



Review

Layered double hydroxides for CO₂ adsorption at moderate temperatures: Synthesis and amelioration strategies

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ABSTRACT

Curving the CO₂ atmospheric levels is one of the challenges of this century, given its direct impact on climate change. Of the several strategies of CO₂ capture and storage, sorption-enhanced water–gas shift (SEWGS) process, a combination of CO₂ adsorption and the water–gas shift reaction, has been appointed as one of the most promising techniques due to its low energy consumption and high efficiency. SEWGS operating settings at both moderate temperature (200–450 °C) and high pressure (more than 10 bar) bring the need to find an adsorbent capable of working at these conditions. Calcined layered double hydroxides (LDH) have been proven to give the best results in this range of pressure/temperatures even though its performance can be greatly improved. Herein, a state-of-art of the research accomplished up until now is presented. Several strategies can be followed to improve the adsorbents performance: the synthesis method, LDH composition, modifications employed to promote their adsorption capacity or how the adsorption conditions can affect their efficiency.

1. Introduction

As a nearly linear relationship has been established between the cumulative carbon dioxide emissions and the increment in global surface temperature, trying to find an effective technique for capturing the emitted carbon dioxide on its source seems to be an essential strategy to decelerate global warming. A total halt of the global warming would still mean that the sea level is to rise for thousands of years due to the energy accumulated in past emissions of CO₂, as established in the technical support of the Climate Change *IPCC Technical Summary* [1]. Carbon capture and storage (CCS) strategies are varied and have started in several projects and configurations [2,3]. One of the most promising ones is the SEWGS reaction, which collects the CO₂ as the production of H₂ takes place and needs to work with an adsorbent capable of operating at moderate temperatures (200–450 °C), high pressures and in the presence of steam. Of the adsorbents available, LDH have been presented as one of the few adsorbents capable of being efficient in these working conditions. LDH are a family of clays with hydrotalcite, Mg₆Al₂CO₃(OH)₁₆·4H₂O, as their most representative member. Their composition consists of an octahedral framework similar to that of brucite (Mg(OH)₂) that forms infinite layers by sharing the edge, with the hydroxide ions located perpendicular to the plane of the layers. These formed sheets are stacked on top of each other and held together

by hydrogen bonding giving two possible symmetries, rhombohedral or hexagonal. In LDH a portion of divalent cations are substituted by trivalent cations which is balanced in the interlayer region with the presence of anions together with water. This family of clays is endowed with a great modification potential for adsorption capacity amelioration as: (1) various M² and M³ cations can be integrated into the structure provided that, among several factors, their ionic radii is not distant to the original ones (2) the proportion of M² and M³ cations can be varied, with the boundaries set near the 1 and 4 M²/M³ ratio and (3) a wide variety of anions can be integrated in the structure, see (Section 5.4). Furthermore, their composition, which usually includes highly abundant metals, and their easy-to-synthesize procedure makes them the perfect candidate for a large-scale system, as the performance of an adsorbent is ultimately linked to its production cost.

Herein, the performance of calcined LDH as CO₂ adsorbents at moderate temperatures has been analyzed: from the synthesis conditions and strategies, to the LDH composition, several methods employed to improve their adsorption capacity and the best adsorption conditions (see Fig. 1), with the main focus established on the adsorbents themselves more than the SEWGS system design challenges.

2. Pre-combustion adsorption

The CO₂ adsorption strategies that can be followed for CCS are

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Nomenclature

CCS	CO ₂ carbon capture and storage
LDH	Layered double hydroxides
MMO	Mixed metal oxides
SEWGS	sorption enhanced water – gas shift
CGM	coal-derived graphitic material
AMOST	aqueous miscible organic solvent treatment
GO	Graphene oxide
MWNTs	Multi-walled carbon nanotubes
AC	Activated carbon
CNF	Carbon nanofibers
LTNS	Layered titanate nanosheets
ZEO	zeolites
PSA	Pressure swing approach
TSA	Thermal swing approach

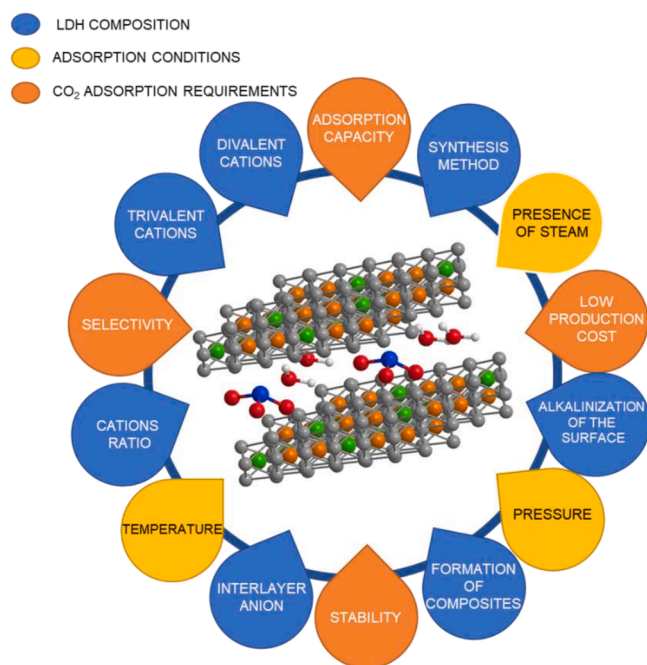


Fig. 1. Fundamental aspects of CO₂ sorption by LDH based systems.

mainly pre-combustion, post-combustion and the oxy-fuel combustion. In SEWGS reaction, pre-combustion technology, primary fuel is first combusted with the aid of steam or oxygen and CO + H₂ are obtained as a result. CO is then converted to CO₂ by means of a water gas shift reaction which requires moderate temperatures (200–450 °C) and high pressures (more than 10 bar). As CO₂ is retained by an appropriate adsorbent, the equilibrium is driven to the right-hand side, thus improving the conversion percentages. SEWGS is one of the most promising technologies due to its combination in a single unit of H₂ production and CO₂ removal. Post-combustion processes retain the CO₂ from the exhaust pipes, at lower temperatures and atmospheric pressure. The last one, oxy-fuel combustion, which consists of the use of almost pure O₂ in combustion, is the least developed to date and also has the largest energy penalty. The best option would be the pre-combustion method if the power plant is of new construction and, on existing plants, post-combustion method is preferred as the plants can be retrofitted to add this capture step in its configuration [4].

Of the available technologies that produce renewable energy from

biomass, the steam reforming of hydrocarbons to produce H₂ is one of the most efficient ones [5]. As H₂ has a high combustion efficiency, is often presented as an alternative to support a sustainable energy development by means of a renewable clean fuel. In the SEWGS pre-combustion operation there is a need for both a high-temperature water-gas shift catalyst and a regenerable CO₂ sorbent in the same reactor [6]. Excess steam is required to guarantee the selective conversion of CO to CO₂ and H₂ and avoid the presence of not-needed secondary reactions that can form undesired products like methane or carbon [7]. The key lies in finding an appropriate CO₂ capturing material in order to obtain an efficient conversion rate. Although this review is intended for SEWGS, other post-combustion processes, where the fumes are still at high temperature, can be performed with LDH [8,9]. This technology not only needs an efficient CO₂ adsorbent but it is essential for it to be stable and able to withstand a continuous course of adsorption-desorption steps.

3. Other adsorbents at moderate temperature

Several adsorbents have been presented as possible candidates (see Table 1). Finding an appropriate adsorbent for the required working conditions is one of the most challenging parts as there are several specifications that must be met: efficiency, selectivity towards CO₂ (other common substances present are Hg, SO₂ or NO_x), thermal and mechanical stability over several cycles, decent sorption-desorption kinetics and good response to the presence of steam. Adsorbents in which the store of CO₂ is under physical forces such as zeolites, activated carbons or aluminas are not capable of adsorbing at moderate temperatures. On the other end, adsorbents with more important chemical interactions e.g. calcium oxide or lithium zirconate need more elevated

Table 1

Comparison of the CO₂ sorbents at moderate temperature [10,15,16,108–110].

