Water adsorbancy of high surface area layered double hydroxides (AMO-LDHs)†

Chunping Chen, Kanittika Ruengkajorn, Jean-Charles Buffet and Dermot O’Hare*

Understanding the water adsorbancy of highly dispersed, high surface area layered double hydroxide (LDH) is of great importance as it directly relates to their hydrophobicity and subsequent use as additives in LDH-polymer nanocomposites. In this study, we have investigated the water vapour uptake response of highly dispersed, high surface area aqueous miscible organic-LDHs (AMO-LDHs) in two relative humidity atmospheres (RH99 and RH60) at 20 °C. We observed that AMO-Mg3Al–CO3 and AMO-Zn2MgAl–CO3 exhibited very high water vapour uptake in an RH99 atmosphere at 20 °C (56 wt% and 20 wt% for Mg3Al–CO3 and Zn2MgAl–CO3 LDH respectively after 120 h). The crystallinity in both ab-plane and c-axis of the LDHs increased with increasing exposure uptake. The water vapour adsorption capacity of the AMO-LDHs can be dramatically reduced by treatment with stearic acid.

Experimental

Materials

Magnesium nitrate hydrate [Mg(NO3)2·6H2O, >99.0%], Aluminium nitrate nonahydrate [Al(NO3)3·9H2O, >98%], stearic acid and zinc nitrate hexahydrate [Zn(NO3)2·6H2O, 99%] were purchased from Sigma-Aldrich. Sodium carbonate (Na2CO3, 

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99.6%) was purchased from Acros Organics. Nitric acid (HNO₃, 70%) and Sodium hydroxide (NaOH) was purchased from Fisher Chemicals.

Synthesis of AMO-Mg₃Al-CO₃-LDH

The metal precursor solution containing 19.2 g Mg(NO₃)₂·6H₂O, 9.38 g Al(NO₃)₃·9H₂O and 100 mL water was added drop-wise into Na₃CO₃ base solution (100 mL water with 5.3 g Na₂CO₃, pH is adjusted to be 10 by 10% HNO₃ solution) within 1 h. The pH was kept constant around 10.0 by drop wise addition of a 4.0 M NaOH solution. After stirring for 16 h at room temperature, the mixture was filtered and washed with deionised (DI) water until pH 7. The wet LDH solid was dispersed in ethanol (1000 mL) followed by re-dispersion in fresh ethanol (600 mL) and stirred at room temperature for 4 h. The AMO-LDH was then isolated by filtration, washed with 400 mL of ethanol and dried under vacuum overnight. AMO-Mg₃Al-CO₃-LDH has the composition [Mg₀.75Al₀.25(OH)₂](CO₃)₀.125·0.5(H₂O)·0.04(ethanol).

Synthesis of AMO-Zn₂MgAl-CO₃-LDH

The general procedure is shown as following: the metal precursor solution containing 6.4 g Mg(NO₃)₂·6H₂O, 14.68 g Zn(NO₃)₂·6H₂O, 9.38 g Al(NO₃)₃·9H₂O and 100 mL water was added drop-wise into Na₃CO₃ base solution (100 mL water with 5.3 g Na₂CO₃) within 1 h. The pH was kept constant around 10.0 by drop wise addition of a 4.0 M NaOH solution. After stirring for 16 h at room temperature, the mixture was filtered and washed with deionised (DI) water until pH 7. The wet solid LDH was treated with ethanol by using AMO method. The AMO-LDH was isolated by filtration and dried under vacuum overnight. AMO-Zn₂MgAl-CO₃ has the composition [Zn₀.5Mg₀.25Al₀.25(OH)₂](CO₃)₀.125·0.06(H₂O)·0.031(ethanol).

Water vapour uptake measurements

The water vapour uptake measurements were carried out according to a modified Callahan’s method. The water vapour uptake was measured in a sealed box at room temperature (20 °C). The relative humidity RH99 and RH60 were generated by saturated solution of KNO₃ and Mg(NO₃)₂ respectively. The detailed measurement procedures are shown in the ESI.

Synthesis of stearic acid modified Zn₂MgAl-CO₃ AMO-LDH

Various amounts of stearic acid (0.25, 0.5, 1 and 2 mmol g⁻¹ LDH) were dissolved in 300 mL of ethanol. 3 g of AMO-Zn₂MgAl-CO₃ was introduced into a stearic acid solution and mixed using a homogeniser for 30 minutes. The obtained suspension was then refluxed at 80 °C for 16 h. The solid was collected by filtration and washed with 600 mL of ethanol followed by drying in an oven at 150 °C for further characterisations and testing. The obtained samples are named as ZMA-Sax where ZMA is AMO-Zn₂MgAl-CO₃ and x the amount of stearic acid (SA).

