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Polyol-modified layered double hydroxides with attenuated basicity for a truly reversible capture of CO_2

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Abstract Dendrimers bearing hydroxyl groups supported by layered double hydroxides (CO_3–LDH) with Mg/Al ratio ranging from 1:1 to 5:1 showed improved properties for the reversible capture of carbon dioxide (CO_2). The adsorption capacity of the starting LDH was due to the intrinsic base-like behavior, and was found to depend on the Mg/Al ratio. When contacted with polyol dendrimers in aqueous media, no intercalation took place. This was explained in terms of low exfoliation grade of LDH and hydrophobic character of the dendrimer molecules. The latter rather adsorb on the external surface of the LDH stacks for low dendrimer loadings, or aggregate into organic clusters for higher contents. Analyses through thermal programmed desorption of CO_2 revealed that dendrimer incorporation advantageously attenuates the basicity strength of the starting LDH support, by lowering the desorption temperature. The OH groups of the organic moiety were found to display an amphoteric character, and act as the main adsorption sites. The weak interactions with CO_2 facilitate easier release of the major part of adsorbed CO_2 at temperature not exceeding 80–100 °C. On polyol organo-LDHs, the reversible CO_2 retention was discussed herein in terms of acid–base interactions. This concept allows envisaging the capture of diverse pollutants and other greenhouse gases by modifying the chemical groups on the dendritic moiety.

Keywords Layered double hydroxide · Polyol dendrimer · Thermal programmed desorption · Carbon dioxide · Reversible capture · Weakly basic sites

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1 Introduction

Greenhouse gases are now recognized as being an important factor of the global warming, and their reduction has become an important issue to be addressed. Among these, carbon dioxide (CO_2) can be retained by basic compounds such as amines and their derivatives, but amine losses during the process turned out to be a major drawback. Improvements have been brought by amine immobilization over solid supports (Chaffee et al. 2007; Sirwardane 2005; Gray et al. 2004), but regeneration requires strong heating for thermal desorption due to strong chemical interaction with CO_2. To overcome this constraint, a judicious route resides in the immobilization of organic moieties bearing high numbers of base sites weakly reactive towards CO_2. This innovative concept will involve a reversible capture of CO_2 through only purely physical adsorption.

Crystalline aluminosilicates such as zeolites and clay minerals are interesting low-cost and widely available gas

adsorbents (Azzouz 2012). For instance, montmorillonite (Mt) was already found to show affinity towards CO_2, owing to the weak base character of the oxygen atoms surrounding the ion-exchange sites (Azzouz et al. 2006). Nonetheless, unless adequate modifications are made, high retention capacity cannot be envisaged on such materials because of their small number of adsorption sites. Besides, diffusion hindrance often takes place due to limited pore sizes (Soares et al. 2004; Santos-Costa et al. 2004; Yong and Rodrigues 2002).

In this regard, Mt intercalation with commercial polyol dendrimers produced higher effectiveness (Azzouz et al. 2010, 2009, 2006). The resulting organo-clay combines physicochemical features arising from both the clay support and organic moiety. Beside the intrinsic affinity of montmorillonite towards CO_2, the OH groups exhibit very weak basicity, expressed in terms of amount of desorbed CO_2, as supported by the relatively low desorption temperature. This basicity is assumed to be induced by the lone electron pair on their oxygen atoms (Azzouz et al. 2010; Saharay and Balasubramanian 2006). The OH groups were found to act as the main adsorption sites by retaining CO_2 via Lewis acid–base (L-AB) interactions (Azzouz et al. 2010, 2009). Such interactions are, by far, much weaker than those involved by amines or other base-like compounds. Consequently, OH-compounds are expected to retain less CO_2 as compared to amines, but should allow easier desorption of the retained gas upon slight heating (Saharay and Balasubramanian 2006; Rodlert et al. 2004).

The incorporation of polyol dendrimers should not shade completely the contribution of the clay support, and slightly more basic clay materials could improve the adsorption capacity, provided that the desorption temperature does not increase. In this regard, anionic clay minerals like layered double hydroxides (LDH) can behave as active supports, owing to their intrinsic basicity (Soares et al. 2004; Santos-Costa et al. 2004; Yong and Rodrigues 2002). They could be regarded as a compromise between amines that display strong chemical interactions and Mt, which exerts only weak physical interactions towards CO_2.

Nevertheless, notwithstanding their intermediate basicity, LDH's still exhibit sufficiently strong interactions with CO_2. These interactions could be attenuated if the accessible adsorption sites belonging to the LDH surface are partially shaded by amphoteric chemical species like polyol dendrimers. The resulting organo-LDHs are expected to display optimum base-like character, judiciously tailored to allow a truly reversible retention of CO_2. All OH-compounds are expected to favor the formation of carbonate-like associations with CO_2, but not necessarily via strong CO_2–OH bindings (Gassensmith et al. 2011). This can be achieved through an optimum compromise between the largest amounts of adsorbed CO_2 and the easiest consecutive desorption with minimum energy consumption, at temperatures close to the ambient value. This concept can also be applied to remove and concentrate diverse gas pollutants, using respiratory systems that operate by repetitive adsorption–desorption cycles. Such adsorbents display lower retention capacity as compared to amines, but they can retain higher CO_2 amounts than polyol-Mt matrices (Azzouz et al. 2010, 2009). Therefore, they are not intended for CO_2 capture from industrial flue gases or for gas sequestration. Besides, they can exert sufficiently strong interaction to retain efficiently CO_2 from gas mixtures at room temperature, but in the meantime, these interactions are sufficiently weak to afford easy consecutive CO_2 desorption even without heating, under forced convection in gas stream or in low CO_2 concentration mixtures.