Adsorbent	advantages	disadvantages
Zeolites	- High stability	- Intolerance towards moisture - Poor adsorption capacity at moderate temperature - Low selectivity towards CO ₂
Magnesium oxide	- Good stability - High theoretical capacity - Low price	- Conversion is promptly prevented, as a monodentate carbonate layer is formed in the surface - Poor kinetics
MMO	- Relatively fast adsorption/desorption rates - High stability - Good mechanical strength in high-pressure - Tolerant towards moisture	- Weak adsorption capacity although easily enhanced with potassium impregnation
Double salts	- Fair adsorption capacity - Stable - Fair kinetics	- A good recipe for a binder to produce pellets from the precipitates has not been found yet. - Response to the presence of water is to be tested - The synthesis technique needs further development in order to scale up to larger quantities
Calcium oxide	- Good adsorption capacity and kinetics	- Elevated regeneration costs - temperature swing regeneration required due to their strong exothermic reaction with CO ₂ - The agglomeration of sorbent particles by sintering diminishes CO ₂ sorption capacity during multiple cyclic sorption/desorption procedures
Lithium zirconate	- Fair adsorption capacity - Stable	- Elevated regeneration costs - Slow sorption rate

temperatures to be competitive apart from requiring a great energy demand to be regenerated and, in addition, some of these chemisorbents may present also difficulties to perform in the presence of water or have poor stability [10,11]. MOF also has shown drawbacks when trying to adsorb CO₂ in the presence of steam [12]. Calcined LDH i.e., MMO present both chemisorption and physisorption capacity and adsorption heat values between zeolites and CaO [13,14]. Even though there is room for improvement when testing its adsorption capacity towards CO₂, it displays good response when in the presence of steam, apart from good stability and kinetics.

There are only a few comparison studies of adsorbents. The performance of five materials when in an integrated gasification and combine cycle are investigated by Singh et al. [15]: two zeolites, LDH, MMO and magnesium double salts. Results show that zeolites only work in temperatures up to 200 °C and water affects its performance, double salts are presented as very promising although the effect of water has not been investigated and its synthesis technique needs further development [16] and MMO is presented as an effective adsorbent at moderate temperature even though the presences of H₂S points to a potential problem. The study on the performance of two adsorbents, alumina and MMO, when promoted with potassium carbonate, a known adsorption-enhancer (see Section 6.2.1.) is presented by Walspurger et al. [17]: apart from having lower initial adsorption capacity, levels obtained of the alumina with potassium do not reach those of the KMMO.

4. Synthesis methods

Co-precipitation is the standard procedure for LDH synthesis as it has been proven to be rapid, green and effective. Nevertheless, each synthesis method derives in different sample morphologies and particle sizes that affect results.

MgAl-CO₃ LDH were synthesized by Gao et al. [18] using various methods: co-precipitation, co-precipitation hydrothermal, urea, urea hydrothermal and urea microwave. The adsorption capacity of the procedures that employed Na₂CO₃ as precipitating agent (co-precipitation) performed better than those of urea, showing double the adsorption capacity. The co-precipitation method performed best in other studies with comparisons with gibbsite interaction [19] and again urea, in this case forming a LDH-AC composite [20]. This fruitful method was further analyzed by Yang and Kim [21] synthesizing MgAl-CO₃ LDH with low and high supersaturation variants. The adsorption performance of the samples was similar although the high-supersaturation MMO showed greater effective adsorption capacity as this method gives lower crystallinity and smaller particle size to the LDH [22].

The use of microwave aging after the co-precipitation has been proven to enhance the adsorption capacity of the samples for several reasons [9,23,24]: in the former, the synthesis of MgAl-CO₃ LDH (M²⁺:M³⁺ ratio 1.65) samples that were subjected to microwave radiation of the precipitating gel, displayed a larger disorganization of the layer stacking and also reduction of average crystallite size, both features beneficial for adsorption. In the latter the microwave irradiation used during the aging process increased the crystallinity of the samples, with enhanced sharpness of the PXRD peaks which could be related to an Oswald ripening effect. Authors suggest that this microwave radiation increased the amount of both basic and acid sites because of an increment on the amount of surface-defective sites [25].

There is a constant pursuit of easy-to-obtain adsorbents that work at a medium range of temperatures and, thus, a one-step synthesis method where the adsorption enhancer is effortlessly included has been sought. Jang et al. [26] studied the use of a hydrothermal method that included the addition of K₂CO₃ to the initial mixture of Mg(OH)₂ and Al(OH)₃ (all three in different proportions) and obtained a 1.26 adsorption capacity for samples with a 3:1:3 ratio of Mg:Al:K. Unintentionally, Cheah et al. [27] found a direct connection between the sodium contents present in the calcined samples and their adsorption capacity. Even though the synthesis procedure followed was consistent throughout the samples,

various percentages of sodium were found in them. Authors claim that even though a washing step till reaching a pH of 7 is commonly utilized after the synthesis, it could lead to the leaching out of the Mg(OH)₂ and the partial dissolution of the LDH and present this fact as the reason why adsorption results are so inconsistent throughout literature. As an excess on sodium encourages the adsorption capacity of the samples (also discussed in Section 6.2.2.), the washing step after the synthesis could be avoided. The synthesis of composites can also be performed in a one-step method as, for example, presented in Qiao et al. [28] work, that synthesized the MgAl-CO₃ LDH using a urea hydrolysis method on a thin film of aluminum foil.

The use of very controlled conditions on the synthesis procedure, helps to the production of adsorbents with distinctive features. Chang et al. [29] employed hexadecyl trimethyl ammonium bromide to form a scaffold-like structure in which CaAl LDH was annealed (see synthesis steps in Fig. 2). Wang et al. [30] employed the facile isoelectric point method, in the presence of restricted pH limits to obtain nanospheric LDH particles, (average size of 20 nm) that improved the results a 33 % due to its negative surface charge when the pH was bigger than the isoelectric point.

The study of the performance of the MMO based on the pH during the synthesis process has been extensively studied by the same authors [31,32]. Synthesizing the Mg₃Al-CO₃ LDH at various pH ranging from 6.5 to 14 and testing their adsorption capacities after calcination gave some interesting results. The final adsorbents had different morphology, chemical composition and pore structure depending on the synthesis pH. At a pH of 10, i.e. equaled to the isoelectric point, a rose-like morphology was obtained, and at higher synthesis pH, mesoporous and more spherical structures appeared. A change of both the interlayer anions and the M²⁺/M³⁺ ratio was also observed when pH ranged from 6.5 up to 10. With this information, a synthesis mechanism was proposed and the results obtained showed that 12 is the best synthesis pH, followed by 10.

4.1. Exfoliation

Several studies have tested the adsorption capacity of exfoliated and calcined LDH [33,34] and, when tested, obtained better results than their 3D counterparts [35,36]. The former synthesized the MgAl-CO₃ LDH using the conventional co-precipitation method and also the aqueous miscible organic solvent treatment (AMOST) which uses acetone to re-disperse and exfoliate the LDH. AMOST-synthesized samples showed better adsorption capacity at various temperatures and Mg/Al ratios. The latter synthesized ZnAl-LDH by a co-precipitation (bulk, 3D) and a bottom-up method (monolayer, 2D) and tested their adsorption capacity on temperatures from 25 to 300 °C. Charge distribution, density of states and charge transfer were studied with the aid of the density functional theory. Results show that even though the adsorption capacity of the monolayer sample was better at low temperatures by a large margin as its physical adsorption behavior is rapid, it greatly decreases with temperature. The bulk sample had a steady adsorption at the whole range and was of a chemical nature.

