Preparation and CO₂ adsorption of amine modified Mg–Al LDH via exfoliation route

Jiawei Wang a,*, Lee A. Stevens b, Trevor C. Drage b, Joe Wood a

a School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, United Kingdom
b School of Chemical and Environmental Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

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In response to the recent focus on reducing carbon dioxide emission, the preparation and characterization of organically functionalized materials for use in carbon capture have received considerable attention. In this paper the synthesis of amine modified layered double hydroxides (LDHs) via an exfoliation and grafting synthetic route is reported. The materials were characterized by elemental analysis (EA), powder x-ray diffraction (PXRD), diffuse reflectance infrared Fourier transform spectrometer (DRIFTS) and thermogravimetric analysis (TGA). Adsorption of carbon dioxide on modified layered double hydroxides was investigated by TGA at 25–80 °C. 3-[2-(2-Aminoethylamino) ethylamino]propyl-trimethoxysilane modified MgAl LDH showed a maximum CO₂ adsorption capacity of 1.76 mmol g⁻¹ at 80 °C. The influence of primary and secondary amines on carbon dioxide adsorption is discussed. The carbon dioxide adsorption isotherms presented were closely fitted to the Avrami kinetic model.

1. Introduction

The increasing atmospheric carbon dioxide concentration is of great concern to mankind, as it can be considered as a leading contributor to global climate change. The main cause for the increase of carbon dioxide concentration since the Industrial Revolution has been suggested to be due to man-made emissions (Hegerl et al., 2007). Among all carbon emission sources, fossil fuel power plants are one of the largest contributors to greenhouse gas emissions. Although amine solvent scrubbing technology is the most established technique available for post-combustion CO₂ capture in power plants, the associated energy penalty and cost make it less attractive economically. This has led to the development of alternative technologies to reduce the energy and cost penalty associated with carbon capture (Figueroa et al., 2008). Solid adsorbents could offer a potential route to significantly reduce the cost of CO₂ capture (Gray et al., 2008). According to Gray et al. (2008), the energy required for solid adsorbent based processes can be significantly lower than that of aqueous processes when the CO₂ adsorption capacity reaches or exceeds approximately 2 mmol g⁻¹. If the CO₂ adsorption capacity of solid adsorbents reaches 3 mmol g⁻¹, the energy reduction is estimated to be least 30–50% compared to the optimum aqueous monoethanolamine (MEA) based process. A range of porous materials have been explored with the key aim of developing materials with a high capacity and selectivity for CO₂ (Choi et al., 2009). Solid sorbent development for post-combustion capture has focussed on porous materials with modified surface chemistry to enhance adsorbent—CO₂ interaction under conditions of low CO₂ partial pressure. Possible techniques for enhancing the adsorption capacity include loading amines onto various types of supports such as mesoporous silicas, including SBA-12 (Zelenak et al., 2008), SBA-15 (Hiyoshi et al., 2005; Zelenak et al., 2008; Zukal et al., 2009), microspheres (Araki et al., 2009). Alternative supports include zeolites (Su et al., 2010; Zukal et al., 2009), MCM-41 (Zelenak et al., 2008) and MCM-48 (Huang et al., 2003; Kim et al., 2005). However grafting or impregnation are also feasible methods of preparation Scheme 1. Layered doubled hydroxides (LDH), also known as hydrotalcite-like compounds, are composed of positively charged layers with charge balancing anions located in the interlayer region. LDH have the general formula [M⁺dh Al₂d(OH)₄d][M⁺h₂dO₄]·xH₂O with x typically in the range between 0.10 and 0.33 (Forano et al., 2006). These materials can be readily and inexpensively synthesized with the desired characteristics for a particular application. LDH and calcined LDH (oxides) are widely used in the areas of catalysis, anion exchange and adsorption.