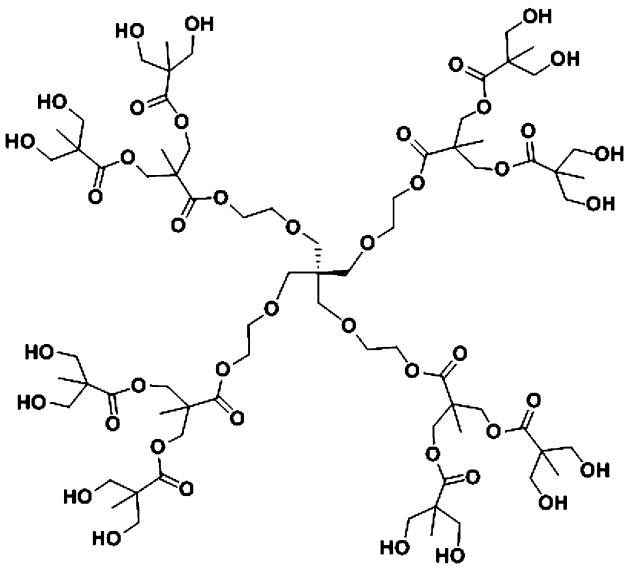
The role of this specific organo-LDH behavior in the retention of the highest CO_2 amounts has to be elucidated. Unraveling the contributions of both the inorganic support and organic moiety could be of great interest to understand the way the physical interactions could be modified to achieve optimum retention of CO_2, followed by easy desorption. For this purpose, attempts were made to retain carbon dioxide on synthetic LDH having different Mg/Al ratio ranging from 1:1 to 5:1, before and after intercalation with commercial Boltorn H20, H30 and H30 dendrimers. The CO_2 adsorption capacity and the retention strength will be assessed through thermal programmed desorption (TPD). The effects of Mg/Al ratio and of the amount of hydroxyl groups on the dendrimers were herein examined and discussed in terms of interactions between CO_2 and the adsorbent.

2 Experimental section

2.1 LDH synthesis and intercalation

Various LDH samples with different Mg/Al molar ratios ranging from 1:1 to 5:1 were prepared through co-precipitation of aqueous solutions of $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$, in the presence of NaOH and Na_2CO_3, according to a conventional procedure (Arus et al. 2010; Vaccari 1998; De Roy et al. 1992; Cavani et al. 1991). Analytical grade reagents (Sigma-Aldrich) were used as such without purification. pH was adjusted at 8–12 in order to improve the product crystallinity. pH higher than 10 was found to reduce significantly the particle size. The precipitate was then washed by centrifugation to reduce pH below 9, then dried at 100–110 °C overnight and further deposited in a desiccator.

Intercalation attempts were achieved through a mere impregnation of dry LDH powder in an aqueous mixture of ethanol and the respective dendrimer (H-20, H-30 or H-40 from Boltorn). These dendrimers possess on average 16, 32



Scheme 1 Idealized molecular structure of the "Boltorn" H20-type dendrimer

and 64 OH groups per molecule, respectively (Scheme 1). Thus, mixtures of 2 g LDH with a 1:1 mol ratio [ethanol:water] solutions containing fixed amounts of dendrimer were gently dried overnight (35 °C) till complete evaporation of the liquid mixture. The resulting organo-LDH samples contain various dendrimer loadings ranging from 0.5 to 3 wt%.

2.2 Characterization

The as-synthesized LDH and organo-LDH samples were fully characterized by scanning electron microscopy (Hitachi S-4300SE/N-VP-SEM instrument), powder X-ray diffraction (P-XRD using a Siemens D5000 instrument, Co-Kα at 1.78897 Å, in the 2-theta range 2–80°) and Fourier transform infrared spectroscopy (Spectrophotometer Brücker Tensor 27 set in the range 400–4,000 cm^{-1}). The chemical composition of the LDH samples was assessed through chemical analysis and energy dispersion X-rays analysis (EDX with an EDAX-Sapphire instrument coupled to the SEM equipment, using a Si(Li) crystal, and an active surface of 10 mm^2. The presence of gold in the EDX patterns is due to the surface metallization during the sample preparation for improving the electric conductivity. Prior to XRD analysis, sealed dry 100 mg samples of LDH and organo-Mt, with particle sizes not exceeding 0.25 mm, were exposed to ambient air at room temperature for 24 h, in order to reach the level of equilibrium moisture. After the LDH intercalation with dendrimers, the XRD analysis was achieved without excessive powder compaction of the powder, in order to avoid undesired preferential orientations.

