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Layered Double Hydroxides (LDHs) based Mixed Metal Oxides (MMOs): Development of Novel Structured Sorbents for CO₂ Capture Applications

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Abstract

Layered double hydroxide (LDHs) based mixed metal oxides (MMOs) are widely studied as the medium to high temperature (200-400 °C) CO₂ capture sorbents. However, most of the studies are carried out using the powdered samples. In order to upgrade these sorbents for industrial scale CO₂ capture, it is important move away from the powdered form and develop structured sorbents. Moreover, CO₂ capture properties of these sorbents needs to be improved in terms of capture capacity and cycling stability. Here we are utilizing a modified amide hydrolysis method to improve the CO₂ capture capacities of LDHs based MMOs. Subsequently, aqueous exfoliation coupled with freeze-drying technique was utilized to develop LDHs based novel MMOs. Exfoliated LDH nano sheets were pelletized (2 mm) to circumvent the challenges associated with powder samples when used in industrial scale applications. The obtained pellets have an average crushing load of 11.1 N and 4.3 MPa of compressive strength, indicating their good mechanical stability. The MMOs pellets showed a narrow distribution of pores (8-10 nm) with very good surface area (264 m²/g) and pore volume (1.27 cm³/g). They also had much improved CO₂ capture capacities at ambient pressure and both, low (2.17 mmol/g, 30 °C) and medium temperature (1.43 mmol/g, 200 °C), compared to previously reported pristine MMOs powder samples. The pelletized structured sorbents also outperformed commercial LDH based pellets by several fold.

Keywords: Layered double hydroxides, aqueous exfoliation, freeze drying, mixed metal oxides, structured sorbents and CO₂ capture.

1. Introduction

Layered solids stand apart from other class of materials and are unique in many ways¹. Their layer-interlayer Chemistry, anisotropic bonding and easily tuneable composition and exceptional properties made them highly sought in many applied areas²⁻⁷. Among the layered solids, layered double hydroxides (LDHs) having the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{-x/n})_x \cdot yH_2O$ {where, $M^{2+} = Mg, Co, Ni, Ca, Zn, M^{3+} = Al, Fe, Ga, A =$ anion (organic or inorganic ions), $0.15 \geq x \leq 0.33$ and $0.5 \geq y \leq 1.0$ } are gaining prominence in many industrially relevant applications in the recent past⁸. Their physico-chemical properties, wide and varied composition, ease of preparation and handling, make them promising candidate materials in sorption and catalysis, as fillers in polymer nanocomposite, as electrodes in electro/photochemical reactions and as drug delivery carriers⁹⁻¹⁴. LDHs and mixed metal oxides (MMOs) derived from them are also employed as CO₂ capture sorbents¹⁵⁻²⁰. However, CO₂ capture performance of LDHs and their MMOs needs significant improvement in terms of capture capacity and cycling stability before considering them for industrial scale CO₂ capture application²¹. Given the raising atmospheric temperatures and imminent threat of global warming, it is of utmost important to speed up the development of better CO₂ capture sorbent materials including LDHs²²⁻²⁵.

Efforts to increase the CO₂ capture performance of LDH based sorbents is an ongoing research²⁶. Various strategies like change in the layer composition, interlayer anion, synthesis method and varying the synthesis parameters have been considered²⁷⁻²⁹. LDH based MMOs are also doped with various dopants to increase the capture capacity and supported with various supports to increase the cycling stability^{30,31}. To exploit the full potential for CO₂ capture of LDHs and their MMOs it is necessary to go beyond the surface and access its interlayer. Exfoliation is a process in which metal hydroxides are pried apart as thinner tactoids of nanometre dimensions³². This exfoliation process leads to materials with higher surface area and provides better accessibility to the interlayer. Exfoliation is a well-known phenomenon for layered solid such as graphite and aluminosilicate clays³³. However, exfoliation studies of LDHs have been only reported recently compared to the other class of layered solids³⁴⁻³⁶. It is shown that modifying the layer charge and interlayer anion of the LDHs is crucial in realizing the successful exfoliation³⁷. Various anions have been used to exfoliate LDHs in various

organic as well as in aqueous solvents³⁷⁻³⁹. From the environmental and sustainability point of view, it is always better to use aqueous solvents^{36,38}. The extent of exfoliation also depends on the synthesis method to some extent. Interestingly, the exfoliated LDHs are restacked to their original form once the solvent is removed from the exfoliated system. Therefore, it is important to retain the LDH layers in the exfoliated state if a high surface area and easy accessibility to interlayer space are to be achieved.

Generally, LDHs and their derived MMOs are powder samples having wide shapes and varied particle sizes, ranging from couple of nano meters to few microns.^{26,40} These irregular and widely dispersed particle sizes of MMOs pose operational issues at large scale industrial applications. The pressure drop and mass transfer issues are commonly encountered while using powder samples.⁴¹ Apart from improving the CO₂ capture capacity and cycling stability, overcoming the particle size issue is a very important aspect on the development of CO₂ capture sorbents. There are efforts to address these issues in other high temperature sorbents like CaO and Li₄SiO₄ by developing structured forms of the materials.⁴²⁻⁴⁶ However, these issues have been largely ignored for LDH based MMOs sorbents.^{47,48}

Here, we are reporting the synthesis of acetate intercalated Mg-Al LDH by modified acetamide hydrolysis and by employing the metal hydroxides as precursors⁴⁹. The high hydration enthalpy of the intercalated acetate ion⁵⁰ was exploited to realize the aqueous exfoliation of the resultant LDH. The exfoliated LDH was then freeze dried to retain the layers in the exfoliated state. The exfoliated freeze-dried LDH was pelletized and tested as a CO₂ capture sorbent at ambient pressure and temperatures ranging from 30 to 300 °C under CO₂ rich and lean conditions (86 and 14% CO₂).

2. Materials and Methods

2.1. Synthesis; All the chemicals, Mg(OH)₂, Al(OH)₃, acetamide were purchased from Sigma Aldrich and used as received. Deionised water (18. MΩ.cm resistivity, Millipore water purification system) was used throughout the experiment. LDHs with Mg/Al = 4 ratio was synthesized (acetamide to metal ion ratio, acetamide/M = 5) In a typical experiment, stoichiometric amounts of Mg(OH)₂, Al(OH)₃ and acetamide were taken in 100 mL of water. The reaction mixture was stirred at room temperature for an hour to get good mixing of the starting precursors. The resultant reaction mixture was transferred to Teflon lined vessel and hydrothermally treated at 180 °C for 24 h. The resultant Mg-Al-acetate LDH was recovered by filtration followed by drying at 65 °C overnight. The exfoliation of the resultant Mg-Al-acetate

LDH was carried out in water. In a typical experiment, 100 mg of Mg-Al-acetate LDH was dispersed in 100 mL of water. The resultant suspension was slowly stirred at RT for 48 h on a magnetic stirrer plate. The exfoliated colloidal suspension of the Mg-Al-acetate LDH was freeze-dried using liquid N₂ and subsequently dried in the freeze dryer. The freeze-dried Mg-Al-acetate LDH powder sample was pelletized into 2 mm pellets using a pellet press. To compare the results of CO₂ capture capacity of the developed pellets, a commercial LDH sample PURAL Mg70 pellets (Sasol) was employed.

2.2. Characterization: Powder X-ray Diffraction (PXRD) patterns of Mg-Al-acetate LDH and its derived MMOs were recorded on a Bruker D8 Advance power diffractometer, using Ge-monochromated Cu-K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$) from a sealed tube, operating at 40kV and 40mA with a LynxEye linear detector in reflectance mode. Data was collected over angular range of 5-70 $^{\circ}2\theta$ with a step size of 0.009 $^{\circ}$ over one hour span. The Fourier Transform Infrared spectra (FTIR) of sample was measured using Perkin Elmer spectrometer in ATR (Attenuated total reflectance) mode (4000 to 600 cm^{-1}). Elemental analysis of Mg²⁺ and Al³⁺ (ICP-OES) was carried out by atomic emission technique using Perkin Elmer Optima 5300DV. A mixture of concentrated nitric acid and hydrochloric acid in the ratio of 1:3 was used to dissolve the LDH. The solution was diluted 20 times prior to analysis. The C, H and N analysis on the LDH samples was carried out by taking approximately 3 mg of sample was placed in a tin capsule and combusted in a high oxygen environment at 950 $^{\circ}\text{C}$ using an Exeter Analytical CE-440 elemental analyser calibrated with acetanilide. Surface area analysis of the sample was carried out by gas adsorption technique (N₂, 77 K) using Micromeritics ASAP 2020 instrument. Prior to the gas adsorption measurement, the sample was degassed for 3 h at 150 $^{\circ}\text{C}$. The surface morphology of the sample is characterized by scanning electron microscopy (SEM) using FEI Quanta FEG SEM. Transmission electron microscopy (TEM) images are acquired using a FEI Titan Themis instrument equipped with a FEI SuperX EDX detector.

