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Acetate intercalated Mg-Al layered double hydroxides (LDHs) through modified amide hydrolysis: A new route to synthesize novel mixed metal oxides (MMOs) for CO$_2$ capture.

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Abstract
Layered double hydroxides (LDHs) based mixed metal oxides (MMOs) are promising high temperature CO$_2$ capture sorbents. In order to improve their CO$_2$ capture capacity, it is crucial to bring in changes to their physicochemical properties such as morphology, particle size, surface area and activity by tuning the synthesis method. Here we are reporting a modified amide hydrolysis method to synthesize LDHs with a mixed morphology having better CO$_2$ capture properties. Acetate intercalated Mg-Al LDHs with two different Mg/Al ratios (3 and 4) were synthesized by employing the metal hydroxides as starting precursors and acetamide as hydrolysing agent. The resultant LDHs crystallized in a new morphology having a combination of both fibrous and sheet like crystallites. The MMOs derived from Mg-Al-acetate LDHs retained the mixed morphology observed in the precursor LDHs. The resultant MMOs showed almost a threefold increase in BET surface, 316 (Mg/Al= 3) and 341 (Mg/Al = 4) m$^2$/g, compared to MMOs derived from anion exchanged Mg-Al-acetate LDH (118 m$^2$/g). The MMOs derived from acetamide hydrolysis captured 1.2 mmol/g and 0.87 mmol/g of CO$_2$ at 200 and 300 °C (atmospheric pressure), respectively. The CO$_2$ capture capacity realized was more than twofold increase compared to CO$_2$ capture capacity of MMOs derived from anion exchanged acetate LDH (0.57 mmol/g) tested under similar conditions. The developed MMOs showed promising CO$_2$ capture (1.0 mmol/g) capacity under industrially relevant CO$_2$ concentration (14%).
1. Introduction

Anthropogenic CO$_2$ emissions are one of the major contributors to the greenhouse gas effect and are responsible for the rise in atmospheric temperatures.$^1$ Carbon capture, usage and storage (CCUS) is one of the required pathways to minimize future emissions as well as capturing already emitted CO$_2$. Adsorption by solid sorbents and absorption by liquid amines are two promising routes to capture anthropogenic CO$_2$. Adsorption by solid sorbents is a well-known technology and it has been successfully tested at industrial scale.$^6,7$ The health and environmental concerns and higher energy penalties limit the widespread implementation of liquid amines to capture CO$_2$. On the other hand, adsorption by solid sorbents is a promising alternative due to (a) ease of operation and handling, (b) wide window of operational temperature, (c) works under both high and low CO$_2$ concentration, (d) selectivity and activity can be tuned, and (e) have low specific heat capacities.$^9-10$

Among the solid sorbents, layered double hydroxide (LDHs) based mixed metal oxides (MMOs) stand apart due to their various physiochemical properties that make them ideal candidate materials for CO$_2$ capture.$^{11-14}$ LDHs are class of layered solids having derived their structure from that of the mineral brucite, Mg(OH)$_2$. LDHs are represented by the general formula $[M^{2+}_{2-x}M^{3+}_x(OH)]^{2+}(A^{-x/n})yH_2O$, where, $M^{2+}$= Mg, Co, Ni, Ca, Zn, $M^{3+}$= Al, Fe, Ga, A= anion(organic or inorganic ions), $0.15 \leq x \leq 0.33$ and $0.5 \leq y \leq 1.0$. LDHs and derived MMOs have been found as catalysts, precursors to catalysts, electrodes in batteries and supercapacitors, sensors, as fillers in nanocomposites, and as sorbents for various applications.$^{17,18}$ Among all the applications of LDHs and MMOs, medium-high temperature (200-650 °C) CO$_2$ capture is one widely studied topic.$^{19}$ LDH derived MMOs are ideal candidate materials for CO$_2$ capture due to (a) fast adsorption/desorption kinetics, (b) large untapped theoretical capture potential, (c) able to work under flue gas conditions, (d) are easy to prepare and handle, and (e) economical and environmentally benign.$^{20,21}$