2.3 Adsorption capacity assessment

Thermal programmed desorption was used to estimate the intrinsic basicity of the LDH support prior to intercalation and the overall base character of the organo-LDH adsorbents. TPD measurements were performed in the temperature range 20 and 240 °C (Azzouz et al. 2010, 2009, 2006). The upper limit of this range was imposed by the thermal stability of the dendrimers which starts to be affected at 280–300 °C. After drying under a nitrogen stream at 140 °C for 3–4 h, the samples were cooled to 20 °C and then saturated with pure dry CO_2. The non-adsorbed CO_2 excess was evacuated. In order to achieve a truly reversible retention of CO_2, a special interest was focused towards the range 20–100 °C, where adsorption is regarded as involving almost purely physical interactions. Under these conditions, measurements of the area described by the TPD pattern provided an accurate assessment of the CO_2 retention capacity (Q_{CO2}), expressed in terms of desorbed mmol CO_2 per gram of dry clay.

3 Results and discussion

3.1 Morphology and chemical composition

The lamellar structure of the as-synthesized LDH's was confirmed by the regular arrangement of the clay mineral layers in compacted stacks with uniform particle size (Fig. 1). All LDH samples displayed almost similar crystallite morphology and particle size. Polygonal 0.4–0.6 μm particles were obtained and no significant impurities resulted from the hydrothermal synthesis procedure, confirming thereby the high purity of the obtained LDH.

Fig. 1 Scanning electron micrograph of a LDH sample with Mg/Al of 2:1

The chemical composition of the synthesized LDH samples fit with that of the initial reactant mixture with satisfactory accuracy. Only a slight discrepancy between the theoretical and the measured chemical compositions not exceeding 1–4 wt% was observed, in agreement with other data (Hyung and Lee 1998). For instance, X-ray energy dispersion analyses (EDX) of an LDH sample having a 2:1 Mg/Al mole ratio gave molar distribution of the main chemical elements of 14.69–15.24 % carbon, 56.90–59.01 % oxygen, 17.91–18.44 % magnesium, and 7.77–8.39 % aluminum (Fig. 2).

This accounts for nearly similar values ranging from 2.20 to 2.30 according to the spot position throughout the whole bulk LDH. This provides clear evidence of a homogenous chemical composition and appreciable purity of the as-synthesized samples.

3.2 Crystallinity and interlayer distance

Layered double hydroxide crystals were identified on the basis of specific xrd lines like 003 (2-Theta = 13–14°) and it harmonic reflexions 006 (at 27°) (Fig. 3). Slight change in the very structure also took place as a result of increasing Mg/Al molar ratio. This is well supported by a reflection splitting around a 2-theta value of 35°. This special feature of LDH-like materials confirms the lamellar structure of the synthesized LDH's. The sharpness of these reflexions is a clear evidence of both the high crystallinity and parallel arrangement of the LDH lamellae. However, the crystallinity was found to slightly increase with decreasing Mg/Al molar ratio, as already reported (Sharma et al. 2007).

A possible explanation is that increasing Mg amount should promote the progressive formation of brucite as an impurity within the LDH frameworks, which undergoes distortions. This is also expected to lower the charge density, which should favor such framework distortions through an attenuation of the strength of the sandwiching effect of the interlayer bivalent anions that maintain the LDH lamellae stuck to each other. This is well supported by the slight shifts of the major peaks to lower 2-theta with increasing Mg/Al molar ratio (Fig. 3). For instance, the 2-theta value for the 003 reflexion decreased from 13.93° (Mg/Al = 1:1) or 13.57° (Mg/Al = 2:1) to 12.77° (Mg/Al = 5:1). This accounts for an increase of the 003 basal spacing from 7.38 (Mg/Al = 1:1) or 7.57 (Mg/Al = 2:1) to ca. 8.04 Å (Mg/Al = 5:1), in agreement with other data (Kang et al. 2004; Solin et al. 1996).

These values are special features of the carbonate form of LDH samples obtained in the presence of air. The sharpness of the xrd reflexions indicates a regular arrangement of the clay lamellae, more particularly in dry CO_2–LDHs and samples with high Mg contents, because unlike other anions, carbonates are usually located in well-defined sites (Thyveetil et al. 2008). Lower Mg/Al ratios are expected to favor high hydration grade through an increase in the charge density. Thus, layers of water molecules could contribute to the measured basal spacing (Yong et al. 2001). Paradoxically, excessive charge density should limit water adsorption, by restricting the interlayer space via an accentuation of the sandwiching effect of the carbonates anions.