Atomic force microscopy (AFM) data was collected by a Dimension Icon[®] AFM (Bruker, Santa Barbara, CA) using the PeakForce Tapping[®] scanning mode at 20 $^{\circ}\text{C}$ with a ScanAsyst-Air[®] probe (Bruker, Santa Barbara, CA) and a nominal spring constant $k = 0.4 \text{ N m}^{-1}$ and nominal tip radius of 2 nm. One drop (10 μL) of the solution was placed on silicon wafer and was left to dry for a few minutes. All the images were analysed using NanoScope Analysis 1.9 software (Bruker, Santa Barbara, CA). The height images were corrected by first-order flattening.

Mechanical characterisation of the exfoliated MMOs pellet samples was carried out using the Mach-I system (Biomomentum Inc, Laval, Canada). Specifically, uniaxial compression using

a flat metal plate was conducted on 16 samples, placed with their longitudinal axis aligned with the compressive axis, with an applied displacement sufficient to crush the samples. The geometrical parameters of the cylindrical samples were first measured, followed by the compression test. The critical force and strength^{42,44} required to crush the sample leading to apparent structural failure, were investigated as a means to evaluate the mechanical behaviour of the samples.

2.3. CO₂ capture studies: Thermal analysis and CO₂ capture studies were performed using a thermogravimetric analyser (TA Instruments, Discovery series TGA 5500). To evaluate the CO₂ capture capacities, pristine 2 mm pellets of exfoliated Mg-Al-acetate LDHs were used instead of preformed MMOs to avoid the CO₂ contamination. Freshly prepared 2 mm pellets of exfoliated LDH were loaded into a platinum pan and decomposed under inert atmosphere (using 100 mL/min N₂, 4h, 400 °C, 10 °C/min). Once the decomposition is over, temperature was brought back to the desired capture temperature and CO₂ gas was switched on (for 2 h) to test the uptake capacity of the resultant MMOs pellets. The CO₂ capture capacity of resultant MMOs pellets was evaluated under two different CO₂ concentrations of 86 and 14 % (mixed with N₂) and at 4 different temperatures (30, 200, 250 and 300 °C). The MMOs pellets of commercial LDH sample PURAL Mg70 were generated and their CO₂ capture capacities tested by employing the same experimental conditions as the one used for exfoliated LDH samples. For comparison, the CO₂ capture capacity of as prepared Mg-Al-acetate LDH pellets was also measured (at 200 °C under 86 % CO₂) by employing the same experimental conditions as the ones used for exfoliated LDH samples. The CO₂ cycling stability of the exfoliated/freeze dried MMOs was carried out at two different temperatures (30 and 200 °C) under 14 % CO₂. The adsorption step at 30 °C was conducted as before (2h), and the regeneration of the carbonated sample was carried out using N₂ gas at 150 °C (2h, 10 °C/min). Similarly, adsorption at 200 °C was carried out for 2h and the regeneration was conducted using N₂ gas at 400 °C (2h, 10 °C/min).

3. Results and Discussion

The metal contents of the resultant compound were determined by ICP-OES and the anion content was established using CHN analysis. The ICP-OES analysis showed a Mg/Al ratio of 3.54 and CHN analysis showed 6.5 wt % of C content for the synthesized LDH. We arrived at

an empirical formula of the resultant compound by combining the results of the chemical analysis as follows; $[\text{Mg}_{0.78} \text{Al}_{0.22} (\text{OH})_2] (\text{CH}_3\text{COO})_{0.22} \cdot 0.5 \text{H}_2\text{O}$. The PXRD pattern of the synthesized Mg-Al-acetate LDH is shown in **Figure S1**. It shows a first basal reflection at 12.40 Å (7.12 °2θ) and second and third basal reflections at 6.31 (14.01) and 4.17 Å (21.29 °2θ), respectively. LDH also shows the 2D reflection corresponding to (110) plane at 1.51 Å (60.98 °2θ). In addition, it shows sawtooth shaped reflection at 2.59 Å (34.50 °2θ), which is characteristic of turbostratically disordered interlayer region⁵⁰. Basal reflections indicate that the acetate ion has fully hydrated in the interlayer³⁸. Intercalation of acetate ion in the interlayer of Mg-Al LDH was further characterized by FTIR (**Figure S2**). The Mg-Al-acetate LDH shows strong vibrations at 1556 and 1414 cm⁻¹, which correspond to antisymmetric and symmetric stretching vibrations of the carboxylate ion, respectively. The broad vibration centered around 3400 cm⁻¹ corresponds to the hydrogen bonded hydroxyl ion⁵¹.

Carboxylate ions including acetate have large hydration enthalpy and this helps in growing the hydration sphere around the central ion⁵⁰. When the acetate intercalated LDHs is immersed in water, due to its high hydration enthalpy, acetate ion drives water molecules into the interlayer space and grows its hydration sphere. The continuous growth of hydration sphere around the acetate ion swells the interlayer space and weakens the coulombic attraction between the successive hydroxide sheets leading to the swollen phase (as depicted in **Figure S3b**). The continuous hydration of the swollen phase leads to the loss of registry between the successive metal hydroxide layers and subsequent exfoliation (as depicted in **Figure S3c**).

In addition to the interlayer anion, the charge on the metal hydroxide layer also plays an important role in achieving the aqueous exfoliation. The higher the substitution of Al³⁺ (greater x values) into the hydroxide layer, the higher the positive charge on the layer, and that results in greater coulombic attraction between the layer-interlayer. LDHs with values of x greater than 0.25 have failed to exfoliate due to the increasing layer-interlayer attraction.³⁸ Hence, the target Mg-Al-acetate LDH with Mg/Al = 4 (x = 0.2) for the present study. Aqueous exfoliation of Mg-Al-acetate LDH was carried out as described in the experimental section. The exfoliated colloidal suspension was stable for several weeks without any solid residue at the bottom of the container. The complete exfoliation and the stability of the exfoliated colloidal suspension was studied by a light scattering (Tyndall effect)³² experiment, as shown in **Figure S4**. The light scattering (Tyndall effect) is seen only when the light scattering particles (exfoliated

hydroxide sheets) dispersed in an otherwise light transmitting medium (water in the present case) show diameters in the nano dimension. The observation of the Tyndall effect by the colloidal suspension (**Figure S4**) confirms the exfoliation of acetate intercalated LDH into the hydroxide sheets having nanometre dimensions.

To retain the LDH in the exfoliated state, the exfoliated colloidal suspension was freeze-dried using liquid N₂ and subsequently dried in a freeze drier. **Figure 1** shows the photographic comparison of the sample before and after exfoliation coupled with freeze-drying. The sample present in the containers (a) and (b) (**Figure 1**) was obtained from exfoliation of the sample in the container (c) (**Figure 1**). The significant increase in sample volume after the exfoliation compared to the pristine sample is evident in **Figure 1**. This provides direct evidence of the beneficial effect of exfoliation on the volume expansion of the sample. The exfoliated-freeze-dried sample was further characterized with TEM (**Figure 2a & b**) to determine the thickness of the exfoliated hydroxide sheets. Based on the scale bar in the TEM images, the thickness of the exfoliated hydroxide sheet can be estimated to be around 5 nm. This indicates that the exfoliated tactoids are roughly 10 hydroxide layers thick (a single hydroxide sheet has a thickness of ~ 0.5 nm).

The successful exfoliation of the Mg-Al-acetate LDH was further studied by AFM techniques, as described in the experimental section. The topographical image of the exfoliated LDH and the corresponding height profiles are given in **Figure S5a** and **Figure S5b**, respectively. The height profiles show that the exfoliated layers have a thickness of around 5 nm. This result corroborates the layer thickness observed in the TEM images (**Figure 2a & b**).