Despite all the promising properties as better CO$_2$ capture sorbent materials, MMOs are yet to live up to their potential due to (a) low CO$_2$ capture, (b) poor thermal and mechanical stability, and (c) capacity fading during cycling.$^{22}$ To overcome these limitations, various attempts to improve their CO$_2$ capture capacity have been reported in the literature.$^{23-24}$ For instance, LDHs are substituted with varied layered metal cations as well as interlayer anions; alkali metals and metal carbonates are doped with LDH based MMOs; To improve the mechanical and thermal stability of MMOs for better CO$_2$ capture and cycling performance, LDHs are supported with zeolites, carbon nanotubes (CNT), graphite oxide (GO).$^{25-28}$ Likewise, different synthesis
methods like aqueous exfoliation and post synthesis washing with organic solvents are also employed to improve the surface area and CO$_2$ capture capacity of MMOs.$^{29,30}$ Furthermore, the properties of MMOs such as basicity, particle size, porosity, morphology can be tuned by altering the combination of pre- and post-synthesis conditions such as composition, synthesis method, starting precursors, time and rate of addition of reagents, supersaturation and drying/washing methods of precursor LDHs.$^{27-29}$ LDHs prepared by one synthesis method differ greatly from those ones prepared by other methods. As an example, LDHs prepared by co-precipitation show ill-defined hexagonal crystallites having submicron particle sizes, whereas LDHs prepared by hydrothermal methods employing homogeneous precipitation from solution (HPFS) methods show crystalline hexagonal morphology with micron sized particles.$^{31,32}$ Similarly, samples prepared with the help of surfactants show distinct morphology and properties compared to those ones prepared without the use of surfactants.$^{33}$ Additionally, different hydrolysing agents such as urea, formamide and acetamide having different hydrolysing constants result in LDHs with different anions, and hence different properties.$^{34-35}$

An improved basicity of LDHs coupled with a varied morphology is expected to generate novel MMOs having better CO$_2$ capture properties. Generally, metal salts such as metal nitrate and chlorides are employed as source of metal cations in the synthesis of LDHs. These precursors’ metal salts are highly acidic and could influence the basicity of the resultant LDHs. Unitary hydroxides such as Mg(OH)$_2$ and Al(OH)$_3$ are highly basic compared to metal salts such as metal nitrates or metal chlorides.$^{36,37}$ Employing these unitary hydroxides as source of metal cations instead of metal salts for LDH synthesis could affect the overall basicity of the resultant LDHs and their derived MMOs. These unitary hydroxide were employed as source of metal cations in synthesizing LDHs with interesting properties.$^{38-40}$ The morphology of the LDHs could be tuned by changing the hydrolysing agent and that will alter the surface properties of the LDHs and their derived MMOs. $^{34-35}$In this paper, we attempted to bring in a new and interesting morphology to the LDHs by modifying the synthesis method and by changing the starting metal precursors.

Modified amide hydrolysis was employed to synthesize Mg-Al-acetate LDHs starting with metal hydroxides instead of metal salts. Acetamide was used as hydrolysing agent to facilitate the nucleation of the metal cations by providing the necessary base (NH$_4$OH) and as well as acts as the source of anions (CH$_3$COO$^-$).$^{41}$ The MMOs derived from the as-synthesized LDHs
are studied for CO₂ capture at different temperatures under both, CO₂ rich (86 %) and lean (14 %) conditions.

2. Experimental

Synthesis: All the chemicals, Mg(OH)₂, Al(OH)₃, acetamide, Mg(NO₃)₂·6 H₂O, Al(NO₃)₃·9 H₂O, NaOH and sodium acetate were purchased from Sigma Aldrich and used as received. Deionised water (18. MΩ.cm resistivity, Millipore water purification system) was used throughout the experiments. LDHs with two different Mg/Al (3 and 4) ratios were synthesized (acetamide to metal ion ratio, acetamide/M = 5). In a typical experiment, stoichiometric amounts of Mg(OH)₂, Al(OH)₃ and acetamide (acetamide/metal = 5) were taken in 100 mL water. The reaction mixture was stirred at room temperature for an hour to get a homogeneous mixture. The resultant reaction mixture was transferred to a 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. For comparison, Mg-Al-acetate (Mg/Al = 3) LDH was prepared by anion exchange reaction (10 times excess acetate ion used) starting from Mg-Al-NO₃ LDH. In this case, the precursor Mg-Al-NO₃ LDH (Mg/Al =3) was synthesized by employing the co-precipitation method (pH 9). The pH of the reaction mixture was maintained at 9 by the constant addition of 1 N NaOH solution (Metrohm auto titrator). The temperature of the reaction mixture was maintained at 70 °C while stirring. Next, 0.5 g of Mg-Al-NO₃ LDH was dispersed in 100 mL of hot deionised water (80 °C) and to this, 10 times excess stoichiometric amount of acetate ion was added in the form of sodium acetate. The reaction mixture was stirred for 24 h at 70 °C on a magnetic stirrer. The resultant Mg-Al-Acetate LDH was recovered by centrifugation and washed with copious amount of water. A commercial LDH Pural Mg70 sample was procured from SASOL for benchmarking the performance of the obtained samples.