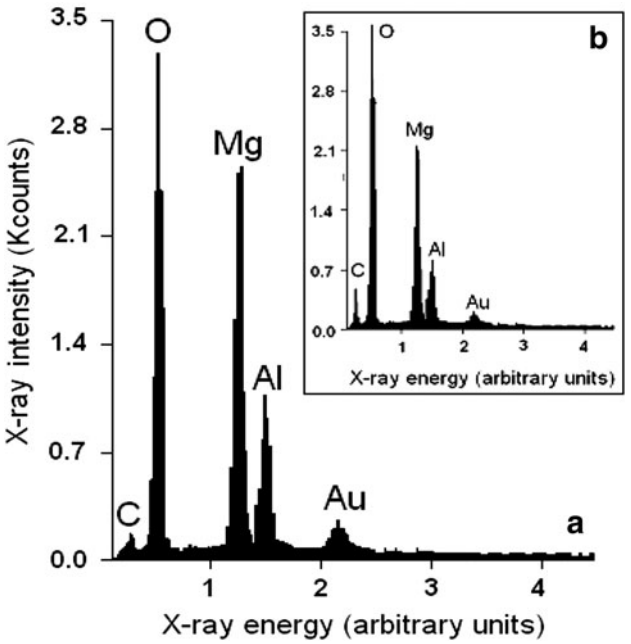


Fig. 2 X-ray energy dispersion pattern of a LDH sample with Mg/Al of 2:1 before (**a**) and after (**b**) incorporation of 1 wt% dendrimer H20

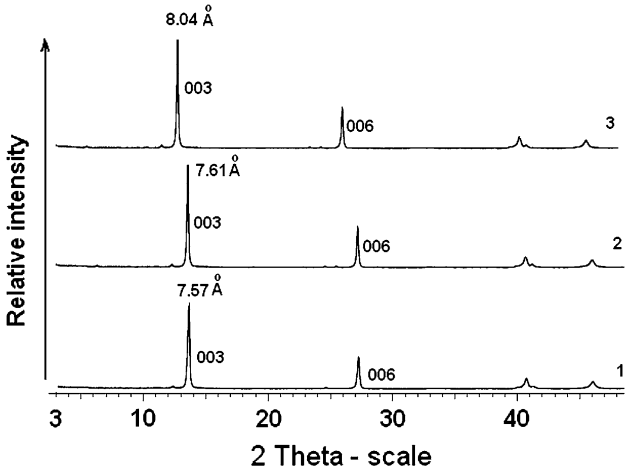


Fig. 3 P-XRD patterns of MgAl–LDH before and after impregnation with H20 dendrimer solution (Co-Kα = 1.78897 Å) **1** As-synthesized MgAl–LDH with a 2:1 Mg/Al ratio; **2** MgAl–LDH (2:1) containing 1 wt% Boltorn dendrimer H20; **3** As-synthesized MgAl–LDH with a 5:1 Mg/Al ratio

3.3 LDH structure

Deeper insights through Fourier transform infrared spectroscopy (FTIR) allowed identifying the LDH structure though sharp peaks in the region 1,550 and 1,650 cm^{-1}, attributed to symmetric and asymmetric stretching absorptions of the C–O and C=O bonds in CO_3^{2-}, and a broad band below 1,000 cm^{-1} corresponding to Mg–OH or Al–OH stretching (Fig. 4). The broad band around 3,400–3,500 cm^{-1} was ascribed to the stretching vibration of OH groups (Kang et al. 2004) The presence of a shoulder suggests the occurrence of two OH groups, presumably those belonging to the very surface of the adsorbent, and free OH groups belonging to water molecules [$\nu(H_2O)$].

A decrease of the Mg content in the LDH samples induced an increase in intensity of the OH-stretching bands (3,500–3,600 cm^{-1}). This indicates an increase of the relative proportion of unassociated OH groups belonging to water molecules at the expense of those attached to the LDH framework, which are supposed to need higher vibration energy. Such an enhancement of the hydration capacity must arise from the increase in the amount of carbonate anions, as supported by the increase in the intensity of the sharp band at 1,350–1,370 cm^{-1}. In the meantime, slight shifts of the OH-stretching bands (3,500–3,600 cm^{-1}) towards lower frequencies (Kloprogge et al. 2002), and of the 1,350–1,600 cm^{-1} band towards higher frequencies were noticed. This confirms, once again, that low Mg/Al ratios provide more compact LDH structures, but with high number of carbonates anions, which, in turn, retain more water, as a result of increasing surface charge.

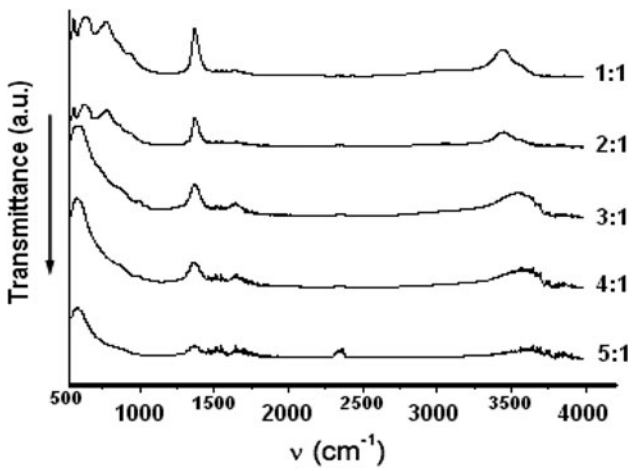


Fig. 4 FTIR spectra of MgAl–LDH at different Mg/Al ratios.