4.2. Calcination temperature

The study of the best performing calcination temperature has been widely realized and there is an agreement for once. The calcination of the samples at 400 °C gave the best results [18,19,33,37–40]. The use of aluminum as M³⁺ dictates this result, as manganese, iron or gallium perform better at lower temperatures [41]. Not only the temperature but the duration of the calcination process can widely change the adsorption perform of the samples as seen in the study presented by Wang et al. [32] whose samples had an increment of more than 50 % on their adsorption capacity if the calcination process was only one hour long instead of six hours. This behavior was also observed by Gao et al. [18] that also noted the importance of an in-situ pretreatment calcination to prevent the

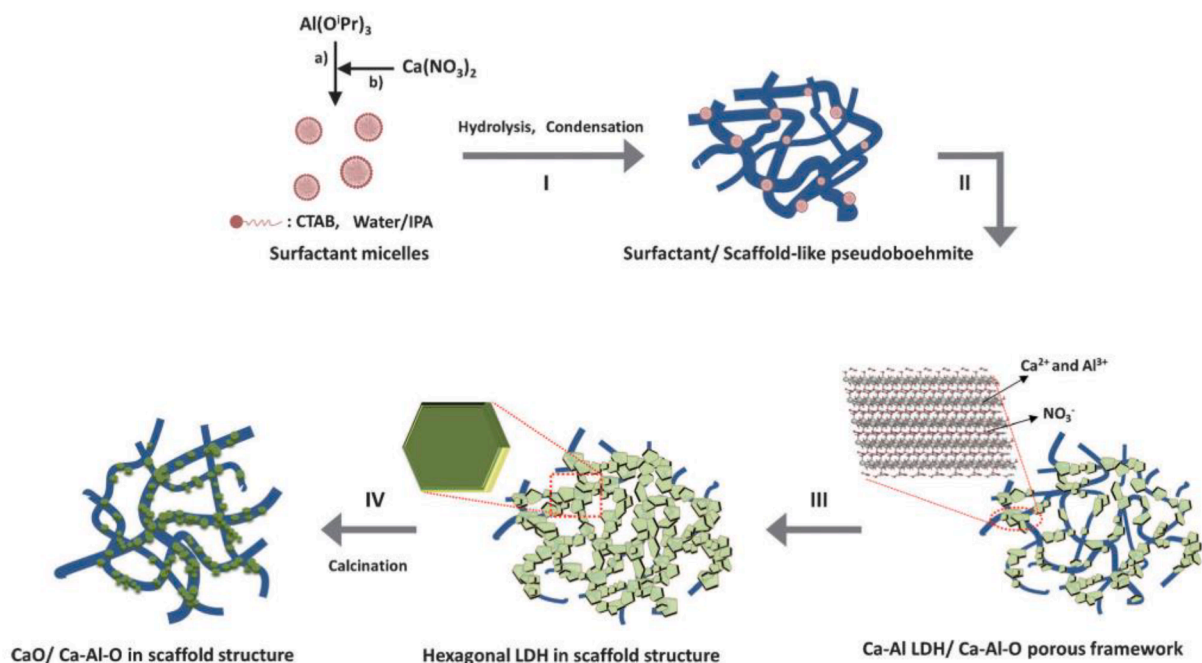


Fig. 2. CaAl LDH with scaffold-like structure synthesis process (Reprinted with permission from [29]).

memory effect as it can really affect the adsorption performance of the samples suggesting that this fact could be responsible for the discrepancies found in the adsorption capacities reported in literature.

4.3. Pellets production

In order to try to overcome the issues that particle size of powder samples generates, a next step on the development of a competitive adsorbent could be the pelletization process. When thinking about their industrial application, the formation of pellets or extrudates made only of LDH or their MMO do not exhibit acceptable mechanical strength. The goal is to obtain an optimized structure with low pressure drop, very stable both chemically and mechanically and with high mass transfer. *Manohara et al.* [42] synthesized Mg_2Al-CO_3 LDH that were modified with melamine, an organic modifier that creates porosity and provides support to the MMO. Various melamine:LDH ratios were tested: from 90:10 to 50:50 and the best results (1.34 mmol of CO_2/g , at 1 bar and $200\text{ }^\circ C$) were obtained with the last one, clearly outperforming those of unmodified MMO (0.35 mmol/g) and commercial (Plural MG70, SASOL) MMO pellets (0.33 mmol/g). *Papa et al.* [43] opted for monoliths: a combination of commercial LDH with a metakaolin-based geopolymer matrix, with a $SiO_2:Al_2O_3$ ratio of 4, as a binder. However, the adsorption capacity of the monoliths was lower than expected due possibly to a partial deactivation of the LDH during the geopolymerization process. Commercial pellets formed out of LDH and with optimized adsorption properties, i.e. modified with potassium can also be found and have been tried with good results [44–46].

5. LDH composition

One of the most attractive features of LDH is the fact that several metals can act as divalent and trivalent cations in its structure, as long as their size does not greatly differ from that of Mg^{2+} and Al^{3+} , present in the original structure. Other possible modification of its structure is the M^{2+}/M^{3+} ratio, which can considerably alter the LDH adsorption performance, and a not so obvious anion selection, as even with its disappearance during the calcination process, provides the LDH with several interlayer distances and, thus, adsorption capacities. Studies performed with regards to these variables are displayed in Table 2.

5.1. Divalent cations

There is a general tendency to use magnesium as M^{2+} as, in general, gives the best results. This was tried and tested by *Gil et al.* [47] synthesizing LDH using cobalt, nickel, magnesium and zinc as M^{2+} and testing the CO_2 adsorption capacity at $200\text{ }^\circ C$ of the MMO obtained after calcination at $400\text{ }^\circ C$. The results show that Mg-containing samples had the best performance, followed by Co-MMO. There are other studies in which magnesium was outperformed or other metals were used as M^{2+} as they provided the adsorbents with other benefits: *Wang et al.* [48] synthesized LDH with several combinations of two of the following divalent cations: Mg, Co or Ca, a $M^{2+}:Al$ ratio of 3 and carbonate as anion. Even though separately Mg gave the best adsorption results followed by cobalt, the best overall adsorption performance was obtained when using a combination of Ca and CO due to a trade-off between its active sites and CO_2 affinity. In the case of *Hanif et al.* [34], exfoliated NiAl LDH with a 3:1 ratio were obtained by an acetone mediated synthesis procedure obtained from *Chen et al.* [49]. The CO_2 capture capacity obtained is 0.66 mmol/g, similar to MgAl samples reported in literature. However, as NiAl have great catalytic properties for CO_2 methanation, a dual function: capture and conversion of CO_2 could be better achieved with these samples. *Huang et al.* [19] synthesized a LiAl LDH with a 3:1 ratio based on the fact that another study by *Wang et al.* [50] obtained good results when doping a MgAl LDH with Li_2CO_3 .

It can be all ultimately related to the number of basic sites. *Hutson et al.* [51] compared the adsorption capacities of various samples with either magnesium or calcium as M^{2+} and several anions. The contribution of the chemisorption and physisorption processes to the total adsorbed was measured by first measuring the total CO_2 adsorbed, removing the physisorbed gas with evacuation at low pressure and then repeating the measurement. The plot of the physisorption and chemisorption capacities vs the basis site density shows a clear correlation of the number of basic sites with the physisorption capacity. This will be further discussed in Section 7, mechanism of adsorption.

5.2. Trivalent cations

Some authors state that while divalent cations provide the basic sites, trivalent cations are responsible for affecting the layer charge density

Table 2
Adsorption capacity of calcined LDH synthesized with various M^{2+}/M^{3+} ratios, anions and adsorption conditions.