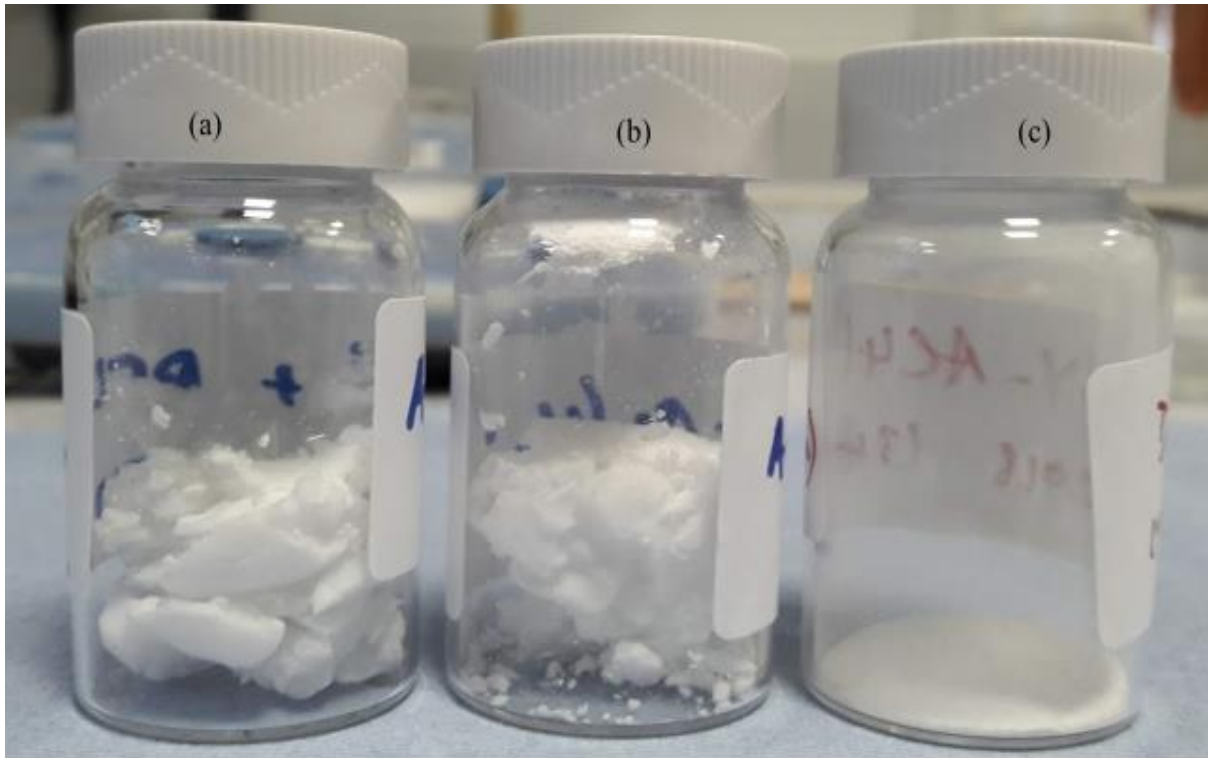


Figure 1. Photographic images of exfoliated (a, b) and non-exfoliated (c) Mg-Al-acetate LDH.

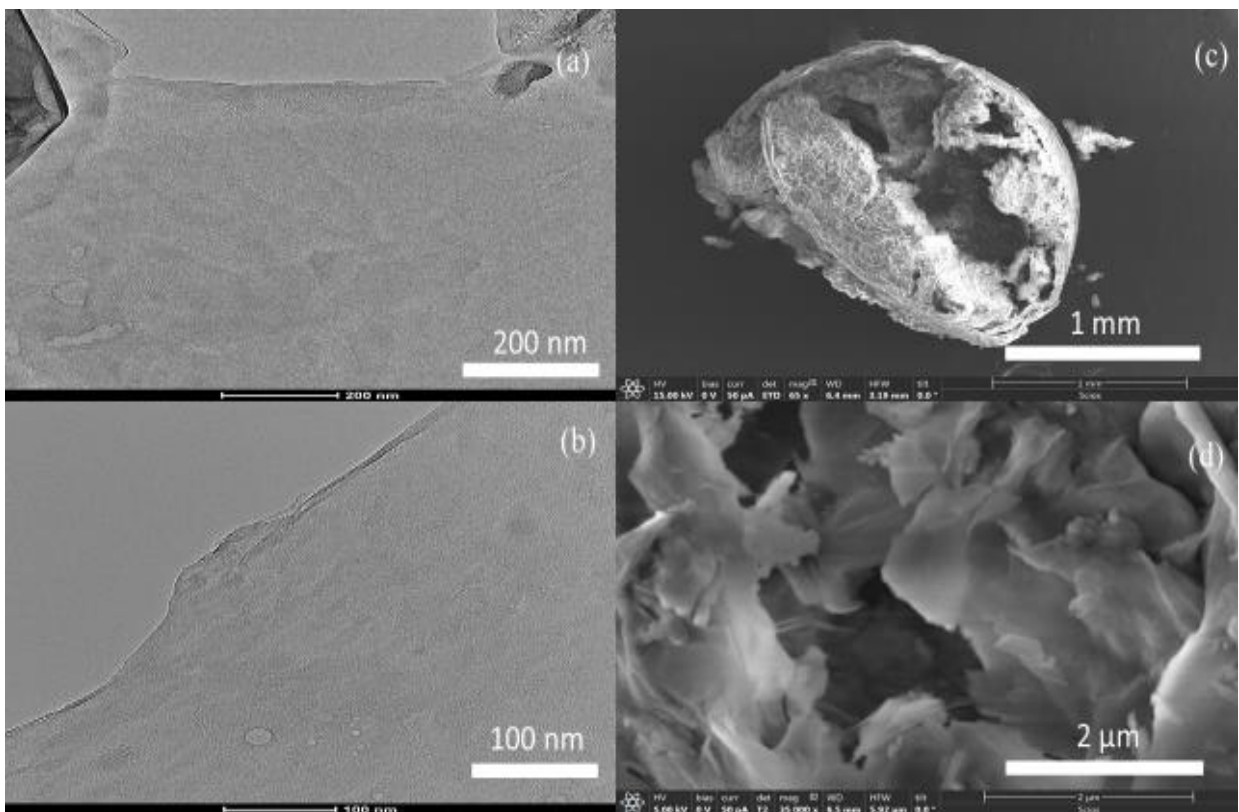


Figure 2. TEM images of exfoliated-freeze-dried LDH (a & b) and SEM images of MMOs pellets prepared from exfoliated-freeze-dried LDH (c & d).

Generally MMOs powder samples show major limitations such as (a) pressure drop across the reactor bed (b) mass transfer/heat transfer⁴¹. To upgrade CO₂ capture sorbent materials for industrial scale CO₂ capture, the sorbent materials should be in the structured shape with well-defined particle sizes^{52,53}. To overcome this challenge, the exfoliated LDH was pelletized into 2 mm pellets (as shown in **Figure S6**) using a pelletizer. Subsequently, the pelletized exfoliated LDH was subjected to thermal decomposition (as described in the experimental section) to get the MMOs pellets.

Surface morphology of the resultant MMOs pellets was characterized using SEM, as shown in **Figure 2c & d**. The MMOs have retained their sheet-like morphology (**Figure 2d**) indicating minimal particle aggregation during the thermal decomposition. The surface area, pore size distribution and pore volume of MMOs pellets were characterized using gas adsorption technique, as described in the experimental section. The exfoliated MMOs pellets show a type IV adsorption isotherm (**Figure 3**), which is characteristic of mesoporous solids⁵⁴. The sample shows H3 type of hysteresis typical of the parallel corrugated platelets⁵⁴. The MMOs pellets show a BET surface area of 264.2 m²/g and 1.27 cm³/g of pore volume. The pore distribution was calculated by the BJH method by using the desorption branch of the isotherm (**Figure S7**). The pores are distributed from 2 to 80 nm range and the majority of them have a pore size of 8 to 10 nm.