Results and discussion

AMO treatment

AMOST treatment of Mg₃Al-CO₃ and Zn₃MgAl–CO₃ produces high surface area and highly dispersed AMO-LDHs with the chemical composition [Mg₀.75Al₀.25(OH)₂](CO₃)₀.125·0.5(H₂O)·0.04(ethanol) and [Zn₀.5Mg₀.25Al₀.25(OH)₂](CO₃)₀.125·0.06(H₂O)·0.031(ethanol) for AMO-Mg₃Al-CO₃ and AMO-Zn₃MgAl-CO₃ respectively (Table S1†). N₂ BET studies show that the specific surface areas for AMO-Mg₃Al-CO₃ and AMO-Zn₃MgAl-CO₃ are 376 and 115 m² g⁻¹, respectively. These values are 5-10 times the values that would be measured for a conventionally prepared LDHs using co-precipitation from water.

Time-dependent water vapour uptake response

The water content of AMO-Mg₃Al-CO₃ and AMO-Zn₃MgAl–CO₃ after drying in vacuum overnight was determined using TGA (Fig. S1†). Both AMO-Mg₃Al-CO₃ and AMO-Zn₃MgAl–CO₃ release high water/AMO solvent corresponding to 21.6 and 11.7 wt% based on a dry weight, respectively. The time-dependence of water vapour uptake was measured in different relative humidity atmospheres. As shown in Fig. 1(a), AMO-Zn₃MgAl-CO₃ adsorbed less than 5 wt% water upon exposition to a low relative humidity, RH60. However, when exposed at high humidity RH99 (Fig. 1(b)), the water vapour uptake dramatically increased up to 20 wt%. AMO-Mg₃Al-CO₃ (Fig. 1(c)) can adsorb water vapour continuously up to 56 wt% based on a dry weight in RH99 humidity over 96 h. This is corresponding to 36 wt% of EMC (equilibrium water content) which belongs to the Class IV (very hygroscopic) according to Callahan’s hygroscopicity classification. We attribute the higher water vapour uptake to the higher surface area for AMO-Mg₃Al-CO₃ (376 m² g⁻¹) compared to AMO-Zn₃MgAl-CO₃ (115 m² g⁻¹). Particle size was also shown to affect water vapour uptake response. As shown in Fig. S2, both platelet samples have similar surface areas, but the sample with the smaller size...
platelets exhibits to higher water vapour uptake owing to their higher surface energy which favours forming hydrogen bonding with water molecules.

Weight losses of AMO-Zn$_2$MgAl–CO$_3$ before and after water vapour adsorption were also measured using TGA as shown in Fig. S3† and collated in Table S2.† Weight loss below 70 °C is mainly attributed to the release of the interparticle water$^{23}$ and AMO-solvent.$^{25}$ The weight loss between 70–180 °C is due to the loss of surface bound water and/or AMO solvent and possibly partially de-hydroxylation.$^{22,28}$ We found that AMO-Zn$_2$MgAl–CO$_3$ contained very low quantities of interparticle pore water and AMO-solvent (1.2 wt% of dry LDH). However, after exposure to at RH99 atmosphere at 20 °C the interparticle pore water dramatically increases to 9.5 and 14.6 wt% after 24 and 72 h, respectively. The water molecules might not only condense in the interparticle space but also diffuse into the surface and the interlayer as observed with amount of surface water increasing from 10.5 to 13.1 wt% after 72 h in RH99.$^{24}$

These results are consistent with those found using XRD. Fig. S4 and Table S3† show no apparent changes in lattice parameters (a and c) for AMO-Zn$_2$MgAl–CO$_3$ and AMO-Mg$_3$Al–CO$_3$ after water vapour adsorption. However, the broadness of both (003) and (110) Bragg reflections decrease after water vapour adsorption. The mean crystalline domain length (CDL) (Table 1) calculated using the Scherer equation reveals that the crystallinity along c-axis and in the ab-plane gradually increases with exposure time. Along the c-axis, the crystalline domain length increases after water vapour adsorption for 120 h from 7.9 to 8.4 nm and 2.9 to 4.6 nm for AMO-Zn$_2$MgAl–CO$_3$ and AMO-Mg$_3$Al–CO$_3$, respectively.

We also observed that the crystalline domain length (CDL) of AMO-LDH samples in the ab-plane dramatically increases with increased water vapour exposure as shown in Table 1 and Fig. 2. The CDL is calculated to be more than 3 and 2 nm larger than that of anhydrous AMO-Zn$_2$MgAl–CO$_3$ and AMO-Mg$_3$Al–CO$_3$ respectively. These findings may be the contributing factor to the observed decrease of the surface area as shown in Fig. S5,† suggesting the possibility for rearrangement of the LDH structure via dissolution-recrystallization of metal hydroxide layers during the water vapour adsorption.