Characterization: Powder X-ray Diffraction (PXRD) patterns were recorded on a Bruker D8 Advance power diffractometer, using Ge-monochromated Cu-Kα1 radiation (λ = 1.5406 Å) 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 °2θ with a step size of 0.009° over one hour span. The Fourier Transform Infrared spectra (FTIR) of samples were measured using Perkin Elmer spectrometer in ATR mode (4000 to 600 cm⁻¹). Elemental analysis of Ca²⁺ 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 3mg of sample and placing them in a tin capsule, followed by combustion in a high oxygen environment at 950 °C using an Exeter Analytical CE-440 elemental analyser calibrated with acetonilide. Surface area analysis of the sample was carried out by gas adsorption technique (N₂, 77 K) using Micromeritics Gemini VII surface analyser. Prior to the gas adsorption measurement, the sample was degassed for 3 h at 150 °C. The surface morphology of the sample was characterized by scanning electron microscopy (SEM) using FEI Quanta FEG SEM.

1.1. CO₂ capture studies: Thermal analysis and CO₂ capture studies were performed using a thermogravimetric analyser (TA Instruments TA 500). Pristine Mg-Al-acetate LDHs were used instead of preformed MMOs to avoid the CO₂ contamination. Freshly prepared LDHs 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 was completed, 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. The CO₂ capture capacity of resultant MMOs was tested under two different CO₂ concentrations, 86 and 14 % (mixed with N₂), and at three different temperatures (200, 250 and 300 °C). For comparison, the CO₂ capture capacity of MMOs generated from the commercial Pural Mg70 LDH was measured at 200 °C under 86 % CO₂ and the same conditions as those used for Mg-Al-acetate LDHs. Next, the cyclic behaviour (10 cycles) of the Mg-Al-acetate (Mg/Al = 3, 4) and commercial Pural Mg70 LDH derived MMOs was investigated under 86 % CO₂. 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

(a) Synthesis and characterization of acetate intercalated LDHs and their derived MMOs

Hydrolysis of acetamide proceeds according to the equation given below;

\[ \text{CH}_3\text{CONH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{NH}_3 \]

Depending on the pH of the reaction medium, hydrolysis of acetamide could be either base or acid catalysed. Synthesis of acetate intercalated LDHs by the conventional co-precipitation or anion exchange reactions requires large excess of acetate ion due to its high solubility in
water (high hydration enthalpy).\textsuperscript{43} On the other hand, acetamide hydrolysis is a better alternative to prepare acetate intercalated LDHs, as explained next. Acetamide hydrolysis generates carboxylic acid (acetic acid) and ammonia. The resultant acetic acid will serve as source for the acetate ion and ammonium will act as base to precipitate the metal hydroxides.\textsuperscript{41} This method is similar to synthesis of LDHs by urea (amide) hydrolysis.\textsuperscript{44} Acetamide hydrolysis was successfully used to prepare Ni-Al-acetate LDHs and attempts to prepare Mg-Al LDHs were largely unsuccessful.\textsuperscript{41} The successful synthesis of metal hydroxides with varied metal cations largely depends on the pH of the reaction medium and this in turn depends on the starting metal ion precursors (Metal nitrates, metal chlorides, metal oxides/metal hydroxides etc.).\textsuperscript{45,37} In the case of Al\textsuperscript{3+} containing LDHs, the synthesis mainly depends on the formation pH of divalent cations, as the Al\textsuperscript{3+} is amphoteric in nature and precipitates in both acidic and basic medium. Specifically, LDHs of Ni\textsuperscript{2+} or Co\textsuperscript{2+} with Al\textsuperscript{3+} form at pH 5-6, whereas Mg-Al LDHs form between pH 9-10.\textsuperscript{45,37} The lower pH of the reaction medium (5-6) and starting metal nitrate as precursors could be the possible reasons for not realizing Mg-Al-acetate LDHs in previous attempts.\textsuperscript{41} In this paper, we have attempted to synthesize Mg-Al-acetate LDHs through acetamide hydrolysis by employing metal hydroxides [Mg(OH)\textsubscript{2} and Al(OH)\textsubscript{3}] as starting precursors for metal cations instead of metal nitrates/chlorides. The basic nature of metal hydroxides compared to largely acidic metal salts, is expected to increase the pH of the reaction medium and thus favour the successful synthesis of Mg-Al-Acetate LDHs.