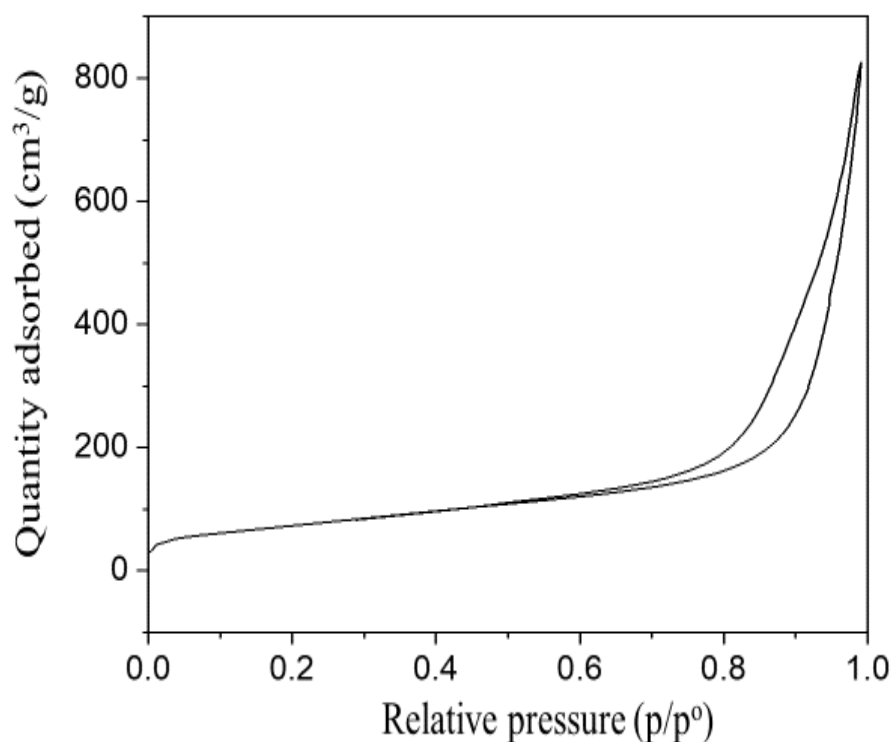


Figure 3. N₂ adsorption isotherm (77 K) of MMOs pellets obtained from exfoliated freeze-dried Mg-Al-acetate LDH (Mg/Al =4).

The mechanical behaviour of the pellets is investigated here to give insights into their ability to withstand external loading which would be present under operational conditions. This was evaluated by measuring the crushing load and the compressive strength of the pellets as described in the methodology section, and shown in Fig. 4. The pellets samples were found to be cylindrical, with a consistent cross-sectional diameter of 1.82mm. The crushing load for all samples is shown in **Figure 4a** and the average value was found to be 11.1 N. The compressive strength of the pellets, on the other hand, was calculated by dividing the crushing load by its cross-sectional area, and its average value was found to be 4.3 MPa (**Figure 4b**). These findings demonstrate the load bearing capability of using such pellet samples under realistic CO₂ capture conditions.

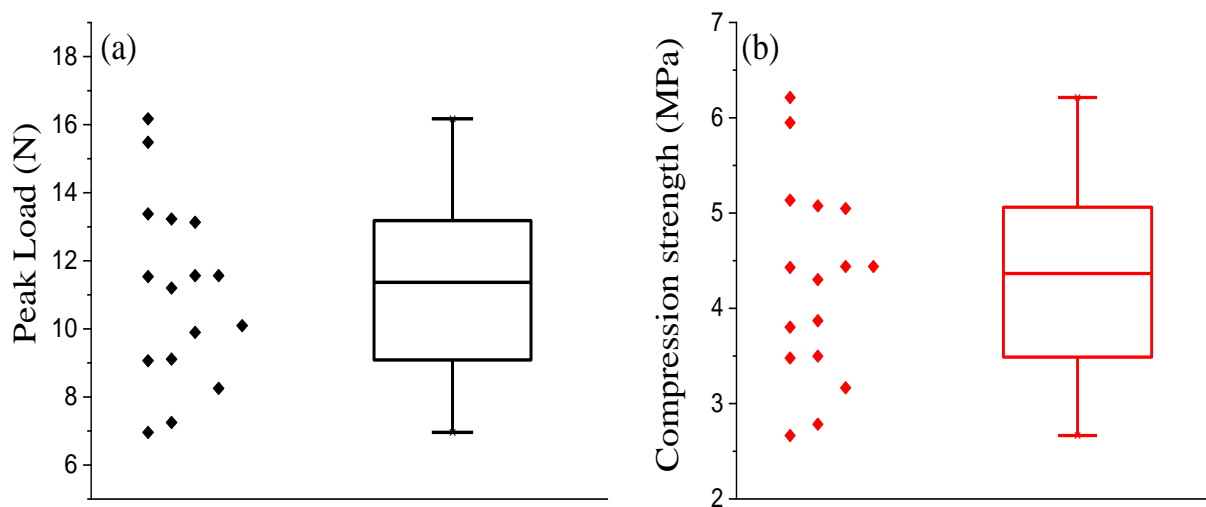


Figure 4. The crushing load (a) and compressive strength (b) of MMOs pellets obtained from exfoliated freeze-dried Mg-Al-acetate LDH (Mg/Al =4). The box represents the median and upper/lower quartiles, and the whiskers the maximum and minimum values.

CO₂ capture studies of the exfoliated MMOs pellets were carried out at atmospheric pressure under different CO₂ concentrations (86 and 14%) and at different temperatures, as described in the experimental section. To benchmark the performance of the synthesized pellets, commercial LDH based MMOs pellets were also tested under the same experimental conditions. Generally, LDH based MMOs are tested for CO₂ capture in the temperature range of 200-250 °C¹⁹. However, due to their intrinsic basicity and porosity, LDH based MMOs offer scope for developing them as CO₂ capture sorbents even at low temperatures. Thus, we have tested the CO₂ capture capacity of the developed exfoliated MMOs pellets at both low (30 °C) and high temperatures (200-300 °C) and compared with commercial LDH based MMOs pellets. The CO₂ capture capacities (under 86 % CO₂) of both, exfoliated MMOs pellets and commercial LDH-based MMOs pellets, are presented in **Figure 5**. Exfoliated MMOs pellets show a CO₂ uptake of 2.17 mmol/g at 30 °C (86 % CO₂). There are hardly any reports for pristine LDH based MMOs pellets in the literature to compare the observed CO₂ capture capacity values (at 30 °C) with. However, the CO₂ uptake achieved for exfoliated pellets is the highest reported so far when compared to pristine LDH based MMOs powder samples (**Table S1**). Interestingly, the CO₂ capture capacity is comparable to some of the best performing physisorbents (powder form) under the similar conditions⁵⁵⁻⁵⁸. On the other hand, the commercial LDH-based MMOs pellets show a CO₂ uptake of 0.6 mmol/g under the same

experimental capture conditions. The exfoliated MMOs pellets show a 3.6 fold increase in CO₂ capture capacity compared to commercial LDH based MMOs pellets at 30 °C. This clearly demonstrates the superior CO₂ capture performance of the exfoliated MMOs pellets compared to the commercial LDH based MMOs pellets at low temperature.

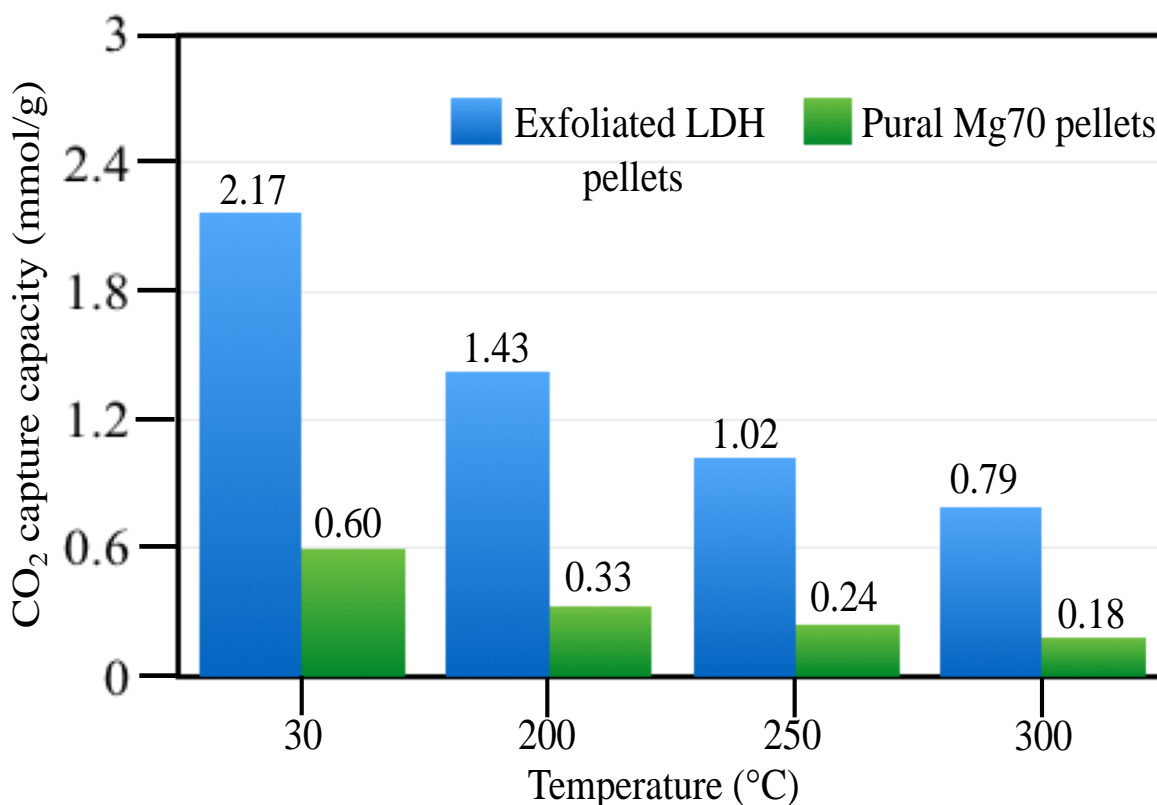


Figure 5. CO₂ capture capacities (mmol/g) of exfoliated freeze-dried LDH based MMOs and commercial LDH based MMOs pellets at atmospheric pressure and as a function of temperature under 86% CO₂.