The use of LDH for adsorption of CO₂ has been investigated, but mainly under conditions of elevated temperature. Yong et al. (2001) reported several commercial hydrotalcite-like compounds...
with adsorption capacities of 0.2–0.5 mmol g\(^{-1}\) at 300 °C and 1 bar of CO\(_2\). They also found that the carbonate anion favours CO\(_2\) adsorption compared to OH\(^-\), and a low content of water can improve adsorption capacity. CO\(_2\) adsorption capacities higher than 1.0 mmol g\(^{-1}\) have been reported by Hutson and Attwood (2008). A CO\(_2\) adsorption capacity of 3.55 mmol g\(^{-1}\) was achieved by Ca–Al LDH with ClO\(_4\)\(^-\) anion at 330 °C and 1 bar. The adsorption capacity of LDH adsorbents can also be enhanced by promotion with potassium salts (Walspurger et al., 2008; Lee et al., 2007).

Amine modified LDHs have been prepared by several different methods. Park et al. (2005) used dodecyl sulfate (DS) intercalated LDH as precursor and added [3-aminopropyl]triethoxysilane (APTS) together with N-cetyl-N,N,N-trimethylammonium bromide (CTAB). The key step for the process was the formation of insoluble DS-CTAB salts and DS molecules were simultaneously replaced by APTS moieties. A process of exfoliation of LDHs followed by grafting of the single layers with aminosilanes has also been proposed (Wypych et al., 2005; Wypych and Satyanarayana, 2005). In-situ grafting of APTS onto the surface of LDHs with the assistance of DS was also reported by Tao et al. (2009a, b).

Compared with the widely studied LDH materials, reported investigations of CO\(_2\) adsorption are lacking for amine grafted LDHs. The aims of this work were to prepare, characterize and for the first time evaluate the CO\(_2\) adsorption capacity of amine modified LDH. In this work, amine modified Mg-Al LDHs prepared via an exfoliation route were characterized by Elemental Analysis (EA), Powder X-Ray Diffraction (PXRD), Diffuse Reflectance Infrared Fourier Transform Spectrometer (DRIFTS) and ThermoGravimetric Analysis (TGA). The exfoliation route were characterized by Elemental Analysis (EA), Powder X-Ray Diffraction (PXRD), Diffuse Reflectance Infrared Fourier Transform Spectrometer (DRIFTS) and ThermoGravimetric Analysis (TGA).

2. Experimental

2.1. Preparation of DS intercalated LDH

The DS intercalated LDH was synthesized by the coprecipitation method of the relevant metal nitrates in DS solution. 4 g of Mg(NO\(_3\))\(_2\)·6H\(_2\)O and 1.95 g of Al(NO\(_3\))\(_3\)·9H\(_2\)O with a molar ratio of 3:1 (Mg\(^{2+}\)/Al\(^{3+}\)) were dissolved in 50 ml distilled water. The solution was added to a 3 g of sodium dodecyl sulfate dissolved in 100 ml distilled water, under vigorous stirring, at a rate of 0.5 ml min\(^{-1}\) at 70 °C. The pH value of the mixture was maintained at 10 by adding 4 M NaOH solution. The mixture was then aged for a further 4 h with the temperature and stirring maintained. The obtained material was filtered and washed with distilled water. The product was dried in a vacuum oven at 70 °C overnight.

2.2. Preparation of amine modified LDH

Aminosilanes were grafted on the LDH surface by the method reported by Wypych et al. (2005). In the method 0.5 g of DS intercalated LDH (MgAl DS) was added to a reaction flask containing 125 ml of toluene. The mixture was subjected to sonication in an ultrasonic bath for 4.5 h at room temperature. After the suspension was kept for about 30 min, an extremely fine, white and voluminous gel formed at the bottom of the reactive flask.

The white gel was reacted with about 15 times the stoichiometric amount of aminosilanes under nitrogen atmosphere for 5 h at 60 °C. The precipitated solid was isolated by filtration and washed with toluene. Finally, the solid was dried under vacuum overnight. Three primary and secondary aminosilanes, 3-aminopropyl triethoxysilane (APTS), N-2-aminooethyl-3-aminopropyl trimethoxysilane (AEAPTS) and 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (DAEAPTS), were used. The corresponding samples were labeled as MgAl N1, MgAl N2 and MgAl N3. MgAl Nx was used as a general designation for all three amine modified LDHs.