3.4 Intrinsic basicity of unmodified MgAl–LDH

Different TPD profiles were obtained in the temperature range 20–240 °C according to the Mg/Al ratio, but as a common feature, all unmodified MgAl–LDH samples showed intrinsic base properties and affinity towards CO_2, in agreements with other studies (Soares et al. 2004; Santos-Costa et al. 2004; Yong and Rodrigues 2002). Here, CO_2 adsorption on LDH's is assumed to involve acid–base interactions (Ficicilar and Dogu 2006; Yang and Kim 2006; Abelló et al. 2005; Yong and Rodrigues 2002; Di Cosimo et al. 1998; Yamamoto et al. 1995). The terminals OH groups of the LDH surface are supposed to display weakly basic character, while the lattice oxygen atoms of the LDH frameworks are supposed to exhibit medium to strong basicity according to their distance to an exchangeable anion (Ding and Alpay 2000). That is why the regeneration of unmodified LDH still needs heating even in the most favorable conditions. In this regard, CO_2 desorption heat of ca. 17 kJ mol^{-1}, i.e. in the same magnitude as for chemical reactions, has been reported (Santos-Costa et al. 2004).

Almost similar desorption peaks were registered in temperature range 30–110 °C (Fig. 5). Since, the CO_2 retention strength should be proportional to the desorption temperature, it results that the major part of the adsorption sites involved exhibit weak basicity strength within the investigated temperature range. This result is of great importance, because below 90–100 °C, CO_2 adsorption can be regarded as being totally reversible, and there is no need of excessive heating for regeneration. At any temperature not exceeding 40–60 °C or under vacuum, the adsorbed amount of CO_2 can be totally removed upon slight heating even as demonstrated by repetitive adsorption–desorption cycles.

The TPD profiles between 110 and 190 °C indicate that LDHs also possess small amounts of adsorption sites with medium basicity. Interestingly, the TPD pattern split in two distinct peaks with increasing Mg/Al ratio up to 5:1, inasmuch as the proportions of weak (20–100 °C) and strong adsorption sites (190–240 °C) increased at the expense of those of medium strength (100–190 °C), which almost thoroughly disappear. MgAl–LDH(5:1) was found to possess the highest amount of weak adsorption sites.

However, the weakest affinity of MgAl–LDH(5:1) towards CO_2 should rather be regarded as being a major benefit for a truly reversible retention of CO_2, inasmuch as the temperature of the desorption peak did not exceed 50–60 °C. At the limit, MgAl–LDH(5:1) could be transformed into an ideal adsorbent totally regenerable at room temperature, if the retention capacity is significantly raised at least up to that of MgAl–LDH(2:1), and that the few strong sites are completely suppressed or shaded. Similar

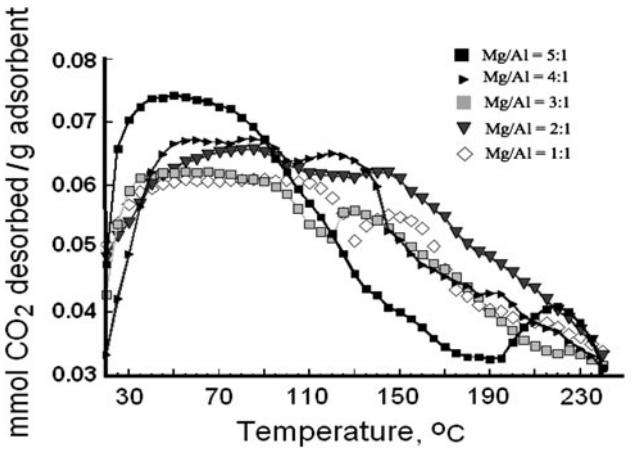


Fig. 5 CO_2-TPD patterns of LDH at different Mg/Al ratios *Filled square* Mg/Al = 5:1, *filled right pointing triangle* Mg/Al = 4:1, *open square* Mg/Al = 3:1, *filled inverted triangle* Mg/Al = 2:1, *diamond* Mg/Al = 1:1

strong basicity has already been identified by a desorption peak around 220 °C for other LDH with a 5:1 Mg/Al ratio (Reijers et al. 2006). Such basicity strength could be dramatically attenuated by incorporation of organic moieties exhibiting weaker basicity strength or calcinations (Bastiani et al. 2004).

3.5 Adsorption capacity of MgAl–LDH

Unmodified MgAl–LDHs were found to behave as effective adsorbents, inasmuch as TPD measurements showed appreciable retention capacities, expressed herein in terms of amounts of desorbed carbon dioxide (Q_{CO2}). TPD measurements between 20 and 240 °C provided Q_{CO2} values ranging from 1.50 to 2.50 mmol. g^{-1} according to the Mg/Al ratio. These values are in the same magnitude of 10–33 mL per gram, accounting for 0.45–1.5 mmol. g^{-1} have been reported for similar LDH's (Forano et al. 2006). The slight discrepancies may arise from the operating conditions, and the temperature range considered for assessing the amount of desorbed CO_2.