We prepared Mg-Al-acetate LDHs with two different Mg/Al = 3, 4 ratios, as described in the experimental section. The metal contents of the resultant compounds were determined by ICP-OES method and the anion content was established using CHN analysis. We derived the empirical formula of the resultant compounds by combining the results of the chemical analysis as follows; [Mg\textsubscript{0.72} Al\textsubscript{0.28} (OH)\textsubscript{2}] (CH\textsubscript{3}COO)\textsubscript{0.28} · 0.4 H\textsubscript{2}O (Mg/Al = 3) and [Mg\textsubscript{0.78} Al\textsubscript{0.22} (OH)\textsubscript{2}] (CH\textsubscript{3}COO)\textsubscript{0.22} · 0.5 H\textsubscript{2}O (Mg/Al = 4). The Mg/Al ratio of the resultant LDHs have slightly deviated from the initial reaction mixture taken for the synthesis. This deviation in the Mg/Al ratio is widely seen in the literature and could be largely due to varied physical constants of two different unitary metal hydroxides involved.\textsuperscript{45}

The PXRD patterns of the Mg-Al-acetate LDHs synthesized by acetamide hydrolysis are shown in Fig.1. Mg-Al-acetate LDH with Mg/Al = 3 shows (Fig.1a) first three basal reflections at 12.34 (7.15), 6.24 (14.16) and 4.16 Å (21.31 °2θ). These basal reflections are matching with the hydrated phase of acetate intercalated LDHs reported in the literature.\textsuperscript{41}
The *d*-spacing of 12.34 Å also indicates the bilayer arrangement of acetate ion perpendicular to the metal hydroxide layers in the interlayer space.\textsuperscript{41,43} Similarly, Mg-Al-acetate LDH with Mg/Al = 4 shows (Fig. 1b) the basal reflections at 12.30 (7.18), 6.21 (14.24) and 4.13 Å (21.50°2θ), which again matches with the hydrated phase of acetate intercalated LDH.\textsuperscript{41} The crystalline nature of both samples is evident from the sharp basal reflections observed in the PXRD pattern. In addition to basal reflections, appearance of turbostratically disordered mid 2θ region (around 35°2θ) and weak 2D reflections (around 60-62°2θ) characteristic of LDHs confirms the formation of Mg-Al-acetate LDHs via acetamide hydrolysis.\textsuperscript{41} The successful synthesis and the intercalation of acetate ion was further characterized by Fourier transformed infrared spectroscopy (FTIR). Mg-Al-acetate LDH with Mg/Al = 3 shows two strong vibrations at 1410 and 1557 cm\(^{-1}\) and they could be assigned to symmetric and antisymmetric stretching vibrations of carboxylic group COO\(^-\), respectively (Fig. 2a).\textsuperscript{46} It also shows a broad vibration centered on 3350 cm\(^{-1}\), and this could be assigned to hydrogen bonded hydroxyl ions and intercalated water molecules.\textsuperscript{46} The shoulder observed at 1340 cm\(^{-1}\) corresponds to the bending mode of \(-\text{CH}_3\) group of acetate ion. The metal-metal (M-M) and metal-oxygen (M-O) vibrations which are present below 1000 cm\(^{-1}\) are not clearly resolved. Similarly, Mg/Al = 4 also shows (Fig. 2b) vibrations at 1340, 1410, 1558 and 3350 cm\(^{-1}\) corresponding to carboxylate and hydroxyl ions, as described above. FTIR spectra of both samples (Mg/Al = 3, 4) corroborates the presence of intercalated acetate ion and also confirms the successful formation of Mg-Al-acetate LDHs. Besides carboxylates (COO\(^-\)), and hydrogen bonded hydroxyl ions (OH\(^-\)) no other vibration are seen in the FTIR spectra, which clearly indicates the absence of any impurities including the starting metal hydroxide precursors. The thermal behaviour of the resultant samples was studied using TGA and results are presented in Fig. S1. Both samples show a mass loss behaviour typical of acetate intercalated LDHs as reported in the literature.\textsuperscript{41} The mass loss observed below 200 °C can be assigned to the elimination of adsorbed and intercalated water. Dehydroxylation and the elimination of intercalated acetate ions were observed between 200-400 °C. The surface morphology of the resultant Mg-Al-acetate LDHs (Fig. 3) was characterized by SEM. Both samples showed an unusual mixed morphology having sheet-like and fibrous-like crystallites. LDHs generally exhibit a hexagonal sheet-like or sandrose morphology.\textsuperscript{47} The observation of fibrous-like crystallites along with sheet-like ones is somewhat unusual and could be due to presence of secondary phases.
To verify the presence of secondary phases as impurities, we compared the PXRD patterns of resultant LDHs with those of starting precursors, i.e. Mg(OH)$_2$, Al(OH)$_3$, and acetamide (Fig. S2). PXRD of the resultant LDHs does not show peaks that correspond to any of the starting precursors. Similarly, FTIR spectra of the starting precursors do not match with the resultant LDHs (Fig. S3), indicating the absence of any of these as secondary phases in the resultant LDHs. However, it has been previously reported that compounds prepared by acetamide hydrolysis show fibrous morphology. The concentration of acetamide in the reaction mixture, time and temperature is known to have significant effect on the morphology of the resultant compounds. Thus, the observed mixed morphology along with fibrous crystallites corroborates previous finding for samples prepared by acetamide hydrolysis. The Ni-Al-acetate LDHs prepared by acetamide hydrolysis by using metal nitrates showed sandrose morphology. The observation of mixed morphology in the present case could be the combined effect of the starting precursors and the concentration of the acetamide.