2.3. Characterization of the samples

Elemental analysis was performed using an Flash EA 1112 Elemental Analyzer (Thermo Electron S.p.A, Milan, Italy), configured to detect carbon, hydrogen, nitrogen and sulfur. The linear calibration method was selected using three calibration standards with 5 mg of vanadium pentoxide (V\(_2\)O\(_5\)) was sealed in tin capsules (8 mm in diameter, 3.0 mm in height, 6H\(_2\)O and 1.95 g of Al(NO\(_3\))\(_3\)·9H\(_2\)O with a molar ratio of 3:1 (Mg\(^{2+}\)/Al\(^{3+}\)) were dissolved in 50 ml distilled water. The solution was added to a 3 g of sodium dodecyl sulfate dissolved in 100 ml distilled water, under vigorous stirring, at a rate of 0.5 ml min\(^{-1}\) at 70 °C. The pH value of the mixture was maintained at 10 by adding 4 M NaOH solution. The mixture was then aged for a further 4 h with the temperature and stirring maintained. The obtained material was filtered and washed with distilled water. The product was dried in a vacuum oven at 70 °C overnight.

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corrected by measuring the response to an empty platinum crucible by the same method.

CO₂ adsorption on liquid amine samples (APTS, AEAAPTS and DAEAPTS) were also measured by TGA. About 20 mg liquid amine sample was placed in the platinum crucible and the temperature of the sample chamber was held isothermally at 25 °C for 10 min in N₂ to remove air from the system. The CO₂ was then introduced and the temperature was ramped to 200 °C at the rate of 10 °C min⁻¹.

3. Results and discussion

3.1. Characterization of amine modified LDH

3.1.1. Elemental analysis

Data from elemental analysis and PXRD are summarized in Table 1. The formula for intercalated and grafted molecules was calculated based on the elemental weight percentage of carbon, nitrogen and sulfur. The formula shows that MgAl DS had 1.87 mmol dodecyl sulfate anion per gram sample, and also captured 0.12 mmol nitrate and 1.04 mmol carbonate anions, which came from the metal salts used to prepare the samples and from atmospheric CO₂. The amount of dodecyl sulfate intercalated reduced to 1.42, 0.98 and 0.85 for MgAl DS N1, N2 and N3 after exfoliation and amine grafting, respectively. This indicates that dodecyl sulfate anions were partially replaced by amine silane molecules. It also shows that more DS anions were replaced with larger aminosilane molecules, which can be explained by the steric effect and larger molecules like DAEAPTS and AEAAPTS occupy more space than APTS.

Based on elemental analysis data, the degree of silylation can also be calculated. Taking APTS as an example a general formula for grafted APTS moieties is C₉H₂₃NO₃Si. When n = 9, the formula is C₃H₇NO₃Si, which is the molecular formula of APTS. In this case there is no reaction between APTS molecules and the LDH layers. When n = 7.5 or 3, correspondingly 1, 2 or 3 ethoxysilane groups react with hydroxyl groups on the LDH layers. Therefore, the degree of silylation reaction for MgAl DS N1 can be calculated from the formula (1):

\[ \text{Degree of silylation} = \frac{9-n}{6} \times 100\% \]  

(1)

The same method can be applied to the other two aminosilanes.

As shown in Table 1, the MgAl N1 shows a degree of silylation of 98%, which means almost all ethoxysilane groups have attached to the LDH layers. MgAl N2 and MgAl N3, however, have only achieved 74% and 61% of the degree of silylation, respectively.

The amine loading (the number of moles of amine per total weight of material) is one of the most important parameters for CO₂ adsorbents, since the availability of basic amine groups influences the CO₂ uptake. MgAl N1, N2 and N3 had amine loading of 2.39, 5.14 and 6.01 mmol N g⁻¹, according to elemental analysis. Normalized by the number of amines in each silane, the actual number of silane molecules grafted for MgAl N1, N2 and N3 were 2.39, 2.57 and 2.00 mmol g⁻¹. The decrease in degree of functionalization was due to the size of the silane molecules (Choi et al., 2009). Larger silanes provide more steric hindrance and lead to smaller degree of surface functionalization.