The Mg/Al ratio was also found to slightly influence the Q_{CO2} value within the temperature range 20–240 °C. MgAl–LDH(5:1) showed the lowest amount of desorbed carbon dioxide (2.30 mmol. g^{-1}), while the highest value (2.50 mmol. g^{-1}) was registered for an Mg/Al ratio of 2:1. Intermediate Al contents appear to be essential requirements for optimum adsorption capacities, as already reported (Hutson and Attwood 2008; Ram Reddy et al. 2006; Bastiani et al. 2004). This could be explained by the fact that intermediate Mg/Al ratios favor optimum compromise between two reverse phenomena, namely: (i) low Mg/Al ratios may promote high surface charge and strong layer-CO_2 interactions to favor adsorption but detrimental structure compactness that hinder CO_2 diffusion; (ii) Conversely, higher Mg/Al ratios produce lower surface charge but higher interlayer space and porosity, which facilitate higher CO_2 accessibility to the adsorption sites. In other words, the favorable enhancement of the CO_2 retention capacity of the LDH based adsorbent is limited by the progressive loss in porosity. For this reason, MgAl–LDH (2:1) was used as starting support material for intercalation.

Below 150 °C, the total amount of desorbed CO_2 accounts for almost 67 and 72 % of the overall retention capacity of MgAl–LDH (2:1) and MgAl–LDH (5:1), respectively. Below, 110–130 °C, these values dropped down to almost 46 and 56 %, respectively, but still remain much higher than those reported for polyol or amine intercalated Mts (Azzouz et al. 2010, 2009). This result confirms once again the intrinsic basicity of the unmodified MgAl–LDH support, as supported by other similar TPD data (Reijers et al. 2006).

Thermal programmed desorption of CO_2 turned out to be a useful and accurate technique to assess not only the amount of adsorbed gas but also the distribution of the adsorption sites according to their strength (Hutson and Attwood 2008). However, care must be taken when dealing with the concept of the reversible capture of CO_2, which involves mere physical interactions between CO_2 and the LDH surface. This cannot be achieved as long as high temperatures are needed for regeneration, because other phenomena like decarbonation also take place (Reijers et al. 2006). At 250–300 °C, irreversible dehydroxylation unavoidably must occur, and should modify the intrinsic properties of the LDH adsorbents. That is probably why, once calcined at 400 °C, unmodified LDH's showed low CO_2 sorption capacity barely attaining 0.5 mmol. g^{-1} (Ram Reddy et al. 2006). Here, for accurate assessments of the amounts of desorbed CO_2, care should be taken to avoid a disruption of the adsorption–desorption equilibrium, otherwise forced release of CO_2 can take place by excessive flow rates of the carrier gas. For this reason, the evacuation of the non-adsorbed CO_2 excess during the purge step was achieved at low and constant throughputs of the carrier gas. Increasing the flow rate of the carrier gas causes CO_2 to desorb easily and spontaneously even at room temperature, more particularly for weakly basic to amphoteric adsorbents. The amounts of desorbed CO_2 measured at a 15 mL min^{-1} flow rate were found to be slightly higher by ca. 15–25 % than those assessed at 50 mL min^{-1}. This provides clear evidence of the occurrence of a truly reversible retention process.

3.6 Effect of intercalation

Unlike other studies (Xi and Davis 2010; Kloprogge et al. 2002), our attempts showed that intercalation of MgAl–

LDH(2:1) with polyol dendrimers, if any, should be negligible and difficult to achieve. Indeed, no shift of the 003 xrd reflexions was observed whatever the concentration of the impregnating solution may be, even though FTIR observations clearly demonstrate the presence of dendrimer molecules on the LDH sample (Fig. 6). This suggests that the dendrimers rather adsorb on the external surface of compact LDH aggregates. Such a behavior was somehow expected, being a special feature of CO_3–LDH.

Fresh MgAl–LDH (2:1) showed many peaks below 1,000 cm^{-1}, two of them being attributed to Mg–OH or Al–OH stretching absorption. These peaks did not seem to be significantly modified by dendrimer incorporation. Calcination, instead, induced significant changes in this region (Spectra 1-a and 1-b), along with a total disappearance of the broad band at 3,400–3,500 cm^{-1} assigned to the stretching vibration of OH groups (Kang et al. 2004).

After dendrimer incorporation, a sharp small peak appeared at ca. 1,600 cm^{-1}, and increased in intensity for larger dendrimer size (Spectra 2–4), or upon saturation overnight with CO_2 (Spectrum 5). The peaks at ca. 1,350 and 1,600 cm^{-1} must be due to symmetric and asymmetric stretching absorption of C–O and C=O bonds. Some of them have already been identified as belonging to the CO_3^{2-} anions. After calcination, decarbonation induced significant modifications of these peaks (Reijers et al. 2006).

As a general feature, by comparison to free CO_3^{2-}, bonded carbonate anion was characterized by a shift towards higher frequency (Vaysse 2001). This explains why, once bonded, carbonate anions acquire rigidity, and consequently need more energy for vibration, deformation and stretching. A weak intensity band observed at 3,000–3,200 cm^{-1} was assigned to the H_2O–CO_3^{2-} bridges. This suggests that water may also contribute to the global retention capacity, in agreement with other data (Bastiani et al. 2004).

