 4 , x is 0.1 to 1 , preferably $x < 1$, more preferably $x = 0.1 - 0.9$, b is 0 to 10 , X is an anion, r is 1 to 3 , n is the charge on the anion X and a is determined by x , y and z , preferably $a = z(1-x)+xy-2$;

b. maintaining the layered double hydroxide water-wet;

c. contacting the water-wet layered double hydroxide with at least one organic solvent, the solvent being miscible with water and having a solvent polarity (P') in the range 3.8 to 9 , wherein contacting the water-wet layered double hydroxide with the solvent comprises dispersing the layered double hydroxide in the at least one solvent; and filtering and then washing the resulting layered double hydroxide with the at least one organic solvent.

2. The process as claimed in claim 1, wherein M is Mg, Zn, Fe, Ca or a mixture of two or more thereof.

3. The process as claimed in any one of the preceding claims, wherein M' is Al, Ga, Fe or a mixture of Al and Fe.

4. The process as claimed in any one of the preceding claims, wherein z is 2 and M is Ca, Mg, or Zn.

5. The process as claimed in any one of the preceding claims wherein M' is Al.

6. The process as claimed in any one of the preceding claims, wherein M is Zn, Mg or Ca, and M' is Al.

7. The process as claimed in any one of the preceding claims, wherein X is selected from halide, inorganic oxyanions, anionic surfactants, anionic chromophores, and/or anionic UV absorbers.
8. The process as claimed in claim 7, wherein the inorganic oxyanion is carbonate, bicarbonate, hydrogenphosphate, dihydrogenphosphate, nitrite, borate, nitrate, sulphate or phosphate or a mixture of two or more thereof.
9. The process as claimed in claim 7, wherein the inorganic oxyanion is carbonate, bicarbonate, hydrogenphosphate, dihydrogenphosphate, nitrite, nitrate, sulphate or phosphate or a mixture of two or more thereof.
10. The process as claimed in any one of the preceding claims, wherein the at least one solvent is selected from acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, dioxane, ethanol, methanol, n-propanol, 2-propanol, tetrahydrofuran or a mixture of two or more thereof.
11. The process as claimed in any one of the preceding claims, wherein the at least one solvent is selected from acetone or ethanol.
12. The process as claimed in any one of the preceding claims, further comprising a step of drying the LDH obtained in step c.
13. The process as claimed in any one of the preceding claims, further comprising subjecting the layered double hydroxide obtained in step c to a thermal treatment, preferably calcination.
14. A layered double hydroxide, prepared according to the process of any of the preceding claims, wherein the layered double hydroxide has a BET pore volume (N_2) in a range of $0.5 \text{ cm}^3/\text{g}$ to $3.5 \text{ cm}^3/\text{g}$ and an apparent density of $0.8 \text{ g}/\text{cm}^3$ or lower.
15. The layered double hydroxide as claimed in claim 14 having a specific surface area (N_2) of greater than $155 \text{ m}^2/\text{g}$.
16. The layered double hydroxide as claimed in claim 14 or 15, wherein the layered double hydroxide has specific surface area (N_2) of $170 \text{ m}^2/\text{g}$ - $700 \text{ m}^2/\text{g}$.

17. The layered double hydroxide as claimed in claim 14 or 15, wherein the layered double hydroxide has specific surface area (N_2) of $250 \text{ m}^2/\text{g}$ - $650 \text{ m}^2/\text{g}$.
18. The layered double hydroxide as claimed in claim 14 - 17, wherein the layered double hydroxide has a de-aggregation factor greater than 2.
19. The layered double hydroxide as claimed in any one of claims 14 - 18, which has been subjected to a thermal treatment, preferably calcination.