The CO₂ capture capacity of the developed exfoliated MMOs pellets was also measured at 200, 250 and 300 °C (86 % CO₂). The MMOs pellets showed CO₂ capture capacities of 1.43, 1.02 and 0.79 mmol/g at 200, 250 and 300 °C, respectively. The observed decrease in CO₂ capture capacity with temperature is commonly reported in the literature ¹⁹. Interestingly, the CO₂ capture capacity obtained at 200 °C for exfoliated MMOs pellets (1.43 mmol/g) is higher than the ones reported so far for pristine/unpromoted LDH based MMOs powder samples (see also **Table S1**, ESI) ^{26,30,59} Generally, powder samples are expected to show better surface properties (surface area, pore volume and pore size) and better CO₂ capture capacities as opposed to their pelletized forms. Due to the additional steps involved in the pellet making process (such as

applying pressure on powder samples), the pellets are expected to have lower values for surface properties, hence lower CO₂ capture capacities compared to the powder samples.

The commercial LDH based MMOs pellets were also tested for CO₂ capture under a rich CO₂ gas stream (86%) at different temperatures (**Figure 5**). They showed CO₂ uptakes of 0.33, 0.24 and 0.18 mmol/g at 200, 250 and 300 °C, respectively, and a similar trend with temperature as exfoliated MMOs pellets. These results show that the developed exfoliated MMOs pellets outperforms the commercial LDH based MMOs pellets. For instance, the CO₂ capture capacity achieved for exfoliated MMOs pellets at 200 °C represents more than a fourfold increase compared to the commercial sample. To investigate the effect of exfoliation and freeze drying on the CO₂ capture properties of the synthesized Mg-Al-acetate LDH, the CO₂ capture capacity of as prepared LDH was also measured at 200 °C (86 % CO₂) after pelletizing the sample. The MMOs pellets generated from the as prepared LDH showed a CO₂ capture capacity of 0.8 mmol/g versus the 1.43 mmol/g observed in the exfoliated/freeze dried MMOs. This clearly shows the effect of exfoliation/freeze drying technique on the superior CO₂ capture performance observed. On one hand, exfoliation has helped in exposing the generally less diffusible interface of the LDHs and thereby increasing the number of active adsorption sites. And, on the other hand, the freeze-drying technique has helped in retaining the LDH in the exfoliated state.

The CO₂ capture capacity of developed MMOs pellets was further studied under low CO₂ concentration (14% CO₂) which mimic the flue gas CO₂ concentration (for example, flue gas from coal fired power plants)⁶⁰. The exfoliated MMOs pellets show 1.75 mmol/g at 30 °C and 1.20 mmol/g of CO₂ capture at 200 °C (**Figure 6**).

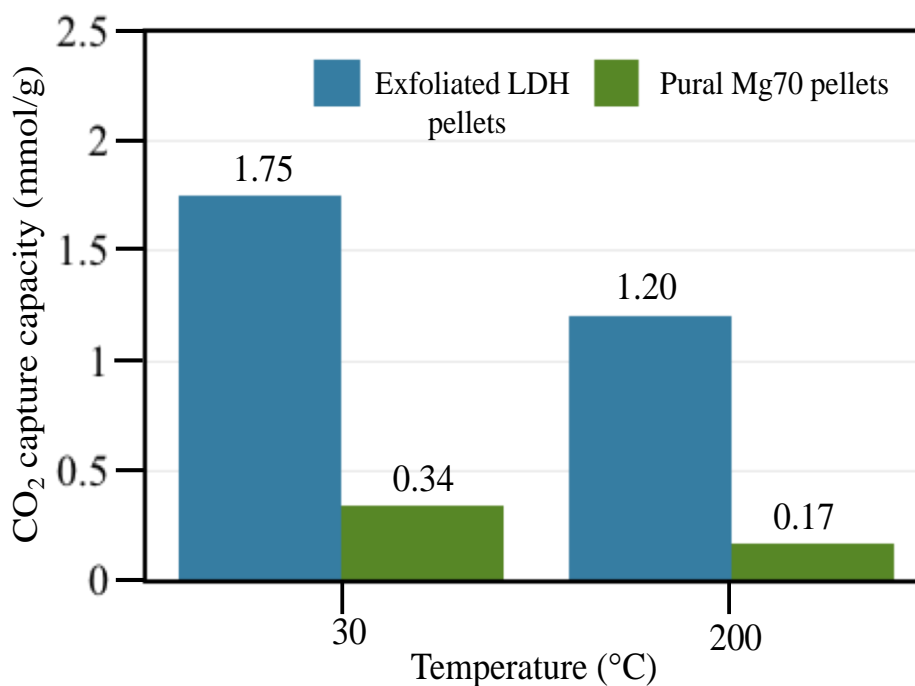


Figure 6. CO₂ capture capacities (mmol/g) of exfoliated freeze-dried LDH based MMOs and commercial LDH based MMOs pellets at atmospheric pressure and as a function of temperature under 14% CO₂.

On the other hand, commercial LDH based MMOs pellets show 0.34 and 0.17 mmol/g of CO₂ capture at 30 and 200 °C, respectively. This shows that exfoliated MMOs pellets show a 5 fold and 7 fold increased CO₂ capture capacity compared to the commercial LDH based MMOs pellets at 30 and 200 °C, respectively. Under the industrially relevant CO₂ gas concentration (14%), the performance of the exfoliated MMOs pellets improved much more significantly compared to the commercial LDH based MMOs pellets. These obtained capture capacity values were compared to those previously reported for LDH based (pristine/unpromoted) MMOs in powder and pellet form (**Table S1**), with much higher values being achieved by the exfoliated freeze-dried LDH based MMOs developed here.

The exfoliated MMOs pellets were tested for CO₂ cycling stability under 14 % CO₂. The adsorption was carried out at 30 and 200 °C and regeneration was carried out at 150 and 400

°C, respectively, as explained in the experimental section. The results from the cyclic study are presented in **Figure 7**.

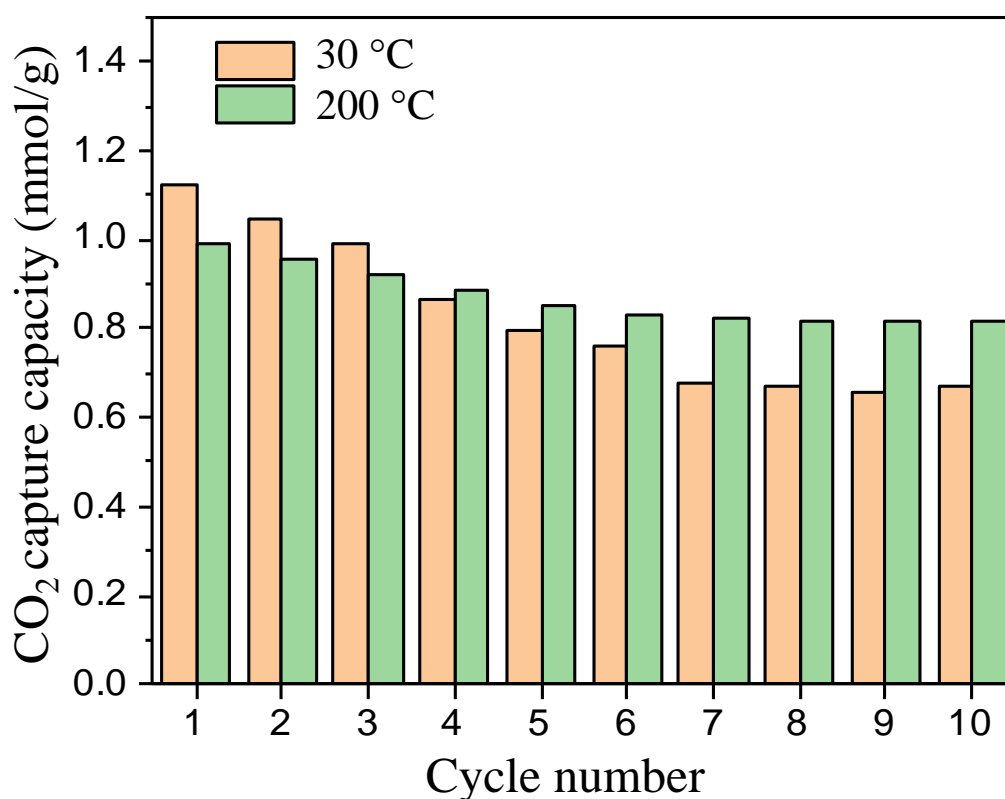


Figure 7. CO₂ cycling data of exfoliated freeze-dried LDH based MMOs at 30 and 200 °C under 14% CO₂.