In order to investigate the effect of the synthesis method and different starting precursors on the CO$_2$ capture properties of the resultant LDH derived MMOs, Mg-Al-acetate LDH (Mg/Al = 3) was prepared by anion exchange reaction starting from Mg-Al-NO$_3$ precursor. The PXRD pattern of anion exchanged Mg-Al-acetate LDH shows (Fig. S4) basal reflections at 12.56 (7.03), 6.33 (13.97) and 4.20 Å (21.14 °2θ). This phase corresponds to hydrated acetate intercalated LDHs. Anion exchanged acetate LDH also shows 2$d$ reflection around 1.50 Å (61.60 °2θ), which corresponds to $ab$ plane of hydroxide sheet. The PXRD pattern also shows the turbostratically disordered reflection at 2.60 Å (34.58 °2θ), typical of hydrated acetate intercalated LDH. Intercalation of acetate was further characterized with FTIR spectra, as shown in the Fig. S5. The sample shows stretching vibrations due to carboxylate ion (1553, 1410 cm$^{-1}$) and hydrogen bonded hydroxyl ion (3312 cm$^{-1}$), confirming the formation of Mg-Al-acetate LDH. The surface of the anion exchanged acetate LDH was characterized by SEM and it shows the surface morphology typical of the LDHs (Fig. S6a & 6b). Interestingly, the mixed morphology having fibrous crystallites observed in the LDHs prepared by acetamide hydrolysis is absent in the anion exchanged acetate LDH.

The targeted LDH derived MMOs for CO$_2$ capture studies were obtained by decomposing Mg-Al-acetate (Mg/Al = 3, 4) LDHs at 400 °C for 4 h under N$_2$ atmosphere. The PXRD patterns of resultant MMOs are shown in Fig. 4. Thermal decomposition of Mg-Al LDHs at or around 400 °C results in the formation of MMOs, and understanding the exact chemical and structural properties of these materials is an ongoing research. The only crystalline
phase observed in the resultant MMOs is MgO and the nature of the aluminium containing oxide/hydroxide is amorphous. MMOs from Mg-Al-acetate LDHs show (Fig. 4a and b) the reflections at 2.10 (43.02 °2θ) and 1.48 Å (62.51 °2θ), which correspond to MgO of the MMOs phase.\textsuperscript{53} The absence of reflections other than the ones corresponding to MgO in the resultant MMOs again confirms the absence of any crystalline impurities/secondary phases in the parent LDHs as well as in the derived MMOs.

The surface morphology of the resultant MMOs was studied using SEM. SEM images of the MMOs are presented in Fig. 5, and MMOs from both LDHs (Mg/Al = 3 and 4) show a similar morphology to the one observed in the parent Mg-Al-acetate LDHs (Fig. 3). MMOs have retained the mixed morphology even after thermal decomposition, which indicates the topotactic conversion from precursor LDHs to resultant MMOs.\textsuperscript{54} The mixed morphology involving fibrous crystallites could influence the properties of the resultant MMOs, which in turn could show different CO\textsubscript{2} capture performance.

The anion exchanged acetate LDH was also decomposed to get MMOs, as described in the experimental section. The PXRD pattern of MMOs derived from anion exchanged LDH is shown in Fig. S7 and it shows peaks due to MgO at 2.08 (43.36) and 1.47 Å (62.92 °2θ) as expected.\textsuperscript{53} The morphology of the resultant MMOs is given in Fig. S6c and 6d and it is similar to the one reported in the literature for LDH derived MMOs.\textsuperscript{55}

The surface area of the resultant MMOs was studied using N\textsubscript{2} gas adsorption technique as discussed in the experimental section. All the samples show the type IV adsorption isotherm characteristic of mesoporous solids (Fig. 6).\textsuperscript{56} The samples show H2 type hysteresis loop between 0.5 to 1.0 pressure range, which is associated with the ink bottle pores indicating mesoporous nature of the MMOs. The surface area of the samples was calculated using the BET method, and pore size and pore volume were calculated by the BJH method and using the desorption branch of the isotherm. The surface properties of all the MMOs are given in the Table 1.
Table 1. Surface properties of MMOs generated from acetamide hydrolysis and anion exchange method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion exchanged (Mg/Al = 3)</td>
<td>118.6</td>
<td>0.25</td>
<td>11.91</td>
</tr>
<tr>
<td>Acetamide hydrolysis (Mg/Al = 3)</td>
<td>316.2</td>
<td>0.68</td>
<td>5.00</td>
</tr>
<tr>
<td>Acetamide hydrolysis (Mg/Al = 4)</td>
<td>341.7</td>
<td>0.75</td>
<td>4.84</td>
</tr>
</tbody>
</table>