FTIR is of great interest to study the adsorbed water molecules in the AMO-LDH and their interaction with AMO-LDH structure. Fig. S6† shows a broad absorption between 400–1100 cm$^{-1}$ which is assigned to the O–M–O bending, M–O stretching and deformation, M–OH deformation and $n_1$ and $n_2$ vibrations of CO$_3$$^{2-}$. The band at 1367 cm$^{-1}$ is ascribed to the $n_3$ of the CO$_3$$^{2-}$ in a symmetric environment. The band at 1639 cm$^{-1}$ can be assigned to an interlayer water bending mode.$^3$ This band becomes more prominent after exposure in an RH99 atmosphere. The broad absorbance in the range of 2800–3800 cm$^{-1}$ is due to stretching of H-bonded OH groups. The band becomes broader with increasing exposure time. By Gaussian peak shape deconvolution on the absorbance mode, more detailed information can be revealed as shown in Fig. 3. There are three main absorption bands (B1: 3052–3270 cm$^{-1}$, B2: 3279–3410 cm$^{-1}$, B3: 3470–3530 cm$^{-1}$), which are assigned to the carbonate, H$_2$O/H$_2$O–H$_2$O bridging mode, the hydrogen bonding of water in highly structured environment in the interlayer galleries and the M–OH stretching with water molecules, respectively.$^{1,29}$ All the –OH stretching bands are shifted to higher wavenumber, which might be due to the stronger hydrogen bonding with a larger concentration of water molecules.

### Table 1: Crystalline domain length of AMO-LDHs before and after exposure to atmosphere with RH99 at 20 °C

| Exposing time (h) | c-axis (nm) | ab-plane (nm) |
|------------------|-------------|---------------|
| Zn$_2$MgAl–CO$_3$–AMO-LDH | 7.9  | 59.5 |
| 5                | 8.0  | 60.2 |
| 24               | 8.2  | 61.6 |
| 72               | 8.2  | 62.5 |
| 120              | 8.4  | 62.9 |
| Mg$_3$Al–CO$_3$–AMO-LDH | 2.9  | 20.5 |
| 120              | 4.6  | 22.6 |

$^a$ Crystalline domain length (CDL) along c-axis is calculated from Scherer equation using full width at half-maximum (FWHM) of the (003) Bragg reflection; the CDL in ab-plane is calculated from Scherer equation using full width at half-maximum (FWHM) of the (110) Bragg reflection.

**Inhibition of water vapour adsorbance**

As discussed above, LDHs, especially those with high surface areas and small particle sizes, exhibit very high water saturation content and a rapid water vapour adsorption rate. We have investigated simple methods to alleviate this issue. Stearic acid is commonly used as a surface modifier for fillers such as calcium oxide, alumina, and magnesium hydroxide to reduce the water vapour adsorption and increase their compatibility with non-polar materials.$^{31-34}$ Traditionally, LDHs are modified with fatty acids (in their salt form), requiring deprotonation.
before use. In this study, the stearic acid was introduced to the AMO-LDHs by post treating in ethanol slurry at 80°C.

The XRD data for AMO-Zn$_2$MgAl–CO$_3$ before and after treatment with different loadings of stearic acid are shown in Fig. 4. The XRD of samples with low stearic acid loadings are consistent with single phase pure LDH exhibiting a series of (00l) Bragg reflections and two well-separated (110) and (113) Bragg reflections at $2\theta = 60^\circ$ and $62^\circ$, that data indicates there is no free crystalline stearic acid present in these samples. The interlayer spacing ($d$(003)) remained the same as the pristine LDH, confirming that the stearic acid is grafted on the surface of LDH instead of intercalating into the interlayer galleries. When the stearic acid loading is higher than 2 mmol g$^{-1}$-LDH, additional reflections at lower $2\theta$ values can be observed. These features could be assigned to crystalline stearic acid. The amount of stearic acid grafted onto the LDH can be is estimated from the TGA data (Table S4†). At low stearic acid treatment ratios most of it is grafted onto the LDH. Dosing the LDHs with 1.0 mmol stearic acid per gram LDH (28 wt%) only resulted in 11 wt% stearic incorporation (by TGA). Dosing the LDHs with 2.0 mmol stearic acid per gram LDH (56 wt%) resulted in 27% incorporation but with substantial crystallisation of stearate acid.