The CO₂ capture capacity at 30 °C drops from 1.75 (fresh sample) to 1.12 mmol/g in the first cycle. This drop in capture capacity is mainly associated with the non-complete regeneration of the sorbent at 150 °C. It has been claimed before that MMOs capture CO₂ through chemisorption only at high temperatures (≥ 200 °C)⁶¹, and this chemisorbed CO₂ is typically regenerated at temperatures ≥ 400 °C. Thus, in principle, only physisorption would have taken place at a temperature of 30 °C. However, the large drop in capture capacity in the first cycle might also be due to some chemisorbed CO₂ being retained in the material. After the first cycle, the sample steadily loses capture capacity, reaching a stable value of 0.67 mmol/g after 10 cycles. The exfoliated MMOs pellets showed a much-improved CO₂ cycling stability at 200 °C compared to the one at 30 °C. The sample at 200 °C showed a reduced capture capacity in the first cycle (0.99 mmol/g) compared to the one measured for the fresh sample (1.2 mmol/g). As in the case at 30 °C, this reduction in capture capacity is most likely due to non-complete

regeneration of the sorbent. At 200 °C, the sample shows a stable working capacity of 0.82 mmol/g after 10 cycles.

4. Conclusions

Novel structured LDH-based materials have been successfully developed for their application as CO₂ sorbents. Our approach was based on the synthesis of Mg-Al-acetate LDH by employing the acetamide hydrolysis method. The hydration enthalpy of intercalated acetate ion was exploited to realize the aqueous exfoliation of metal hydroxide layers. The exfoliated colloidal suspension was freeze-dried to retain the layers in the exfoliated state. The exfoliation coupled with freeze-drying technique helped in increasing the volume of the LDH sample by several folds. The development of structured sorbents is key to their further implementation in industrial-scale applications, so the exfoliated LDH material was further pelletized (2 mm). Mechanical characterisation data demonstrated a promising level of loading bearing capability and compressive strength of such pelletized samples. The exfoliated MMOs pellets were evaluated for CO₂ capture at atmospheric pressure and from 30 to 300 °C under both, CO₂ rich and lean conditions. It was inferred that exfoliation helped in exposing the less diffusible interface of the LDH, and thereby in increasing the number of active adsorption sites for CO₂ capture. The CO₂ capture capacities obtained for exfoliated MMOs pellets (2.17 mmol/g at 30 °C and 1.43 mmol/g at 200 °C) are comparable or even better than CO₂ capture values reported for powder MMOs samples under similar conditions. Also, these novel exfoliated MMOs pellets outperform the commercial ones by several folds. The exfoliated MMOs pellets showed a much improved cycling stability at both low (30 °C) and high temperature (200 °C) under industrially relevant (14 %) CO₂ concentration.

Associated Content

PXRD and FTIR of Mg-Al-acetate LDH, schematic of aqueous exfoliation, Tyndall effect of exfoliated LDH colloidal suspension, AFM images of exfoliated LDH colloidal suspension, photographic images of exfoliated/freeze dried LDH pellets, BJH pore size distribution of MMOs pellets and a comparison table of CO₂ capture performance for pristine MMOs sorbents are given as supporting information.

Declaration of Competing Interest

No conflict of interest exists in the submission of this manuscript. The work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part.

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Reference

- (1) Ruiz-Hitzky, E.; Casal, B. Intracrystalline Complexation by Crown Ethers and Cryptands in Clay Minerals. In *Chemical Reactions in Organic and Inorganic Constrained Systems*; Springer Netherlands: Dordrecht, 1986; pp 179–189. https://doi.org/10.1007/978-94-009-4582-1_14.
- (2) Lagaly, G.; Beneke, K. Intercalation and Exchange Reactions of Clay Minerals and Non-Clay Layer Compounds. *Colloid Polym. Sci.* **1991**, *269* (12), 1198–1211. <https://doi.org/10.1007/BF00652529>.
- (3) Mallouk, T. E.; Gavin, J. A. Molecular Recognition in Lamellar Solids and Thin Films. *Acc. Chem. Res.* **1998**, *31* (5), 209–217. <https://doi.org/10.1021/ar970038p>.
- (4) Kovtyukhova, N. I.; Wang, Y.; Berkdemir, A.; Cruz-Silva, R.; Terrones, M.; Crespi, V. H.; Mallouk, T. E. Non-Oxidative Intercalation and Exfoliation of Graphite by Brønsted Acids. *Nat. Chem.* **2014**, *6* (11), 957–963. <https://doi.org/10.1038/nchem.2054>.
- (5) Thompson, M. E. Use of Layered Metal Phosphonates for the Design and Construction of Molecular Materials. *Chem. Mater.* **1994**, *6* (8), 1168–1175. <https://doi.org/10.1021/cm00044a015>.
- (6) Sotiles, A. R.; Baika, L. M.; Grassi, M. T.; Wypych, F. Cation Exchange Reactions in Layered Double Hydroxides Intercalated with Sulfate and Alkaline Cations (A(H₂O)₆)[M₂₊₆Al₃(OH)₁₈(SO₄)₂]·6H₂O (M₂₊ = Mn, Mg, Zn; A₊ = Li, Na, K). *J. Am. Chem. Soc.* **2019**, *141* (1), 531–540. <https://doi.org/10.1021/jacs.8b11389>.
- (7) Zhao, Y.; Jia, X.; Waterhouse, G. I. N.; Wu, L. Z.; Tung, C. H.; O'Hare, D.; Zhang, T. Layered Double Hydroxide Nanostructured Photocatalysts for Renewable Energy Production. *Adv. Energy Mater.* **2016**, *6* (6). <https://doi.org/10.1002/aenm.201501974>.
- (8) Tian, R.; Liang, R.; Wei, M.; Evans, D. G.; Duan, X. Applications of Layered Double Hydroxide Materials: Recent Advances and Perspective; D. M. P. Mingos, Ed.; Springer international publishing, 2016; pp 65–84. https://doi.org/10.1007/430_2015_205.
- (9) Cavani, F.; Trifirò, F.; Vaccari, A. Hydrotalcite-Type Anionic Clays: Preparation,