The MMOs generated from the acetamide hydrolysis show very good surface area compared to the MMOs generated from the anion exchanged method. The observed large surface areas of MMOs generated from the acetamide hydrolysis are amongst the highest values reported so far for LDH based MMOs.\textsuperscript{30} The synthesis method along with mixed morphology involving fibrous crystallites could be a major factor in creating that high surface area.

(b) CO₂ capture studies of MMOs derived from acetate intercalated LDHs

CO₂ capture studies on MgO and MMOs derived from Mg-Al LDHs are usually carried out around 200-250 °C. The mechanism of CO₂ adsorption over MMOs is not yet clear, but it is broadly assumed that it is due to chemisorption.\textsuperscript{57} The earlier studies of CO₂ capture on MMOs showed the evidence for metal-carbonate formation during the CO₂ sorption over LDHs derived MMOs.\textsuperscript{58} The MgO present in the MMOs is found to be active phase for the formation of metal carbonates. Assuming chemisorption as the adsorption mechanism, one would expect that the formation of metal carbonates would take place based on the amount of MgO present in the MMOs. However, the amount of CO₂ capture realized for LDH derived MMOs is very negligible (2-5 %) when compared to the amount of MgO present.\textsuperscript{22}

In this work, CO₂ capture studies of resultant MMOs are carried out as described in the experimental section. The CO₂ capture performance of the obtained MMOs was evaluated from 200 to 300 °C at atmospheric pressure and under both, CO₂ rich (86 % CO₂) and more diluted (14 % CO₂) conditions, and it is presented in Fig. 7.
MMOs derived from 4:1 LDH showed a CO$_2$ capture capacity (86 % CO$_2$) of 1.19 mmol/g at 200 °C, which decreased to 0.87 mmol/g at 300 °C. This reduction in capture capacity from 200-300 °C is similar to the ones previously reported in the literature.$^{30}$

However, the CO$_2$ capture capacity observed at 200 °C is one of the highest values reported so far for pristine/unpromoted MMOs (Table 2).$^{20,59}$ The observed CO$_2$ capture capacity represents a very significant improvement compared to the capture capacity previously reported for acetate LDH derived MMOs (0.56 mmol/g).$^{60}$ Similarly, MMOs derived from 3:1 LDH showed better CO$_2$ capture capacities than previously reported values, with a capture capacity of 1.02 mmol/g (86 % CO$_2$) at 200 °C and 0.7 mmol/g at 300 °C.$^{60}$ MMOs derived from 4:1 LDH showed better CO$_2$ capture capacities at all temperatures than those derived from 3:1 LDH. The higher uptake could be due to the higher amount of Mg$^{2+}$ present in the MMOs derived from 4:1 LDH. For comparison, the CO$_2$ capture capacity of MMOs derived from commercial LDH Pural MG70 (Mg/Al = 2.33) was tested at 200 °C under 86 % CO$_2$. The sample showed a CO$_2$ capture capacity of 0.67 mmol/g which is much lower than the capture capacity achieved for the MMOs derived from Mg-Al-acetate LDHs synthesized from acetamide hydrolysis. The CO$_2$ capture profiles of MMOs derived from both 3:1 & 4:1 LDHs were studied at 200, 250 and 300 °C and are given in Fig. S8. All the samples show a very rapid initial uptake of CO$_2$ followed by a slow and steady uptake. None of the samples reach equilibrium within 2h of experimental time. However, the samples capture more than 80 % of CO$_2$ within the first 10-15 min compared to the overall capture capacity achieved over 2h (inset of Fig. S8).

The MMOs derived from Mg-Al-acetate LDHs were also tested under more industrially relevant flue gas CO$_2$ concentrations (14 %). Under those conditions, MMOs derived from 4:1 LDH show a CO$_2$ uptake of 0.97 mmol/g at 200 °C whereas MMOs derived from 3:1 LDH show 0.80 mmol/g. The amount of CO$_2$ captured by both MMOs decreases as the temperature increases from 200 to 300 °C. The observed CO$_2$ capture capacities of MMOs derived from the acetamide hydrolysis are compared with the literature reported CO$_2$ values of pristine MMOs, as shown in the Table 2. It can be seen that MMOs generated from the Mg-Al-acetate LDHs synthesized by modified acetamide hydrolysis show better CO$_2$ capture capacities than previously reported ones.