Divalent cation	Trivalent cation	$M^{2+}:M^{3+}$ ratio	Anion	Adsorption conditions	CO ₂ adsorption capacity	Reference
Mg Co Ca Co + Mg Mg + Ca Ca + Co	Al	3:1	CO ₃ ²⁻	350 °C, 1 atm, 8% CO ₂	1.13	[49]
					1.03	
					0.87	
					1.05	
					1.28	
					1.39	
					3.10	
					1.68	
					2.50	
					2.55	
Co	Al	4:1 2:1	CO ₃ ²⁻	200 °C, 0.81 bar	0.53	[48]
					1.78	
					0.66	
Ni	Al (exfoliated)	3:1	CO ₃ ²⁻	200 °C, 1.2 bar	0.66	[34]
					0.51	
Li	Al	3:1	CO ₃ ²⁻ Cl ⁻ NO ₃ ⁻	200 °C, 1 atm	0.16	[19]
					0.16	
Mg	Al Fe Mn Ga	3:1	CO ₃ ²⁻	200 °C, 1 atm	0.41	[42]
					0.462	
					0.270	
Mg	Al Fe	2:1	CO ₃ ²⁻	450 °C	0.422	[104]
					0.24	
Mg	Al + Ga	3:1	CO ₃ ²⁻	200 °C, 0.7 atm	0.016	[56]
					1.4	
Mg	Al + Ga	2:1	CO ₃ ²⁻	300 °C, 1.08 bar	1.82	[57]
					1.70	
Mg	Al + Ga	2:1	CO ₃ ²⁻	300 °C, 1.05 bar	0.7	[24]
					1.15	
Mg	Al + Ga	2:1	CO ₃ ²⁻	400 °C, 0.9 bar	0.7	[24]
					1.15	
Mg	Al + Ga	2:1	CO ₃ ²⁻	300 °C, 1 bar	1.15	[58]
					0.51	
Mg	Al	1.5 2.5 3 3.5 4	CO ₃ ²⁻	200 °C, 1 atm	0.57	[38]
					0.71	
					0.74	
					0.6	
					0.45	
Li	Al	1:1 2:1 3:1 4:1 5:1	CO ₃ ²⁻	300 °C, 1 bar	0.44	[19]
					0.51	
					0.49	
					0.49	
					0.5	
Mg Mg	Al Al	2:1 1:1	CO ₃ ²⁻ OH ⁻ CO ₃ ²⁻ NO ₃ ⁻ SO ₄ ²⁻ HCO ₃ ⁻ Cl ⁻	300 °C, 1 bar	0.4	[62]
					0.53	
Mg	Al	3:1	CO ₃ ²⁻ NO ₃ ⁻ SO ₄ ²⁻ HCO ₃ ⁻ Cl ⁻	200 °C, 1 atm	0.21	[31]
					0.10	
Mg	Al	3:1	Stearate C ₁₇ H ₃₅ COO ⁻	300°C, 1 atm, flow CO ₂ : 40 mL/ min	0.18	[74]
					1.25	
Mg	Al	3:1	acetic acid (C2) butyric acid (C4) caproic acid (C6) octanoic acid (C8) capric acid (C10) dodecanoic acid (C12) tetradecanoic acid (C14) palmitate acid (C16)	200 °C, 1 atm	0.51	[37]
					0.57	
Mg	Al	4:1	Acetate	200 °C, 1 atm 86 % CO ₂	0.53	[75]
					0.61	
Mg + Ca	Al	1:2:1	CO ₃ ²⁻ Oxalate stearate	600 °C, 15% CO ₂	0.77	[72]
					0.76	
Mg	Al	2:1	CO ₃ ²⁻ (CH ₃ COO) ₃ BH ⁻	300 °C, 1 bar 300 °C	0.91	[58]
					0.69	
Mg	Al	2:1	triacetoxyborohydride Cl ⁻ SO ₄ ²⁻ BrO ₃ ⁻ ClO ₄ ⁻ CO ₃ ²⁻	300 °C, Pco2 1 bar	0.22	[65]
					0.03	
Mg	Al	3:1	Fe(CN) ₆ ³⁻ Cl ⁻ ClO ₄ ⁻ CO ₃ ²⁻	300 °C, 108 KPa	0.44	[68]
					0.16	
Mg	Al	3:1	Fe(CN) ₆ ³⁻ Cl ⁻ ClO ₄ ⁻ CO ₃ ²⁻	300 °C, 1 atm	0.62	[73]
					0.25	
Mg	Al	3:1	stearate	300 °C, 1 atm	0.27	[73]
					0.11	
Ca	Al	2:1	adamantanecarboxylate	600 °C	0.71	[76]
					1.01	
Ca	Al	2:1	adamantanecarboxylate	600 °C	6.18	[76]
					6.18	

[52] while others affirm that the presence of alumina enhances the basicity of the MMO [53]. An extensive analysis of the effect of M^{3+} in both the optimal adsorption and calcination temperatures was performed by Wang et al. [41]: choosing always magnesium as M^{2+} , carbonate as anion and a M^{2+}/M^{3+} ratio of 3:1, aluminum, iron, gallium and manganese were tested as M^{3+} . Al, Fe and Mn give between 0.41 and 0.46 mmol of CO_2 while the adsorption of the gallium sample only reaches 0.27 mmol. In general, adsorption at 200 °C gives better results and the best calcination temperature varies depending on the M^{3+} . Authors suggest that the presence of a quasi-amorphous phase can be a key issue for the MMO to get a high CO_2 adsorption capacity. Hadj-Abdelkader et al. [54] compares the results of two MMO of magnesium with aluminum or iron and a 2:1 ratio obtaining best results with aluminum.

5.2.1. Gallium

Even though the use of only gallium as M^{3+} seemed to give poor adsorption results, its addition in small quantities has been proven to significantly increase the adsorption capacity of the MMO. This was first tested by Yavuz et al. [55], where Mg/(Al + Ga) LDH with various percentages of Gallium (from 0 to 100 %) were synthesized. The CO_2 adsorption capacities of the samples were best when, in addition to an impregnation with K_2CO_3 , the sample had 10 % gallium as M^{3+} , obtaining 1.40 mmol/g while the sample with K_2CO_3 but no gallium adsorbed only 0.467 mmol/g and the sample with gallium but no potassium adsorbed 0.531 mmol/g. The combination of both gallium and potassium seemed to have a sort of synergistic effect. Authors attribute the reinforcement of the layered structure, as gallium made the MMO more robust and stable through multiple cycles, to be the primary cause of this adsorption increment. Based on these results, Miguel et al. [56] synthesized Mg/(Al + Ga) LDH with a M^{2+}/M^{3+} ratio of 2 and a Al:Ga ratio of 9:1 and a 20 % K, Cs or Sr content, and tested the adsorption capacity of the samples at 300 °C. The sample that had both potassium and gallium gave the best results, with 1.82 mmol/g as working capacity. Other experiments performed with the same proportions (Mg/(Al + Ga) LDH with a M^{2+}/M^{3+} ratio of 2 and a Al:Ga ratio of 9:1) gave better results than the MMO with no promoters [9,24,57].

5.3. M^{2+}/M^{3+} ratio

There has been quite an exhaustive research on the ideal ratio between the divalent and trivalent metals, examples of ratios from 0.4:1 to 20:1 can be found. However, some controversy arises when claiming ratios lower than 2 or higher than 4. The ratio of pure LDH phases is often difficult to obtain: elemental analysis of the metal content of the LDH can give inaccurate results if, for example, phases such as $M^{2+}(OH)_2$, $M^{2+}(OH)_3$ or $M^{3+}OOH$ are present [58] and X-ray diffraction patterns only sometimes detect other phases as they are prone to be amorphous [59].