- Properties and Applications. *Catal. Today* **1991**, *11* (2), 173–301.
[https://doi.org/10.1016/0920-5861\(91\)80068-K](https://doi.org/10.1016/0920-5861(91)80068-K).
- (10) Reichle, W. T. Catalytic Reactions by Thermally Activated, Synthetic, Anionic Clay Minerals. *J. Catal.* **1985**, *94* (2), 547–557. [https://doi.org/10.1016/0021-9517\(85\)90219-2](https://doi.org/10.1016/0021-9517(85)90219-2).
- (11) Patel, R.; Park, J. T.; Patel, M.; Dash, J. K.; Gowd, E. B.; Karpoomath, R.; Mishra, A.; Kwak, J.; Kim, J. H. Transition-Metal-Based Layered Double Hydroxides Tailored for Energy Conversion and Storage. *Journal of Materials Chemistry A*. Royal Society of Chemistry 2017, pp 12–29. <https://doi.org/10.1039/c7ta09370e>.
- (12) Li, E.; Xu, Z. P.; Rudolph, V. MgCoAl-LDH Derived Heterogeneous Catalysts for the Ethanol Transesterification of Canola Oil to Biodiesel. *Appl. Catal. B Environ.* **2009**, *88* (1–2), 42–49. <https://doi.org/10.1016/j.apcatb.2008.09.022>.
- (13) Nagendra, B.; Mohan, K.; Bhoje Gowd, E. Polypropylene/Layered Double Hydroxide (LDH) Nanocomposites: Influence of LDH Particle Size on the Crystallization Behavior of Polypropylene. *ACS Appl. Mater. Interfaces* **2015**, *7* (23), 12399–12410. <https://doi.org/10.1021/am5075826>.
- (14) Ma, R.; Sasaki, T. Nanosheets of Oxides and Hydroxides: Ultimate 2D Charge-Bearing Functional Crystallites. *Advanced Materials*. December 1, 2010, pp 5082–5104. <https://doi.org/10.1002/adma.201001722>.
- (15) Pardakhti, M.; Jafari, T.; Tobin, Z.; Dutta, B.; Moharreri, E.; Shemshaki, N. S.; Suib, S.; Srivastava, R. Trends in Solid Adsorbent Materials Development for CO₂ Capture. *ACS Appl. Mater. Interfaces* **2019**, *11* (38), 34533–34559. <https://doi.org/10.1021/acsami.9b08487>.
- (16) Hutson, N. D.; Attwood, B. C. High Temperature Adsorption of CO₂ on Various Hydrotalcite-like Compounds. *Adsorption* **2008**, *14* (6), 781–789. <https://doi.org/10.1007/s10450-007-9085-6>.
- (17) Hanif, A.; Dasgupta, S.; Divekar, S.; Arya, A.; Garg, M. O.; Nanoti, A. A Study on High Temperature CO₂ Capture by Improved Hydrotalcite Sorbents. *Chem. Eng. J.* **2014**, *236*, 91–99. <https://doi.org/10.1016/j.cej.2013.09.076>.
- (18) Garcia-Gallastegui, A.; Iruretagoyena, D.; Gouvea, V.; Mokhtar, M.; Asiri, A. M.;

- Basahel, S. N.; Al-Thabaiti, S. A.; Alyoubi, A. O.; Chadwick, D.; Shaffer, M. S. P. Graphene Oxide as Support for Layered Double Hydroxides: Enhancing the CO₂ Adsorption Capacity. *Chem. Mater.* **2012**, *24* (23), 4531–4539. <https://doi.org/10.1021/cm3018264>.
- (19) Wang, Q.; Tay, H. H.; Zhong, Z.; Luo, J.; Borgna, A. Synthesis of High-Temperature CO₂ Adsorbents from Organo-Layered Double Hydroxides with Markedly Improved CO₂ Capture Capacity. *Energy Environ. Sci.* **2012**, *5* (6), 7526–7530. <https://doi.org/10.1039/c2ee21409a>.
- (20) Gao, Y.; Zhang, Z.; Wu, J.; Yi, X.; Zheng, A.; Umar, A.; O'Hare, D.; Wang, Q. Comprehensive Investigation of CO₂ Adsorption on Mg-Al-CO₃ LDH-Derived Mixed Metal Oxides. *J. Mater. Chem. A* **2013**, *1* (41), 12782–12790. <https://doi.org/10.1039/c3ta13039h>.
- (21) Manohara, G. V.; Maroto-Valer, M. M.; Garcia, S. The Effect of the Layer-Interlayer Chemistry of LDHs on Developing High Temperature Carbon Capture Materials. *Dalt. Trans.* **2020**, *49* (3), 923–931. <https://doi.org/10.1039/C9DT03913A>.
- (22) Sharma, U.; Tyagi, B.; Jasra, R. V. Synthesis and Characterization of Mg-Al-CO₃ Layered Double Hydroxide for CO₂ Adsorption. *Ind. Eng. Chem. Res.* **2008**, *47* (23), 9588–9595. <https://doi.org/10.1021/ie800365t>.
- (23) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon Dioxide Capture: Prospects for New Materials. *Angewandte Chemie - International Edition*. August 16, 2010, pp 6058–6082. <https://doi.org/10.1002/anie.201000431>.
- (24) Wang, Q.; Luo, J.; Zhong, Z.; Borgna, A. CO₂ Capture by Solid Adsorbents and Their Applications: Current Status and New Trends. *Energy and Environmental Science*. January 2011, pp 42–55. <https://doi.org/10.1039/c0ee00064g>.
- (25) Fernández, J. R.; Garcia, S.; Sanz-Pérez, E. S. CO₂ Capture and Utilization Editorial. *Ind. Eng. Chem. Res.* **2020**, *59* (15), 6767–6772. <https://doi.org/10.1021/acs.iecr.0c01643>.
- (26) Wang, J.; Zhang, Y.; Altaf, N.; O'Hare, D.; Wang, Q. CHAPTER 1. Layered Double Hydroxides-Derived Intermediate-Temperature CO₂ Adsorbents. In *Inorganic Materials Series No. 1*; Wang, Q., Ed.; The Royal Society of Chemistry, 2018; pp 1–

60. <https://doi.org/10.1039/9781788013390-00001>.
- (27) Jang, H. J.; Lee, C. H.; Kim, S.; Kim, S. H.; Lee, K. B. Hydrothermal Synthesis of K₂CO₃-Promoted Hydrotalcite from Hydroxide-Form Precursors for Novel High-Temperature CO₂ Sorbent. *ACS Appl. Mater. Interfaces* **2014**, *6* (9), 6914–6919. <https://doi.org/10.1021/am500720f>.
- (28) Wang, Q.; Wu, Z.; Tay, H. H.; Chen, L.; Liu, Y.; Chang, J.; Zhong, Z.; Luo, J.; Borgna, A. High Temperature Adsorption of CO₂ on Mg-Al Hydrotalcite: Effect of the Charge Compensating Anions and the Synthesis PH. *Catal. Today* **2011**, *164* (1), 198–203. <https://doi.org/10.1016/j.cattod.2010.10.042>.
- (29) Yavuz, C. T.; Shinall, B. D.; Iretskii, A. V.; White, M. G.; Golden, T.; Atilhan, M.; Ford, P. C.; Stucky, G. D. Markedly Improved CO₂ Capture Efficiency and Stability of Gallium Substituted Hydrotalcites at Elevated Temperatures. *Chem. Mater.* **2009**, *21* (15), 3473–3475. <https://doi.org/10.1021/cm900834g>.
- (30) Bhatta, L. K. G.; Subramanyam, S.; Chengala, M. D.; Olivera, S.; Venkatesh, K. Progress in Hydrotalcite like Compounds and Metal-Based Oxides for CO₂ Capture: A Review. *J. Clean. Prod.* **2015**, *103*, 171–196. <https://doi.org/10.1016/j.jclepro.2014.12.059>.
- (31) Lee, J. M.; Min, Y. J.; Lee, K. B.; Jeon, S. G.; Na, J. G.; Ryu, H. J. Enhancement of CO₂ Sorption Uptake on Hydrotalcite by Impregnation with K₂CO₃. *Langmuir* **2010**, *26* (24), 18788–18797. <https://doi.org/10.1021/la102974s>.
- (32) Manohara, G. V.; Kunz, D. A.; Kamath, P. V.; Milius, W.; Breu, J. Homogeneous Precipitation by Formamide Hydrolysis: Synthesis, Reversible Hydration, and Aqueous Exfoliation of the Layered Double Hydroxide (LDH) of Ni and Al. *Langmuir* **2010**, *26* (19), 15586–15591. <https://doi.org/10.1021/la103108f>.
- (33) Gardolinski, J. E. F. C.; Lagaly, G. Grafted Organic Derivatives of Kaolinite: II. Intercalation of Primary n-Alkylamines and Delamination. *Clay Miner.* **2005**, *40* (4), 547–556. <https://doi.org/10.1180/0009855054040191>.
- (34) Leroux, F.; Adachi-Pagano, M.; Intissar, M.; Chauvière, S.; Forano, C.; Besse, J. P. Delamination and Restacking of Layered Double Hydroxides. *J. Mater. Chem.* **2001**, *11* (1), 105–112. <https://doi.org/10.1039/b002955f>.