Fig. 5 shows the FTIR spectra of AMO-Zn$_2$MgAl–CO$_3$ modified with different loadings of stearic acid. The characteristic bands assignable to stearic acid can be found in all modified samples at 2920, 2852, 1545 and 1472 cm$^{-1}$, these features correspond to CH$_2$ antisymmetric and symmetric stretching, COO$^-$ antisymmetric stretching and a CH$_2$ scissor mode, respectively. These absorbances grow in intensity with increasing stearic acid loading.

Furthermore, the H$_2$O bending mode at 1639 cm$^{-1}$ disappears and the –OH stretching band in the region of 2800–3800 cm$^{-1}$ becomes much lower in intensity than a pristine LDH. The data indicates that the stearic acid treatment imparts hydrophobicity and so can effectively prevent water molecules penetrating the LDH layers. Stearic acid commonly displays a carbonyl stretching band due to dimerisation at 1698 cm$^{-1}$ instead of a carboxylate band at 1575 cm$^{-1}$.

In this study, a carbonyl band is not observed in all stearic acid modified samples. We believe that the stearic acid is deprotonated by the basic LDH surface and so dimerisation is inhibited. Similar behaviour has been observed for other inorganic basic materials such as Mg(OH)$_2$ and CaCO$_3$.31,32,35
The solid state $^{27}$Al NMR spectroscopic data are shown in Fig. S7. AMO-Zn$_2$MgAl–CO$_3$ exhibit a resonance at ca. –15 ppm typical of octahedral Al sites ($O_h$) within the LDH. After surface modification with stearic acid, an extra low intensity resonance at ca. 50 ppm (tetrahedral Al sites ($T_d$)) can be observed, indicating that some Al$_3^+$ ions migrate from octahedral sites to complex with stearate anions. The ratio of octahedral to tetrahedral Al$^{3+}$ sites was calculated by integrating the NMR resonances and are collated in Table S5.† The Al$^{3+}$ $T_d$: $O_h$ site ratio increases from 100 : 0.5 to 100 : 15 after stearic acid treatment with a loading of 0.25 mmol g$^{-1}$-LDH. This data confirms that stearate has successfully been grafted onto the LDH surface. This conclusion is also consistent with the $N_2$ BET surface area (Fig. S8†) and pore volume (Fig. S9†) results. Both the $N_2$ specific BET surface area and pore volume slightly decrease with increasing loading with stearic acid up to 1 mmol g$^{-1}$-LDH (attributed to surface coverage of the modifier). We observe that the particles become significantly aggregated if the loading reaches 2 mmol g$^{-1}$-LDH; resulting in a dramatic drop in surface area and pore volume.

The water contents of all samples were measured using TGA at 180 °C. The water content of AMO-Zn$_2$MgAl–CO$_3$ is ca. 11.7 wt% of dry basis and after thermal treatment at 150 °C is still 2.4 wt%. For stearic acid treated samples, the water content dramatically reduces from 2.4 to 0.9 wt% as a function of stearic acid loading from 0 to 2 mmol g$^{-1}$-LDH. The water vapour uptake response of AMO-Zn$_2$MgAl–CO$_3$ after surface treatment with stearic acid was investigated by exposing the modified samples to a RH99 atmosphere at 20 °C.

As shown in Fig. 6, the stearic acid modified AMO-Zn$_2$MgAl–CO$_3$ has a much reduce hydrophilicity with dramatically reduced water vapour affinity. With a stearic acid loading of only 0.25 mmol g$^{-1}$-LDH, the water vapour uptake after 96 h can be reduced from 34 to 18 wt% of dry LDH. Further increasing the stearic acid loading up to 2 mmol g$^{-1}$-LDH can effectively reduce the saturation water capacity below 8 wt% of dry LDH after 150 h. These results suggest that the use of stearic acid for surface modification on LDH can provide a viable strategy to obtain LDH with less water content and low water vapour uptake, which is promising in the water sensitive applications.

**Conclusions**

In summary, we have investigated the water vapour uptake behaviour of a new generation of aqueous miscible organic layered double hydroxides. We found that the as prepared AMO-Zn$_2$MgAl–CO$_3$ and AMO-Mg$_2$Al–CO$_3$ exhibit high saturation water content of 21.6 and 11.7 wt% (on dry basis) respectively. The AMO-LDH with highest surface area and/or smallest particle size exhibits the greatest water vapour adsorption capacity. The majority of the adsorbed water was thought to reside in the interparticle region while some resides on the surface and in the interlayer galleries of LDH. The crystallite domain length in both $ab$-plane and $c$-axis increased with increasing water vapour exposure time. A simple surface modification method using stearic acid dramatically reduces the water vapour affinity an uptake rate, which should enable these highly dispersed materials to be used as additives in polymer composites and/or in pharmaceutical delivery systems.

**Conflicts of interest**

There are no conflicts to declare.

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