Some authors chose to examine the lower end of the M^{2+}/M^{3+} ratio, usually because of the use of commercial LDH (SASOL) in their experiments. Zhu et al. [60] tested the adsorption capacity of commercial LDH at 400 °C along with Mg and Al oxides. Samples were calcined at 450 °C for 3 h and MG63 (2:1) gave higher adsorbance than MG30 (0.55:1) and MG70 (3:1) in the samples with no potassium. After performing an exfoliation process, sample MG63 still displayed the best CO_2 adsorption capacity [35]. Authors claim that although Mg-O sites are believed to be where CO_2 adsorbs, an increment in Al^{3+} adds more defects in the LDH layers, which in turn might further activate Mg-O sites making them more reactive to CO_2 . Yong et al. [61] tested the adsorption capacity of MG30, MG50 (1:1) and MG70 at 300 °C and 1 bar and the results are similar, as MG50 and MG70 obtained better results than MG30. Miguel et al. [56] considered these results but took into account that a ratio lower than two cannot avoid the electrostatic repulsion between nearby trivalent metals, when octahedrally coordinated [62] thus selecting a 2:1 ratio as also did Silva et al. [9], Yamamoto et al. [63] and Rocha et al.

[64].

Gao et al. [18] carried out a systematic investigation of the ratios and tested the Mg:Al ratio (from 1.5 to 4) of MgAl- CO_3 at 200 °C and in situ pre-calcination at 400 °C in N_2 for 1 h. The samples with ratios of 3 and 3.5 were clearly superior. A better understanding of these results can be found in Gao et al. [65] who, with the help of molecular dynamics simulations, studied the static and dynamic adsorption behavior of the MMO with various ratios (from 1 to 4.5). Sample with ratio 3 had the highest adsorption which is explained by a higher CO_2 diffusion barrier and the fact that, in this sample, magnesium atoms attract more surrounding atoms, particularly oxygen. Authors claim that theoretical results between samples are not as divergent as in experimental ones [18] as simulation takes into account only physisorption (electrostatic and van der Waals forces) but not chemisorption which could also play an important role.

Several other factors can alter the results such as potassium impregnation of the samples or the use of a different M^{2+} . Reijers et al. [10] tested the CO_2 adsorption capacity at 400 °C of various commercial LDH (MG30, MG50, MG61 and MG70) after a K-loading and calcination at 400 °C for 4 h. Strangely enough, the best results were obtained by the sample with the lowest magnesium ratio and the worst for the sample with more magnesium. Using lithium, Huang et al. [19] synthesized LiAl- CO_3 LDH with ratios ranging from 1 to 5 and tested their adsorption capacity at 200 °C, ratio 3, 4 and 5 were better, 3 gave a 0.51 mmol/g CO_2 adsorption which was comparable to the most used LDH Mg₃Al- CO_3 (0.50 mmol/g).

As stated above, results of samples with a M^{2+}/M^{3+} higher than four must be approached with caution, as they are not straightforward to explain. Trying to synthesize samples with higher ratios makes sense as the incorporation of Al^{3+} in the structure can attenuate the surface basicity of the clays and, thus, their ability to interact with the CO_2 [66]. Salomé Macedo et al. [8] synthesized MgAl- CO_3 LDH with several M^{2+}/M^{3+} ratios (from 2 to 20) by the co-precipitation method and tested their CO_2 adsorption capacity at 1 bar and 300 °C. Results show that the amount adsorbed increases from 0.6 to 1.6 at a ratio of 7 and decreases again to adsorb 0.8 at a ratio of 20. Authors find that this superior capacity of the sample of ratio 7 can be related to its BET surface or the interlayer distance and especially to the quantity of basic sites, this last factor also corroborated by Hutson and Attwood [67]. Even though several works try to relate the adsorption capacity of the samples with the BET surface, it has been proven that it does not exist [56,68], as it N_2 molecules cannot enter the LDH interspace [69].

Kim et al. [14] tested the adsorption capacity of MgAl samples with molar ratios from 3 to 30. The adsorption behavior at 240 °C showed that the sample with ratio 20 had the best uptake, at 9.27 mmol/g. PXRD patterns show the presence of Mg(OH)₂, NaNO₃, and Na₂CO₃ in the samples with a ratio bigger than 12. Interestingly, these samples with a bigger ratio showed a unique adsorption process consisting of two steps: a low loading that transitions to a very high CO_2 loading with time. Apart from the ratio, authors suggest that the presence of NaNO₃ in the structure (which originates from the magnesium nitrate precursor and increases together with the ratio) might be related to the adsorption increment until ratio 20 and decrease at higher ratios because of pore blockage of the samples. Other studies also show a better adsorption capacity when the ratios were high [21,29,70]. The latter synthesized CaAl LDH with ratios ranging from 1 to 7 and tested their adsorption capacity at 700 °C. The highest calcium content showed the highest adsorption capacity. The presence of Ca(OH)₂ is found from the ratio-4 sample and above in PXRD. Sometimes is the impregnation of the LDH with basic elements what makes a difference in regards to the behavior or the samples with several M^{2+}/M^{3+} ratios. Qin et al. [37] studied the adsorption capacity of the MgAl LDH (ratios from 3 to 20) intercalated with palmitate acid and synthesized considering two methods (co-precipitation and calcination-rehydration) with a loading of alkali metals. Results, taken at 200 °C with a constant flow of high purity CO_2 (40 mL/min), show an adsorption capacity decrease as the ratio increases if there

is no alkali loading and the opposite if a 15 % Li/Na/K loading is employed.

5.4. Interlayer anion

Carbonate (CO_3^{2-}) is the anion that has been proven to work best when compared to hydroxyl [61], chloride, bicarbonate, nitrate, sulfate, bromate, perchlorate, [19,31,64] oxalate or stearate [71] triacetox-yborohydride [57] ferrocyanide [67] or triacetoxhydroborate, [64]. When compared to hydroxide ion (OH^-), as carbonate is larger (which means a wider interlayer spacing) and also has higher charge than OH^- , CO_3^{2-} better performance seems straightforward. However, that does not seem to be the case of larger molecules that act as interlayer anions. Rocha et al. [64] compared the adsorption capacity of various anions such as chloride, sulfate or bromate with carbonate. Results demonstrate that there is not direct relation between the adsorption capacity of the carbonate sample and the c -parameter (calculated from PXRD, and related to the thickness of the interlayer distance), i.e. a bigger interlayer molecule does not translate to greater adsorption capacity. Authors found no correlation to other properties such as the volume and size of the pores or surface area and associate the better performance of carbonate to its morphological and chemical properties, especially its “sand rose” structure whereas other samples formed a “stone” structure. Salomé Macedo et al. [8] also found that interlayer distance cannot be linked to the adsorption capacity when using carbonate. In another experiment, Rocha et al. [57] used triacetox-yborohydride as interlayer anion in an attempt to enlarge the interlayer distance and thus, help the dopant K to be better dispersed into the material. While they achieved an increment of the space between layers, the sample with carbonate had the same increase in its sorption capacity when impregnated with potassium than the sample synthesized with triacetox-yborohydride. Li et al. [72] succeeded in introducing potassium in the layer structure by the synthesis of the LDH with the intercalation of the long-carbon-chain stearate anion, see Fig. 3. TGA test results at 300 °C for 60 min show a 0.71 mmol/g of CO_2 adsorption capacity by the carbonate-anion sample with no potassium and 1.11 mmol/g with potassium (+55.9 %) vs 1.01 and 1.93 mmol/g when stearate was used as anion (+90.8 %). Wang et al. [73] synthesized $\text{Mg}_3\text{Al}-\text{CO}_3$ and Mg_3Al -stearate LDH by a co-precipitation method and obtained an increment in the interlayer

distance from 0.78 nm (carbonate) to 3.54 nm (C18, stearate) and in the adsorption capacity. Authors also found that the memory effect of the Mg_3Al -stearate sample was not significant and related its better adsorption capacity to an increment in the surface basicity (O^{2-}), its lower degree of crystallinity and a more stable quasi-amorphous structure. While the size of the interlayer anion is not directly related to adsorption in smaller molecules as carbonate comes in first, it can greatly influence adsorption past a certain point in the carbon chain length. In addition to study the effect of Mg/Al ratios (see previous section), Qin et al. [37] tested the adsorption capacity of the calcined LDH with anions of various length, from two carbons to sixteen. The direct relation of these two factors is not clear in short anions, from C2 to C8, but it steadily increases from there on, obtaining 0.91 mmol/g in the sample with palmitate (C16).