The reduced CO$_2$ capture capacity of MMOs under 14 % compared to 86 % CO$_2$ is as expected due to lower partial pressure of CO$_2$. However, the CO$_2$ uptake under 14 % CO$_2$ is higher than
most of the values reported for MMOs even under 100 % CO$_2$.\textsuperscript{59,61} This significant increase in CO$_2$ capture could be due to the combination of different factors including the starting metal ion precursors, the synthesis method, hydrolysing agent as well as the observed morphology. Generally, metal salts (nitrates, chlorides) are employed as precursors to metal ions in the synthesis of LDHs, which are highly acidic. In the present case, highly basic metal hydroxides are used as metal ion precursors and this could have slightly altered the basicity of the resultant LDHs. This change in starting precursors could have also altered the local pH and this in turn could have a significant effect on the nucleation and growth of the LDH. This was evident from the unsuccessful previous attempts to prepare Mg-Al- acetate LDHs starting with metal nitrates using the acetamide hydrolysis.\textsuperscript{41}

**Table 2. Comparison of CO$_2$ capture capacities of Mg/Al LDH based MMOs reported in the literature with the MMOs generated from the acetamide hydrolysis method.**

<table>
<thead>
<tr>
<th>Precursor LDH Sample</th>
<th>CO$_2$ capture Temperature (°C)</th>
<th>CO$_2$ concentration (%)</th>
<th>CO$_2$ capture Capacity (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Al-CO$_3$</td>
<td>200</td>
<td>100</td>
<td>0.8</td>
<td>62</td>
</tr>
<tr>
<td>Mg-Al-CO$_3$</td>
<td>200</td>
<td>50</td>
<td>0.9</td>
<td>63</td>
</tr>
<tr>
<td>Mg-Al-Pl</td>
<td>200</td>
<td>100</td>
<td>0.91</td>
<td>64</td>
</tr>
<tr>
<td>Mg-Al-CO$_3$</td>
<td>240</td>
<td>100</td>
<td>0.83</td>
<td>65</td>
</tr>
<tr>
<td>Mg-Al-St</td>
<td>200</td>
<td>100</td>
<td>1.15</td>
<td>66</td>
</tr>
<tr>
<td>Mg-Al-St</td>
<td>300</td>
<td>100</td>
<td>1.01</td>
<td>67</td>
</tr>
<tr>
<td>Mg-Al-CO$_3$</td>
<td>200</td>
<td>100</td>
<td>0.74</td>
<td>68</td>
</tr>
<tr>
<td>Mg-Al-Ac</td>
<td>200</td>
<td>100</td>
<td>0.51</td>
<td>64</td>
</tr>
<tr>
<td>Mg-Al-CO$_3$</td>
<td>300</td>
<td>100</td>
<td>0.62</td>
<td>69</td>
</tr>
<tr>
<td>SASOL MG70</td>
<td>200</td>
<td>86</td>
<td>0.67</td>
<td>This work</td>
</tr>
<tr>
<td>Mg-Al-Ac</td>
<td>200</td>
<td>86</td>
<td>1.20</td>
<td>This work</td>
</tr>
<tr>
<td>Mg-Al-Ac</td>
<td>200</td>
<td>86</td>
<td>1.02</td>
<td>This work</td>
</tr>
<tr>
<td>Mg-Al-Ac</td>
<td>200</td>
<td>14</td>
<td>0.97</td>
<td>This work</td>
</tr>
<tr>
<td>Mg-Al-Ac</td>
<td>200</td>
<td>14</td>
<td>0.80</td>
<td>This work</td>
</tr>
</tbody>
</table>

CO$_3$= Carbonate, Pl= Palmitate, St= Stearate, Ac= Acetate. The CO$_2$ capture capacities reported in the Table 2 are measured using TGA technique.
The surface properties of MMOs depend on the morphology and any change on that morphology will alter their properties. The combination of starting precursors along with the hydrolysing agent and synthesis method have resulted in a new mixed morphology involving fibrous and sheet-like crystallites for the resultant Mg-Al-acetate LDHs.