3.1.2. PXRD

In Fig. 1, only PXRD patterns for MgAl DS and MgAl N3 are shown for clarity. All amine modified LDH samples have similar PXRD patterns apart from the peak positions of (003) and (006). The pattern for MgAl DS had the (003) and (006) reflections at 26.2 and 13.0 Å, corresponding to a basal spacing of 26.1 Å. The value was close to the previously reported values in the literature of 26.2 Å (Wypych et al., 2005) and 26.5 Å (Park et al., 2005; Tao et al., 2009a). As observed from Fig. 1, at the 2θ value equal to 60°, overlapping of the peaks corresponding to the (113) and (110) reflections occurred, which is usual for LDHs with large interlayer spacing (Herrero et al., 2009). After exfoliation and amine grafting, the sharpness and intensity of the reflections (003) and (006) reduced dramatically and a broad reflection was observed in the 2θ range of 15–30°. This indicates that the crystallinity of the system decreased after restacking of the layers. However, the non-basal reflections (012) and (110) were preserved, which indicates that the structure of the layers was conserved (Crepaldi et al., 2002).

The d-spacing was calculated as \[ d_{(003)} = \frac{\partial d_{(006)}}{2} \] (Herrero et al., 2009) and the values are listed in Table 1. MgAl N1, grafted with APTS, has a d-spacing of 24.1 Å, which was reduced from 26.1 Å of MgAl DS. As the size of grafted aminosilanes increased, the d-spacing of corresponding surface modified LDHs increased.

![Fig. 1. PXRD patterns for samples MgAl DS and MgAl N3.](image-url)

Table 1

Data of element analysis and PXRD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental weight (%)</th>
<th>Formula for intercalated and grafted molecules (mmol g⁻¹)†</th>
<th>Degree of silylation</th>
<th>d spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl DS</td>
<td>0.17</td>
<td>(C₁₂H₂₃SO₄)₁₂(NO₃)₀.₁₂(CO₃⁻)ₐ₀.₀₄</td>
<td>–</td>
<td>26.1</td>
</tr>
<tr>
<td>MgAl N1</td>
<td>3.35</td>
<td>(C₁₂H₂₃SO₄)₂₄(C₁₃H₂₅H₂₃N₇O₃Si)₂₆₉₈</td>
<td>98%</td>
<td>24.1</td>
</tr>
<tr>
<td>MgAl N2</td>
<td>7.20</td>
<td>(C₁₂H₂₃SO₄)₄₈(C₁₃H₂₅H₂₃N₇O₃Si)₂₃₉₃</td>
<td>74%</td>
<td>28.5</td>
</tr>
<tr>
<td>MgAl N3</td>
<td>8.42</td>
<td>(C₁₂H₂₅H₂₃Si₄₈(C₁₃H₂₅H₂₃N₇O₃Si)₂₆₇₇</td>
<td>61%</td>
<td>28.7</td>
</tr>
</tbody>
</table>
The \( d \)-spacing of MgAl N2 and N3 were increased to 28.5 and 28.7 Å, respectively. The increase of \( d \)-spacing implies the intercalation of grafted aminosilanes into LDH layers.

### 3.1.3. TGA

Fig. 2 shows the TGA and corresponding differential thermogravimetry (DTG) profiles of DS and amine modified LDHs. For DS intercalated LDH, the TGA profile shows four weight loss steps. The first one was from 25 to 150 °C with a total weight loss of 10.5%, attributed to the removal of surface adsorbed and interlayer water molecules (Tao et al., 2009a). The second step was from 150 to 300 °C with a decomposition peak at 224.8 °C in the DTG curve. A total weight loss of 31.1% was recorded during this step, which was thought to be related to dehydroxylation of LDH. Further dehydroxylation and dodecyl sulfate decomposition occurred over the temperature range from 300 to 850 °C with a total weight loss of 12.0%. The final step of 9.1% weight loss above 850 °C was attributed to the decomposition of the residual sulfate salt (Herrero et al., 2009).