3.7 CO_2 adsorption on organo-LDH

A first overview of the data obtained indicates that dendrimer incorporation modified considerably the TPD profile of the starting LDH sample (Fig. 7). Even though the resulting polyol-LDH's are expected to combine physicochemical features arising from both the LDH support and organic moiety, the presence of polyol dendrimers appears to shade the intrinsic properties of the LDH support. A major change resides in the appearance of a new desorption peak between 50 and 120 °C. This is a precise and reliable indicator of the enhancement of the amphoteric character at the expense of the basicity strength of the starting LDH surface. Similar phenomenon has already been reported on Mt-based adsorbents (Azzouz et al. 2010, 2009).

Within this temperature range, the CO_2 retention capacity increased by almost two times after intercalation

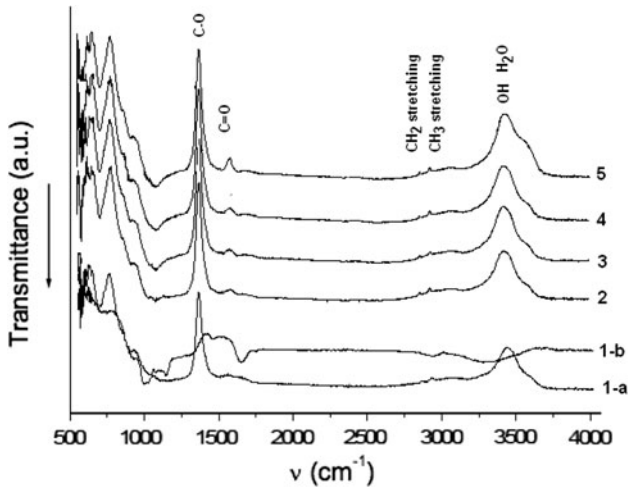


Fig. 6 FTIR patterns of MgAl–LDH(2:1) before (**1a**, **1b**) and after intercalation (**2**–**5**). These spectra were registered with LDH samples impregnated for 24 h with aqueous solutions of various polyol dendrimers having the same concentration (1 wt%). The samples were then dried overnight at 40 °C, in the present of the liquid solution without filtration **1** Before intercalation: **1a** uncalcined starting LDH; **1b** after calcination at 450 °C for 3 h; **2** uncalcined and intercalated with dendrimer H20; **3** uncalcined and intercalated with dendrimer H30; **4** uncalcined and intercalated with dendrimer H40; **5** uncalcined and intercalated with dendrimer H20 and further saturated with CO_2 at room temperature overnight

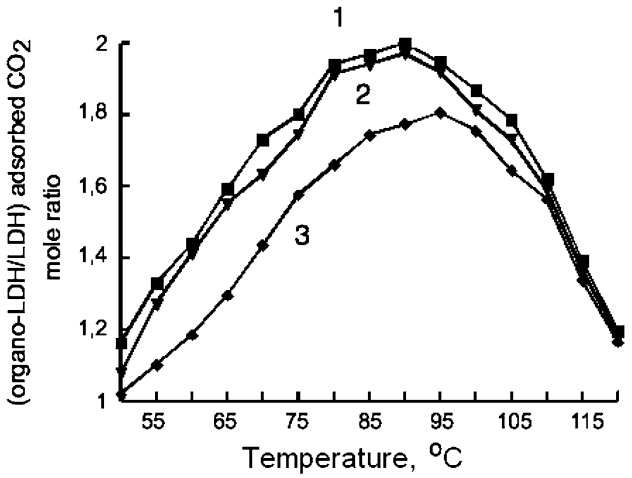


Fig. 7 Relative TPD patterns of organo-LDH after intercalation as reported to that of LDH (2:1) **1** MgAl–LDH–H30; **2** MgAl–LDH–H40; **3** MgAl–LDH–H20. The starting LDH with an Mg/Al ratio of 2:1 was impregnated for 24 h with various 1 wt % aqueous solution of Boltorn dendrimer H20, H30 and H40. The samples were then dried overnight at 40 °C, without filtration. The (organo-LDH/LDH) adsorbed CO_2 mole ratio was calculated by dividing every experimental point of a TPD pattern for a given organo-LDH at a given temperature by the corresponding point of a TPD pattern of the unmodified LDH at the same temperature