To evaluate the effect of synthesis method and starting precursors on the CO$_2$ capture performance of the materials, we also tested the CO$_2$ capture capacity of MMOs derived from anion exchanged Mg-Al-acetate LDH. They showed 0.57 mmol/g of CO$_2$ capture at 200 °C, under 86 % CO$_2$. This observed CO$_2$ capture capacity is similar to the reported value (0.56 mmol/g) for acetate LDH derived MMOs under similar testing conditions. This clearly highlights the need for alternative strategies in developing improved LDH based MMOs for medium-high temperature CO$_2$ capture applications. The MMOs derived from Mg-Al-acetate LDHs synthesized by acetamide hydrolysis were tested for cyclic CO$_2$ stability and results were compared with the CO$_2$ cyclic stability of MMOs derived from commercial LDH, Pural Mg70. The results are presented in Fig. 8. The MMOs derived from Mg-Al-acetate LDH (Mg/Al = 4) retained 65% (0.77 mmol/g CO$_2$) of their initial capture capacity after 10 adsorption/regeneration cycles. On the other hand, MMOs generated from Mg-Al-acetate LDH (Mg/Al = 3) showed a better stability as the capture capacity loss was of around 28% after the 10 cycles period. This improved CO$_2$ cycling stability might be attributed to the additional aluminium present in the sample compared to the MMOs having Mg/Al = 4 (lower aluminium content). The commercial LDH based MMOs sorbents (Pural MG70) show 35 % loss in capture capacity after 10 cycles. The CO$_2$ capture capacity retained by the commercial LDH based MMOs after 10 cycles (0.43 mmol/g) is much less compared to the MMOs derived from the Mg-Al-acetate LDHs (0.77 mmol/g). Overall, MMOs derived from Mg-Al-acetate LDHs synthesized by modified acetamide hydrolysis show better CO$_2$ capture and cycling stability compared to the MMOs derived from anion exchanged and commercial LDHs.
4. Conclusions

In this work, we have successfully developed LDH based novel MMOs with a mixed morphology and enhanced performance for high temperature (200-300 °C) CO₂ capture applications. The sorbents were synthesised by altering the starting precursors, synthesis method and hydrolysing agent. Mg-Al-acetate LDHs with two different Mg/Al (3, 4) ratios were synthesized by employing metal hydroxide as precursors and acetamide as hydrolysing agent. The acetamide acts as both, a pH regulator and the source of acetate ions. The resultant acetate intercalated LDHs crystallizes in a new morphology having both fibrous and sheet-like particles. Interestingly, the derived MMOs retain the mixed morphology of the precursor LDHs. These MMOs showed high specific surface areas (316-341 m²/g) and enhanced CO₂ capture capacities under both, 86 and 14 % CO₂ atmospheres, at ambient pressure. For instance, the CO₂ uptake at 200°C (1.20 mmol/g) was almost double than the one achieved by MMOs derived from anion exchanged acetate LDH (0.57 mmol/g) and commercial LDH (0.67 mmol/g). The MMOs derived from Mg-Al-acetate LDHs synthesized by modified acetamide hydrolysis show better CO₂ capture capacities compared to the MMOs derived from anion exchanged and commercial LDHs. They also showed improved cyclic stability compared to commercial LDH based MMOs. The starting precursors, synthesis method and hydrolysing agent used in this study have shown a positive effect on the CO₂ capture performance of resultant MMOs.

Acknowledgments

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Figures

Fig. 1 PXRD patterns of Mg-Al-acetate LDHs prepared by acetamide hydrolysis (a) Mg/Al = 3 and (b) Mg/Al = 4. Values given on reflections are corresponds to $d$-spacing in Å.
Fig. 2 FTIR spectra of Mg-Al-acetate LDHs prepared by acetamide hydrolysis (a) Mg/Al = 3 and (b) Mg/Al = 4.
Fig. 3 SEM images of Mg-Al-acetate LDHs prepared by acetamide hydrolysis (a, b) Mg/Al = 3 and (c, d) Mg/Al = 4.
Fig. 4 PXRD patterns of MMOs derived from Mg-Al-acetate LDHs prepared by acetamide hydrolysis (a) Mg/Al = 3 and (b) Mg/Al = 4. Values given on reflections correspond to \( d \)-spacing in Å.
Fig. 5 SEM images of MMOs derived from Mg-Al-acetate LDHs prepared by acetamide hydrolysis (a, b) Mg/Al = 3 and (c, d) Mg/Al = 4.
**Fig. 6** $\text{N}_2$ adsorption isotherms (77 K) of MMOs derived from Mg-Al-acetate LDHs prepared by acetamide hydrolysis and anion exchange method.

- Mg/Al = 4
- Mg/Al = 3
- Mg/Al = 3 (anion exchanged)
Fig. 7 CO₂ capture capacity under 86 and 14 %CO₂ of MMOs derived from Mg-Al-acetate LDHs synthesized by acetamide hydrolysis as a function of temperature.
Fig. 8. CO$_2$ capture cycling study (under 86% CO$_2$) of MMOs derived from Mg-Al-acetate LDHs synthesized by acetamide hydrolysis and Pural MG70 LDH. The carbonation was carried out at 200 °C and the regeneration was carried out at 400 °C.