When aminosilanes were bonded to the LDH surface, the thermal decomposition showed significantly different behavior. The most obvious difference was that the weight loss of MgAl N\( x \) in the process of dehydroxylation (150–300 °C) was much less than the one recorded in the sample of MgAl DS. This can be explained by the reaction of –OH group with silanol during grafting reaction (Tao et al., 2009a). It was followed by decomposition of alkyl chain in the temperature range of 300–850 °C with a total weight loss of about 50%. A further 8–9% weight loss was recorded at about 850 °C, corresponding to the residual sulfate salt decomposition, which was similar to the TGA of MgAl DS.

### 3.1.4. DRIFTS

The DRIFTS spectra of DS and amine modified LDHs are shown in Fig. 3. The spectrum of MgAl DS had a broad band in the region 3200–3700 cm\(^{-1}\), which can be attributed to the stretching vibration of internal and hydrogen-bonded hydroxyl groups and adsorbed water molecules. The bending vibration of hydroxyl group also gave a band at 1634 cm\(^{-1}\). The DS molecules showed a group of characteristic bands (Wypych et al., 2005) at 2955, 2920 and 2852 cm\(^{-1}\) (C–H stretching bond) and 1466 cm\(^{-1}\) (C–H bending bond) of the organic skeleton and at 1209, 1061 and 823 cm\(^{-1}\) (–SO\(_4\)). A band at 1382 cm\(^{-1}\) is attributed to nitrate ions, co-intercalated with DS (Crepaldi et al., 2002; Wypych et al., 2005). In the spectra of MgAl N\( x \), new bands related to N–H bonds were observed in the region of 3200 and 1570 cm\(^{-1}\).

### 3.2. Adsorption of carbon dioxide

A typical TGA curve for CO\(_2\) adsorption capacity measurement is shown in Fig. 4. At stage 1, the sample was pre-treated at 105 °C for 30 min under N\(_2\). The weight loss at this stage was attributed to the loss of absorbed water. In stage 2 the sample was cooled to the required temperature for the CO\(_2\) adsorption test. A slight weight gain was caused by N\(_2\) adsorption on the sample. After the sample temperature was stable (stage 3), the gas input was switched to CO\(_2\) and the associated weight gain was assumed to be due to the adsorbed CO\(_2\).

Fig. 5 shows the CO\(_2\) adsorption capacity of amine modified LDHs at four different temperatures, where each sample had the same pre-treatment as described above. The amount of carbon dioxide adsorbed on MgAl N1 was about 1.0 mmol g\(^{-1}\) in the

![Fig. 2. TGA and DTG profiles of MgAl DS and MgAl N\( x \).](image-url)

![Fig. 3. DRIFTS spectra of DS and amine modified layered double hydroxides.](image-url)
temperature range tested, which is within the range of values 0.57–2.05 mmol g\(^{-1}\) reported in the literature for CO\(_2\) adsorption on APTES modified mesoporous silica (Hiyoshi et al., 2005; Huang et al., 2003; Zelenak et al., 2008). The amine efficiency is defined as the ratio of the amount of CO\(_2\) adsorbed to the number of amine groups in the sample and thus provides a measure of how effective the grafted amines are in augmenting the adsorption capacity of the materials for CO\(_2\). The amine efficiencies for the samples tested in this study were in the range of 0.41–0.48 mol CO\(_2\) mol\(^{-1}\)N, which is close to the maximum efficiency of 0.5 based on carbamate formation mechanism (Satyapal et al., 2001). Under dry conditions, two moles of amine groups are required to remove every mole of CO\(_2\) to form carbamate.