- (35) Liang, J.; Renzhi, M.; Iyi, N.; Ebina, Y.; Takada, K.; Sasaki, T. Topochemical Synthesis, Anion Exchange, and Exfoliation of Co-Ni Layered Double Hydroxides: A Route to Positively Charged Co-Ni Hydroxide Nanosheets with Tunable Composition. *Chem. Mater.* **2010**, *22* (2), 371–378. <https://doi.org/10.1021/cm902787u>.
- (36) Manohara, G. V. Exfoliation of Layered Double Hydroxides (LDHs): A New Route to Mineralize Atmospheric CO₂. *RSC Adv.* **2014**, *4* (86), 46126–46132. <https://doi.org/10.1039/c4ra08865d>.
- (37) Ma, R.; Liu, Z.; Li, L.; Iyi, N.; Sasaki, T. Exfoliating Layered Double Hydroxides in Formamide: A Method to Obtain Positively Charged Nanosheets. *J. Mater. Chem.* **2006**, *16* (39), 3809–3813. <https://doi.org/10.1039/b605422f>.
- (38) Iyi, N.; Ebina, Y.; Sasaki, T. Water-Swellable MgAl-LDH (Layered Double Hydroxide) Hybrids: Synthesis, Characterization, and Film Preparation. *Langmuir* **2008**, *24* (10), 5591–5598. <https://doi.org/10.1021/la800302w>.
- (39) Hibino, T.; Kobayashi, M. Delamination of Layered Double Hydroxides in Water. *J. Mater. Chem.* **2005**, *15* (6), 653–656. <https://doi.org/10.1039/b416913a>.
- (40) Bhatta, L. K. G.; Subramanyam, S.; Chengala, M. D.; Olivera, S.; Venkatesh, K. Progress in Hydrotalcite like Compounds and Metal-Based Oxides for CO₂ Capture: A Review. *J. Clean. Prod.* **2015**, *103*, 171–196. <https://doi.org/10.1016/j.jclepro.2014.12.059>.
- (41) Levenspiel, O. Chemical Reaction Engineering. *Industrial and Engineering Chemistry Research*. Third. Wiley: New York 1999, pp 4140–4143. <https://doi.org/10.1021/ie990488g>.
- (42) Ma, L.; Qin, C.; Pi, S.; Cui, H. Fabrication of Efficient and Stable Li₄SiO₄-Based Sorbent Pellets via Extrusion-Spheronization for Cyclic CO₂ Capture. *Chem. Eng. J.* **2020**, *379* (July 2019), 122385. <https://doi.org/10.1016/j.cej.2019.122385>.
- (43) Sun, J.; Liu, W.; Hu, Y.; Wu, J.; Li, M.; Yang, X.; Wang, W.; Xu, M. Enhanced Performance of Extruded-Spheronized Carbide Slag Pellets for High Temperature CO₂ Capture. *Chem. Eng. J.* **2016**, *285*, 293–303. <https://doi.org/10.1016/j.cej.2015.10.026>.
- (44) Yang, Y.; Liu, W.; Hu, Y.; Sun, J.; Tong, X.; Chen, Q.; Li, Q. One-Step Synthesis of

- Porous Li₄SiO₄-Based Adsorbent Pellets via Graphite Moulding Method for Cyclic CO₂ Capture. *Chem. Eng. J.* **2018**, *353* (July), 92–99.
<https://doi.org/10.1016/j.cej.2018.07.044>.
- (45) Manovic, V.; Anthony, E. J. Reactivation and Remaking of Calcium Aluminate Pellets for CO₂ Capture. *Fuel* **2011**, *90* (1), 233–239.
<https://doi.org/10.1016/j.fuel.2010.07.054>.
- (46) Blamey, J.; Al-Jeboori, M. J.; Manovic, V.; Fennell, P. S.; Anthony, E. J. CO₂ Capture by Calcium Aluminate Pellets in a Small Fluidized Bed. *Fuel Process. Technol.* **2016**, *142*, 100–106. <https://doi.org/10.1016/j.fuproc.2015.09.015>.
- (47) Li, S.; Ribeiro, A. M.; Shi, Y.; Moreira, M. N.; Cai, N.; Rodrigues, A. E. Synthesis, Pelleting, and Performance Evaluation of a Novel K-Promoted γ -Alumina/MgAl-Layered Double Oxide Composite Adsorbent for Warm Gas H₂/CO₂ Separation. *Ind. Eng. Chem. Res.* **2015**, *54* (28), 7154–7163. <https://doi.org/10.1021/acs.iecr.5b01342>.
- (48) Papa, E.; Medri, V.; Paillard, C.; Contri, B.; Natali Murri, A.; Vaccari, A.; Landi, E. Geopolymer-Hydrotalcite Composites for CO₂ Capture. *J. Clean. Prod.* **2019**, *237*, 117738. <https://doi.org/10.1016/j.jclepro.2019.117738>.
- (49) Manohara, G. V.; Vishnu Kamath, P.; Milius, W. Reversible Hydration and Aqueous Exfoliation of the Acetate-Intercalated Layered Double Hydroxide of Ni and Al: Observation of an Ordered Interstratified Phase. *J. Solid State Chem.* **2012**, *196*, 356–361. <https://doi.org/10.1016/j.jssc.2012.06.017>.
- (50) Kumar, P. P.; Kalinichev, A. G.; Kirkpatrick, R. J. Molecular Dynamics Simulation of the Energetics and Structure of Layered Double Hydroxides Intercalated with Carboxylic Acids. *J. Phys. Chem. C* **2007**, *111* (36), 13517–13523.
<https://doi.org/10.1021/jp0732054>.
- (51) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*; 2008. <https://doi.org/10.1002/9780470405888>.
- (52) Valizadeh, B.; Nguyen, T. N.; Smit, B.; Stylianou, K. C. Porous Metal–Organic Framework@Polymer Beads for Iodine Capture and Recovery Using a Gas-Sparged Column. *Adv. Funct. Mater.* **2018**, *28* (30), 1–6.

<https://doi.org/10.1002/adfm.201801596>.

- (53) Cousin-Saint-Remi, J.; Van Der Perre, S.; Segato, T.; Delplancke, M. P.; Goderis, S.; Terryn, H.; Baron, G.; Denayer, J. Highly Robust MOF Polymeric Beads with a Controllable Size for Molecular Separations. *ACS Appl. Mater. Interfaces* **2019**, *11* (14), 13694–13703. <https://doi.org/10.1021/acsami.9b00521>.
- (54) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87* (9–10), 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.
- (55) Vorokhta, M.; Morávková, J.; Řimnáčová, D.; Pilař, R.; Zhigunov, A.; Švábová, M.; Sazama, P. CO₂ Capture Using Three-Dimensionally Ordered Micromesoporous Carbon. *J. CO₂ Util.* **2019**, *31*, 124–134. <https://doi.org/10.1016/j.jcou.2019.03.001>.
- (56) Shi, X.; Xiao, H.; Azarabadi, H.; Song, J.; Wu, X.; Chen, X.; Lackner, K. S. Sorbents for Direct Capture of CO₂ from Ambient Air. *Angew. Chemie* **2019**. <https://doi.org/10.1002/ange.201906756>.
- (57) Singh, G.; Lakhi, K. S.; Sathish, C. I.; Ramadass, K.; Yang, J. H.; Vinu, A. Oxygen-Functionalized Mesoporous Activated Carbons Derived from Casein and Their Superior CO₂ Adsorption Capacity at Both Low- And High-Pressure Regimes. *ACS Appl. Nano Mater.* **2019**, *2* (3), 1604–1613. <https://doi.org/10.1021/acsanm.9b00059>.
- (58) Modak, A.; Jana, S. Advancement in Porous Adsorbents for Post-Combustion CO₂ Capture. *Microporous and Mesoporous Materials*. Elsevier B.V. March 1, 2019, pp 107–132. <https://doi.org/10.1016/j.micromeso.2018.09.018>.
- (59) Yang, Z. zhu; Wei, J. jing; Zeng, G. ming; Zhang, H. qing; Tan, X. fei; Ma, C.; Li, X. cheng; Li, Z. hao; Zhang, C. A Review on Strategies to LDH-Based Materials to Improve Adsorption Capacity and Photoreduction Efficiency for CO₂. *Coordination Chemistry Reviews*. Elsevier B.V. May 1, 2019, pp 154–182. <https://doi.org/10.1016/j.ccr.2019.01.018>.
- (60) Song, C.; Pan, W. Tri-Reforming of Methane: A Novel Concept for Catalytic Production of Industrially Useful Synthesis Gas with Desired H₂/CO Ratios. *Catal.*

Today **2004**, 98 (4), 463–484. <https://doi.org/10.1016/j.cattod.2004.09.054>.

- (61) León, M.; Díaz, E.; Bennici, S.; Vega, A.; Ordóñez, S.; Auroux, A. Adsorption of CO₂ on Hydrotalcite-Derived Mixed Oxides: Sorption Mechanisms and Consequences for Adsorption Irreversibility. *Ind. Eng. Chem. Res.* **2010**, 49 (8), 3663–3671. <https://doi.org/10.1021/ie902072a>.