Another factor to consider is the method used to integrate the anion into the structure. Manohara et al. [74] synthesized MgAl LDH with two ratios (3 and 4) and acetate as interlayer anion. Acetamide hydrolysis and anion exchange were tested to load the acetate and the samples at 200 and 300 °C. The acetamide hydrolysis method showed better results with an uptake at 200 °C of 1.20 mmol/g (anion exchange method only adsorbed 0.57 mmol/g). A change in the morphology and particle size of the samples as the hydrolysis sample crystallized in both fibrous and sheet-like particles with high surface area and better stability can explain the different outcome. The integration of adamantanecarboxylate in CaAl LDH employing a co-hydration method was also studied by Manohara et al. [75]. This anion has great thermal and mechanical stability and the ability to transform into a support if decomposed into a controlled manner. Results, after calcining the samples at 700 °C and testing their adsorption capacity at various temperatures, were best at 600 °C with a 6.18 mmol/g adsorption capacity.

6. Methods employed to improve the adsorption capacity of the LDH

Although LDH are the best performing adsorbents on the moderate-temperature range, there is still a lot of room for improvement when referring to their adsorption capacity, their mechanical stability in multicycle (adsorption–desorption) processes and their kinetics, which are below those found in physisorbents. Several strategies can be taken:

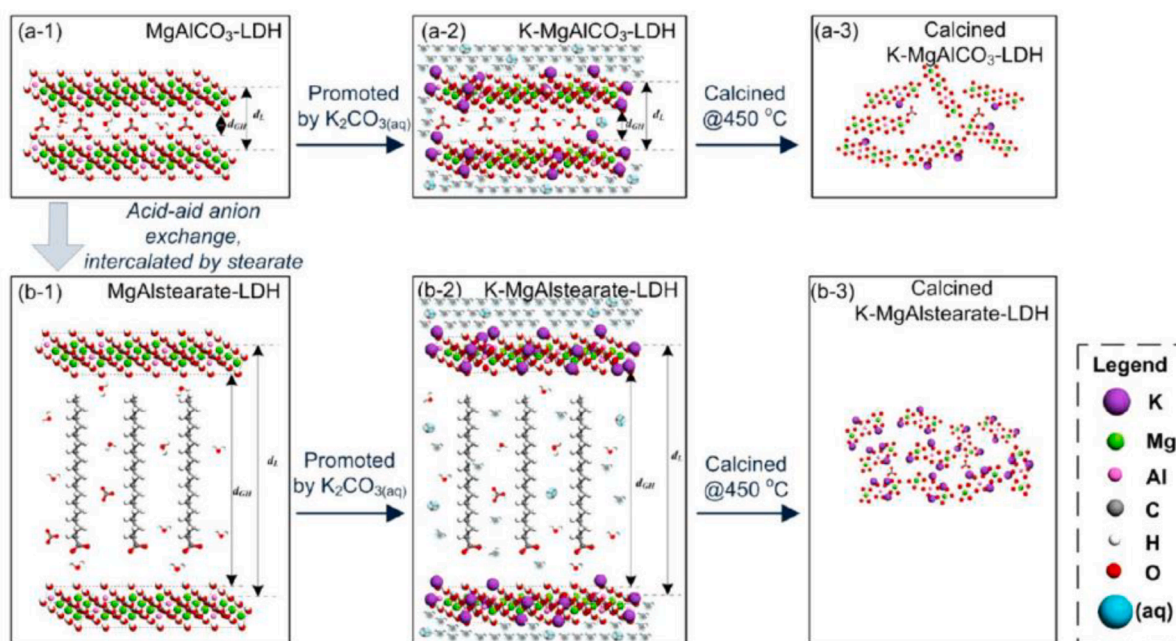


Fig. 3. Stearate intercalation and surface promotion synthesis scheme (Reprinted with permission from [72]).

some refer to the study of the synthesis process and internal structure of the LDH (cations, M^{2+}/M^{3+} ratio, anions, see Section 5) and others try to improve the adsorption capacity by either combining the LDH with other materials in order to either form composite/hybrid adsorbents or to alkalinize the LDH surface by a simple impregnation procedure. A third way of obtaining an improvement in the MMO performances is to study the best working conditions: temperature, pressure or steam content which will be described in Section 8.

6.1. Composites of LDH with supports

The study of the co-joined effect of MMO with a material that provides the composite with mechanical stability and at the same time acts as a base were the MMO can be well dispersed, usually outperforms the adsorption capacity of the MMO on its own. The MMO-composites tested up until now are displayed in Table 3.

One of the most studied supports is graphene oxide (GO) [33,68,76,77]. Based on its structure and charge Garcia-Gallastegui et al. [76] tested its compatibility with LDH. Both are formed of planar sheets but with complementary surface charges, negative for GO and positive for LDH. Using an in situ coprecipitation of the LDH into various proportions of GO (from 7 to 83 %), the sample with less amount of GO was chosen to provide a double coating of LDH on each flake of GO as represented in Fig. 4 and gave the best adsorption results, a 60 % improvement on the LDH adsorption capacity. The well-dispersed structure of the new compound increased also its stability and gave better results than MWNTs and alumina support, (see following paragraph). Based on this results, Wang et al. (2015) [33] synthesized and delaminated Mg_3Al-NO_3 and combined it with delaminated graphite oxide to form the nanocomposite by simply mixing the two components in suspension. The results are almost equal to those obtained by Garcia-Gallastegui et al. [76] and were further improved by Mohd Sidek et al. [77] with the addition of a third component to the structure, layered titanate nanosheets, that even at a very modest dose (0.3 wt%), strongly prevented the structure from self-aggregating.

The use of multi walled carbon nanotubes (MWNT) and alumina as supports has also been studied by Garcia-Gallastegui et al. [78]. The open supporting framework gave both stability throughout multiple cycles, maximized CO_2 accessibility to the adsorbent and minimized coarsening effects. However, a less morphological compatibility to the LDH meant a higher concentration of MWNT was needed (40 % wt.) in order to render similar results. Bhatta et al. [79] also explored the hybrid performance by synthesizing the compound in a similar manner, a one-step coprecipitation method and using 30 % wt. of MWNT which provided a better particle dispersion.

Table 3

Adsorption capacity of several MMO composites.

LDH	Composite	Adsorption conditions	CO_2 adsorption capacity before/after modification (mmol/g)	Reference
Mg_2Al-CO_3	CGM	300 °C, 1 bar	0.26/0.49	[39]
Mg_2Al-CO_3	7% GO	300 °C	0.28/0.45	[77]
Mg_2Al-CO_3	40% MWNTs	300 °C, 0.2 bar	0.3/0.42	[79]
$MgAl-CO_3$	30% MWNTs	300 °C	0.30/0.53	[80]
Mg_3Al-CO_3	Ac	200 °C 1 atm	0.148/0.185	[20]
$MgAl-CO_3$	Al foil	200 °C	--/0.56	[28]
$Mg_{20}Al-CO_3$	10% GO	260 °C 1 atm	--/0.77	[69]
$MgAl-LDH$	30% GO, 0.3% LTNS	300 °C	0.58/0.78	[78]
Mg_3Al-NO_3	6.54% GO	200 °C	0.24/0.47	[33]
Mg_2Al-CO_3	90% CNF	250 °C	0.1/1.3	[82]
Mg_3Al-CO_3	ZEO	200 °C	1/4	[81]