For the samples MgAl N2 and MgAl N3, the grafted aminosilanes not only have primary amine end groups, but also have secondary amine sites in their linkers. MgAl N2 had a CO\(_2\) adsorption capacity of 1.1 mmol g\(^{-1}\) at 25 °C, which decreased to 0.8 mmol g\(^{-1}\) at 40 °C. At 60 and 80 °C, the CO\(_2\) adsorption capacity increased to 1.2 mmol g\(^{-1}\). Although the CO\(_2\) adsorption capacity of MgAl N2 was higher than that of MgAl N1, the amine efficiency of MgAl N2 was in the range of 0.15–0.24, which was less than that of MgAl N1. The CO\(_2\) adsorption capacity of MgAl N3 showed a steady increase from 0.74 mmol g\(^{-1}\) at 25 °C to 1.75 mmol g\(^{-1}\) at 80 °C. The trend is different from the previous results of hexagonal mesoporous silicas (HMSs) modified by DAEPTS, the same aminosilane used for preparation of MgAl N3, reported by Knowles et al. (2006). They reported that the CO\(_2\) adsorption capacity of the DAEPTS modified HMS decreased from 1.34 mmol g\(^{-1}\) at 25 °C to 0.45 mmol g\(^{-1}\) at 75 °C. This suggests that positively charged MgAl brucite-like layers might affect CO\(_2\) adsorption in a way which is different from silica based supports. The amine efficiency of MgAl N3 increased from 0.12 at 25 °C to 0.39 at 80 °C. Knowles et al. (2006) reported the AEPAPTS and DAEAPTS modified HMSs had an amine efficiency of about 0.3. The authors suggested that the lower amine efficiencies than APTS modified HMS were due to reduced accessibility of CO\(_2\) to the surface amine groups, as longer hydrocarbon chains might lead to reduced mobility and relative proximity of amine pairs. Comparing adsorption capacities in the current study with those reported in the literature, Lwin and Abdullah (2009) reported adsorption capacity of 30 mg g\(^{-1}\) (0.68 mmol g\(^{-1}\)) at 25 °C for CuAl-1.0 hydrotalcite, which decreased to 22 mg g\(^{-1}\), (0.5 mmol g\(^{-1}\)) at 150 °C. The adsorption of 0.74 mmol g\(^{-1}\) recorded in this study at 25 °C was only slightly higher than that measured by Lwin and Abdullah (2009), but the marked increase in adsorption that occurred with increasing temperature up to 80 °C in this work was in contrast with their study. This suggests that the amine modified adsorbents reported here would be useful in higher temperature capture processes, such as post-combustion capture.

To understand CO\(_2\) adsorption of grafted amine at different temperatures, the CO\(_2\) adsorption of three liquid amines was measured by TGA as well. The results are shown in Fig. 6. APTS showed a steady weight gain from 28 to 80 °C and started to lose weight at temperatures above 80 °C. This indicates that CO\(_2\) begins to react with APTS from even the low temperature of 28 °C. However, AEAPTS and DAEAPTS showed very different behaviors for CO\(_2\) uptake. While the weight gain for AEAPTS before 73 °C was slow compared to APTS, it showed a sudden increase after that. Similar behavior was observed for DAEAPTS where the transition temperature at which the weight gained started to rapidly increase was 84 °C. The slower weight gain of AEAPTS and DAEAPTS at low temperature could be caused by their higher viscosity and therefore additional mass transfer limitation for CO\(_2\) adsorption. The existence of transition temperature for AEAPTS and DAEAPTS suggests that primary amine sites and secondary amine sites have different initial reaction temperatures for CO\(_2\) adsorption, as APTS has only primary amine sites and AEAPTS and DAEAPTS have primary and secondary amine sites.
Fig. 7 shows the initial CO$_2$ adsorption rate over each sample at different temperatures. For all three samples, the CO$_2$ adsorption rate increased with temperature. At every temperature tested, MgAl N1 always had the highest adsorption rate. This can be explained since the secondary amine has a slower reaction with CO$_2$ than primary amine (Harlick and Sayari, 2006). With increasing number of secondary amine sites, the CO$_2$ adsorption rate decreased in the order of MgAl N1 > MgAl N2 > MgAl N3. The adsorption rates reported by Lwin and Abdullah (2009) were strongly dependent upon temperature with CuAl-2.0 adsorbent displaying carbon dioxide adsorption rates in the range 1–16 mg g$^{-1}$ min$^{-1}$ (0.02–0.36 mmol g$^{-1}$ min$^{-1}$) at 150–600 °C adsorption temperatures. However in this work, adsorption rates of up to 0.4 mmol g$^{-1}$ min$^{-1}$ were observed at the much lower temperatures, suggesting that the amine modified layered double hydroxides display a superior rate of adsorption.