with dendrimers 30 and 40, and by ca. 1.8 times with dendrimer H20. The mere incorporation of organic OH groups within a LDH structure was found to raise the CO_2 adsorption capacity up to 2.0–2.5 mmol. g^{-1}. These Q_{CO2} values are still higher than that reported for amine-containing LDH's (Wang et al. 2012). This result is of great importance, because it opens new prospects for harmless and nontoxic OH-compounds such as starch, cellulose and other wood components to be used as alternatives to amine-based adsorbents. Here, different adsorbents are expected to behave differently towards CO_2. Unless assessed in similar conditions, more particularly for similar specific surface area, CO_2 retention capacities (CRC) provided by literature cannot be compared. For instance, notwithstanding their relatively much higher affinity towards CO_2, amine-bridged mesoporous polysilsesquioxane (Qi et al. 2011) or amine-impregnated mesoporous silicas (Chao Chen et al. 2009) gave CRC values not exceeding 5 mmol. g^{-1}, even under the most favorable operating conditions. A wide variety of activated carbons showed appreciable specific surface area, but CO_2 uptakes of only 2.3–2.5 mmol. g^{-1} (Martín et al. 2010). In addition, cesium-modified X zeolite diplayed CRC of ca. 227 μmol.g^{-1} (Díaz et al. 2008). This value accounts for an uptake of 10 mg CO_2 per gram, and seems to be higher than that reported for solid amines (174.5 μmol.g^{-1}), but the latter showed much lower specific surface area of only 27 m^2 g^{-1} (Gray et al. 2002). Favorable effect was also registered in humid conditions (Chao Chen et al. 2009), indicating that water also contributes to CO_2 retention.

Q_{CO2} was found to vary according to the LDH based adsorbent as follows: LDH-H30 > LDH-H40 > LDH-H20 >> LDH. This sequence globally corresponds to decreasing number of hydroxyl groups belonging to the organic moiety except for LDH-H40, which is supposed to bear more OH groups as compared to H30 (64 versus 32 per idealized molecular structure). A plausible explanation is that large size dendrimers like H40 tend to aggregate into hydrophobic clusters on the external surface of compact LDH particles, and thereby offer smaller number of accessible OH groups. This is well supported by the lack of intercalation observed by xrd analyses. Q_{CO2} appears to be proportional to the density of the OH groups, as long as these sites remain accessible. This confirms unequivocally that the incorporated OH groups act as the main adsorption sites, by shading the direct contribution of the LDH surface, at least within the investigated temperature range.

Large size dendrimers were also found to display slightly weaker basicity strength, inasmuch the desorption peaks for LDH-H30 and LDH-H40 appeared at a lower temperature (ca. 85 °C) than for LDH-H20 (ca. 95 °C). LDH-H30 even turned out to be the most effective in the reversible capture of CO_2. This performance results from a compromise between the highest adsorption capacity and lowest desorption temperature possible.

3.8 Role of hydroxyl groups

The hydroxyl groups incorporated within a LDH structure display affinity towards CO_2 via optimum interactions for effective adsorption of CO_2 followed by easy desorption upon slight heating at only 20–40 °C (Saharay and Balasubramanian 2006; Rodlert et al. 2004). They can be regarded as a compromise between unmodified LDH that display relatively stronger interactions and Mt that exerts only weak physical interactions towards CO_2. Their optimum base-like character can be judiciously tailored to allow the reversible retention of CO_2 through adequate procedures that confer them weaker basicity strength, but high number of adsorption sites. On the one hand, the acid–base interaction could be attenuated by covering the accessible adsorption sites belonging to the LDH surface with amphoteric chemical species like polyols. On the other hand, high adsorption capacities require high number of OH groups. This can be achieved by increasing either the dendrimer loading or the length of its dendritic organic chains, as long as the detrimental hydrophobic effect still remains negligible. That is, the occurrence of these two opposite effects imposes a limit to the maximum retention capacity, when the formation of dendrimer clusters starts to reduce the number of accessible OH groups.

In all cases, the measured amounts of desorbed CO_2 were higher than the calculated numbers of incorporated OH groups, confirming thereby previous data (Azzouz et al. 2010). This suggests that the major part of CO_2 adsorbs in multilayers via other interactions with CO_2 and water molecules previously adsorbed. In other words, this deviation from the 1:1 stoichiometry must arise from a pseudo-condensation of CO_2, on layers of precursors such as carbonate-like associations and/or H_2O–CO_3^{2-} bridges previously formed (Gassensmith et al. 2011; Yong et al. 2001). This finding still remains to be elucidated through deeper investigations in this direction.

4 Conclusions

The insertion of polyol dendrimers in LDH's resulted in hybrid surfaces with optimum affinity towards CO_2 and improved adsorption capacity. These properties arose from an attenuation of the relatively strong base character of the starting LDH material by the insertion of an increased number of amphoteric OH groups. The latter were found to act as the adsorption sites. Each OH group displays a sufficiently weak basicity to exert only physical interactions towards more than one CO_2 molecule. These interactions

were sufficiently strong to retain appreciable amounts of CO_2 of almost 1.5–2.5 mmol. g^{-1} at temperatures not exceeding 80 °C. These results clearly demonstrate the contribution of the OH groups in the improvement of the adsorptive properties of LDHs and the possibility to achieve a truly reversible capture of CO_2 at low temperatures close to the ambient value. Easy regeneration requires weak interaction towards CO_2, and could be achieved only at the expense of the adsorption capacities. However, simultaneous increase of the adsorption sites for CO_2 turned out to be a judicious route to obtain effective adsorbents. This opens new prospects to apply the concept of reversible capture for other pollutants and greenhouse gases by modifying the chemical functions of the organic moiety.

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