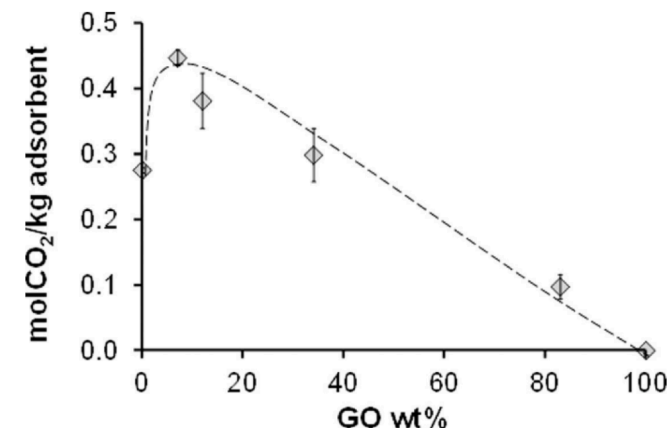
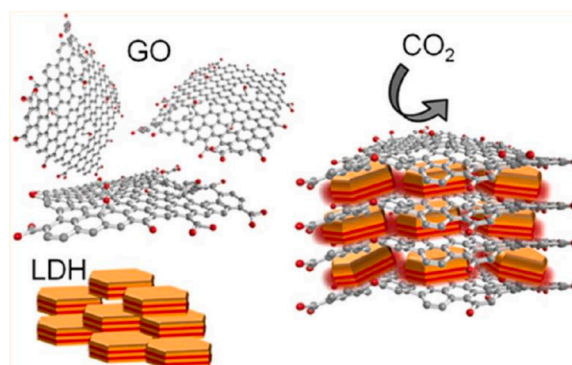


Fig. 4. LDH/GO structural combination and combination performance (Reprinted with permission from [76]).

The use of Activated Carbon (AC) has been studied by Zhu et al. [20] which only improved the results by a shy margin. The incorporation of zeolites by Othman et al. [80] and carbon nanofibers (CNF) by Meis et al. [81] gave excellent performances although there is a lack of data as neither CNF alone or LDH with no zeolites were tested for comparison purposes.

The selection of an adequate support must be thoroughly thought over, as the main advantages of LDH are their non-expensive and easy-to-synthesize nature, a reasonably prized support would fit LDH better. With that in mind, Bhatta et al. [38] used a graphitic material obtained from coal as support of the adsorbent with a simple synthesis technique. Results show that adsorption capacity of the composite doubled that of

LDH on its own, even though its performance through the adsorption–desorption cycles suffered at first. Qiao et al. [28] synthesized a multilayer LDH/MgCO₃ thin film on an aluminum foil that also provided all the aluminum needed by a urea hydrolysis method. By studying the synthesis time (12 h), temperature (140 °C) and Mg/urea ratio (1:1), a stable compound that retained 0.4 mmol CO₂/g after 20 cycles was obtained.

6.2. Impregnation

6.2.1. Potassium

Several pathways have been proposed to clarify the potassium role in the adsorption process. Walspurger et al. [82] state that the promotion of LDH with K₂CO₃ can encourage the carbonation of periclase (MgO). The formation of MgCO₃ can be catalyzed by a high enough concentration of a carbonate species such as K-CO₃-Al in equilibrium with CO₂. Another approach, not antagonistic but complementary, is considered by both Hoffman and Pennline [83] and Yang and Kim [21] and explains the increase in adsorption capacity of the LDH in the presence of potassium carbonate as: K₂CO₃ + CO₂ + H₂O \rightleftharpoons 2KHCO₃ + heat, with no direct involvement of the LDH. It should be pointed out that even though steam has been proven to improve adsorption results (see Section 8.3), the impregnation with K₂CO₃ and no steam supply also promotes adsorption. Zhu et al. [60] clarified the adsorption mechanism of potassium in calcined LDH with the use of *in-situ* Fourier transform infrared spectroscopy (FTIR). Two adsorption mechanisms were found: in samples with a high Mg/Al ratio, K-Mg double carbonates form after the CO₂ adsorption providing the sample with high thermodynamic stability and permitted an increment in the operating temperatures; the increase in Al³⁺ content adds more defects in the LDH layers, thus further activating Mg-O sites and enhancing the interaction between potassium and

unsaturated oxygen sites and the formation of unidentate carbonates which gave superior results when CO₂ was at low concentration. Several adsorption studies of LDH impregnation with potassium at moderate temperatures (from 200 to 400 °C) have been performed with the results obtained pre- and post-impregnation displayed in Table 4 and Fig. 5, as it can be seen, it works at each temperature. Impregnating the calcined LDH samples with K₂CO₃ is a quite a straightforward process that can give a mayor improvement in the adsorption capacity of the samples. Even so, the use of various solvents can lead to mayor differences in their performance. Zhu et al. [84] impregnated exfoliated Mg₃Al-CO₃ LDH nanosheets with 20 % wt. K₂CO₃ using six solvents (water, acetone, ethanediol, ethanol, DMAC, and methanol) and a posterior rota-evaporation under vacuum procedure. As the impregnation with water produced a re-stacking of the LDH layers, the use of organic solvents was tested, leaving the exfoliated structure intact. The use of ethanediol to impregnate the samples provided the best adsorption results, with an improvement of more than 200 %. In this study they improve the results by exfoliating the LDH and using the active centers placed in the inner surface of the layers, something also exploited by Li et al. [72] with a different approach, using a big anion (stereate) in the interlayer and thus opening a gap big enough for potassium to enter the inner active sites.

Numerous studies have researched the appropriate amount of K in order to achieve the best results, too much of a quantity may block the pores and thus active sites which can lead to a loss in the overall adsorption. Bhatta et al. [38] and Wang et al. [33] tried various percentages of K₂CO₃, from 5 to 25 % and found 15 % to be the best. As seen in Table 4, 15 and 20 % are the most used percentages. The only result found which was out of this tendency is that obtained by Lee et al. [85] on commercial LDH (MG30, MG50, and MG70). The increase in adsorption capacity of the samples with 35 % K₂CO₃ doubles that of the samples calcined with 20 %.

Table 4
Potassium promoted MMO performances.