3.3. Kinetic study

Kinetic information was obtained by isothermal adsorption of amine modified LDHs at different temperatures (i.e. 25, 40, 60 and 80 °C). The isothermal graphs of MgAl N$_x$ are presented in Fig. 8. All the isotherms of CO$_2$ adsorption were fitted by Avrami model (Avrami, 1939)

$$C_t = C_e [1-e^{-k_A n_A}]^{n_A}$$

where $C_t$ represents the amount of CO$_2$ adsorbed at time $t$, $C_e$ is the amount of CO$_2$ adsorbed at equilibrium, $k_A$ is the Avrami kinetic constant and $n_A$ is the Avrami exponent. The Avrami model was used extensively to model phase transitions and crystal growth of materials (Jackson, 2004), and recently used to describe the adsorption of anionic dyes (Cestari et al., 2006) and CO$_2$ (Serna-Guerrero and Sayari, 2010) on amine-functionalized silicas. To determine the adequacy of the Avrami model fit to the adsorption data reported in this work, an error function based on the normalized standard deviation was calculated

$$Err(\%) = \sqrt{\frac{\sum (C_{t(exp)} - C_{t(cal)})^2}{N-1}} 	imes 100$$

where $Err$ (%) is the error function, $C_{t(exp)}$ is the experimental data of the amount of CO$_2$ adsorbed at time $t$, $C_{t(cal)}$ is the amount adsorbed as calculated by the Avrami model and $N$ is the total number of experimental points.

For each isotherm, the values of $C_e$, $n_A$ and $k_A$ were calculated from experimental data through linear regression. The results are presented in Table 2. The calculated Avrami exponent for MgAl N2 varied from 0.79 at 25 °C to 0.27 at 80 °C. According to Cestari et al. (2006), the order of this model reflects the complexity of the reaction mechanisms or the occurrence of more than one reaction.

Fig. 8. Isotherms of CO$_2$ adsorption on MgAl N$_x$ at different temperatures. Experimental data are shown as points and Avrami model by curves. (a) MgAl N1, (b) MgAl N2, (c) MgAl N3.
The materials were characterized by EA, PXRD, DRIFTS and TGA. It is the first time that CO₂ adsorption data has been reported for amine modified LDHs. The highest adsorption capacity for CO₂ was achieved at 1.75 mmol g⁻¹ by MgAl N3 at 80 °C and 1 bar. The LDHs with only primary amine groups had the highest adsorption rate at any temperature. The Avrami model has provided a good experimental-simulation fit for the CO₂ adsorption isotherms on amine modified LDHs. The relatively high capacity at 80 °C together with favorable rates of adsorption make the amine modified layered double hydroxides suitable for use in post combustion carbon capture processes.

Notation

\[ A \] Arrhenius pre-exponential factor, min⁻¹  
\[ C_e \] amount of CO₂ adsorbed at equilibrium, mmol g⁻¹  
\[ C_t \] amount of CO₂ adsorbed at time \( t \), mmol g⁻¹  
\[ C_e(\text{exp}) \] experimental data of the amount of CO₂ adsorbed at time \( t \) calculated by the Avrami model, mmol g⁻¹  
\[ E_a \] activation energy, KJ mol⁻¹  
\[ \text{Err} \] error function, %  
\[ k_A \] Avrami kinetic constant, min⁻¹  
\[ n_A \] Avrami exponent  
\[ N \] total number of experimental points  
\[ T \] absolute temperature, K

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