	LDH	modification	Adsorption conditions	CO ₂ adsorption (mmol/g)		Reference
				before modification	after modification	
1	Mg ₂ Al-CO ₃	20 % Na/KNO ₃	200 °C, P _{CO2} = 1 atm	0.41	1.07	[86]
2		20 % K ₂ CO ₃	350 °C, P _{CO2} = 1 atm		1.19	
3		20 % NaNO ₃	200 °C, P _{CO2} = 1 atm		0.95	
4		20 % KNO ₃	200 °C, P _{CO2} = 1 atm		0.83	
5	Ni ₃ Al-CO ₃	10 % NaNO ₃	200 °C, 1.2 bar	0.66	0.85	[34]
6	Mg ₂₀ Al ₁₋₁₆ C (palmitate)	55 % Li-Na-K	200 °C	0.34	3.21	[37]
7	Mg ₃ Al-CO ₃ /AC	K ₂ CO ₃	200 °C, 1 atm	0.156	0.194	[20]
8	Mg ₂ (Al _{0.9} Ga _{0.1})-CO ₃	0.13 % K ₂ CO ₃	200 °C, 0.7 atm	0.531	1.400	[55]
9	Mg ₃ Al-NO ₃ /GO nanosheets	15 % K ₂ CO ₃	200 °C, 1 atm	0.47	0.6	[33]
10	LiAl ₂ -CO ₃	20 % K ₂ CO ₃	200 °C, 1 atm	0.51	0.83	[19]
11	Mg ₃ Al-CO ₃	20 % K ₂ CO ₃	200 °C, 1 atm	0.83	1.21	[30]
12	Mg ₂ Al-CO ₃	20 % K ₂ CO ₃	300 °C, P _{CO2} = 0.15 bar	0.45	0.67	[89]
13	Mg ₂ Al-CO ₃	5 % Na	300 °C, P _{CO2} = 0.15 bar	0.45	0.65	
14	Mg ₂ Al-CO ₃	10 % Cs	300 °C, P _{CO2} = 0.15 bar	0.45	0.64	
15	Mg ₂ Al-CO ₃	20 % K ₂ CO ₃	300 °C	0.94	1.43	[9]
16	Mg ₂ Al-CO ₃	15 % K ₂ CO ₃	300 °C	0.26	0.52	[38]
17	Mg ₂ (Al _{0.9} Ga _{0.1})-CO ₃	20 % K	300 °C, 1.08 bar	0.45	1.82	[56]
18		20 % Cs			1.4	
19	Mg ₃ Al-stearate	12.5 % K ₂ CO ₃	300 °C	1.01	1.93	[72]
20	MgAl-CO ₃	20 % K ₂ CO ₃	300 °C, 1 bar	0.45	0.65	[79]
21	MgAl-CO ₃ /MWCNT			0.85	1.12	
22	Mg ₃ Al-CO ₃	20 % K ₂ CO ₃	400 °C	0.42	1.46	[84]
23	MG-30	20 % K ₂ CO ₃	400 °C, 2 bar, P _{CO2} 0.40 bar	0.10	0.76	[88]
24		20 % Cs ₂ CO ₃			0.44	
25	MG30	35 % K ₂ CO ₃	400 °C, 1 atm	0.10	0.94	[85]
26	Mg ₃ Al-CO ₃	20 % K ₂ CO ₃	400 °C oC	0.53	0.85	[31]
27	Mg ₃ Al-CO ₃	18.5 % K, 1.5 % Na	350 °C, 1.34 bar	0.28	1.109	[105]
28	Mg ₃ Al-CO ₃	20 % K ₂ CO ₃	400 °C, 1 atm	0.22	0.83	[60]
29	Mg _{0.70} Al _{0.30} (CO ₃)	22 % K ₂ CO ₃	400 °C, 1 bar	0.06	0.37	[17]
30	Mg ₄ Al-CO ₃	20 % K ₂ CO ₃	350 °C	0.454	0.96	[92]
	Mg/Al ratio 0.6	20 wt% K ₂ CO ₃	400 °C, up to 24 bar		1.5	[46]
	Mg ₂ Al-CO ₃	20 % K ₂ CO ₃	450 °C, 1.13 bar	0.26	0.77	[21]
	Mg ₂ Al-CO ₃	20 % K ₂ CO ₃	350 °C	0.52	1.78	[23]
	Mg ₂ (Al _{0.9} Ga _{0.1})-CO ₃	20 % K ₂ CO ₃	400 °C, 15 % CO ₂		1.23	[24]

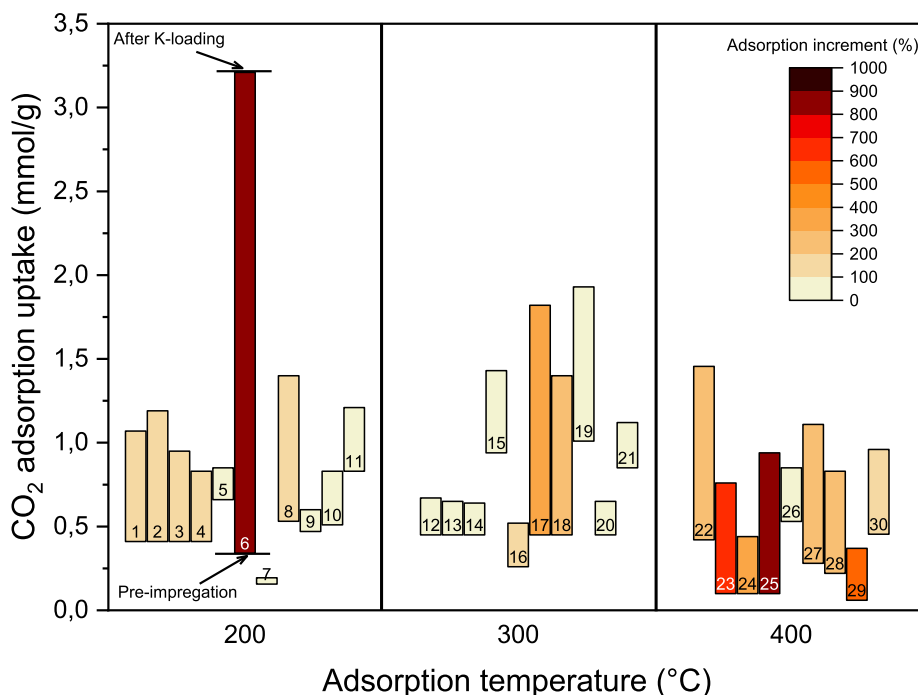


Fig. 5. Increment on the CO₂ adsorption capacity when impregnated with K₂CO₃.

There is a lack of research on the use of other forms of potassium to enhance the LDH adsorption capacity. Sun *et al.* [86] studied the effects of NaNO₃, KNO₃, Na/KNO₃, and K₂CO₃ (20 wt% doped amount for each salt) impregnated on a commercial hydrotalcite MG60 (Mg:Al ratio of 1.91) by adding H₂O and ethanol (ratio 1:1) as a way of dispersing the salts evenly on the LDH surface. Results show two behaviors: the impregnation of the calcined LDH with either NaNO₃, KNO₃, Na/KNO₃ had analogous results (~100 % increment in adsorption capacity) that also followed the response of the MMO and the best adsorption results were obtained at 200 °C (see Fig. 6a). In contrast, the impregnation of the samples with K₂CO₃ worked best at temperatures ranging from 300 to 400 °C (Fig. 6b), making them more compelling for SEWGS working conditions. This behavior of potassium was studied with Raman and FTIR concluding that nitrates do not react with CO₂ during adsorption but increase the number of active sites with basic properties. Carbonates however, form a K-O-Mg bond which promotes adsorption although with a slower regeneration rate compromise.

6.2.2. Other alkali metal cations

Although less explored than potassium carbonate, sodium carbonate has similar characteristics and is inexpensive which makes it a potential candidate for the enhancement of the CO₂ uptake by calcined LDH. Min *et al.* [87] tested several proportions of NaNO₃ and MG70 (a commercial hydrotalcite) and the best performance was obtained with a 0.35:1 Na₂CO₃:LDH ratio. As shown by Kim *et al.* [14], the presence of NaNO₃ on the surface of a mixed oxide with a high Mg/Al ratio and, therefore, with a similar structure to that of MgO, can promote the rapid generation of both active MgO sites and carbonates needed for the formation of MgCO₃ crystals. The amount of NaNO₃ content has to be appropriate, as an excess of nitrate comes with a blockage of the pores and a reduction of the available surface. Hanif *et al.* [34] calcinated Ni-Al LDH only at 200 °C, as they found by TGA that the impregnation with NaNO₃ brings stabilization to the structure and restricts the loss of interlayer water (favorable for the fixation of CO₂), thus improving the adsorption capacity by 28 % and the added advantage of a lower energy penalty.

Apart from sodium, other basic metals such as cesium and strontium have been also tested as modifiers. Oliveira *et al.* [88] tested the adsorption capacity of three commercial LDH (MG30, MG50, MG70)

without further modification and with potassium and cesium impregnated at 20 % wt. For the following adsorption conditions: 400 °C, 0.4 bar CO₂ partial pressure and in the presence of steam, potassium gave always better results than cesium, which also displayed better results than the MMO on its own (0.10 mmol/g). The sample with highest adsorption capacity was MG30 with potassium (0.76 mol/kg) and the sample that worked best with cesium was MG70-C (0.41 mmol/g). Similar results were obtained by Miguel *et al.* [56] when modifying Mg/Al + Ga LDH with either potassium, cesium or strontium: K performed the best, followed by Cs and Sr lowered the results obtained by the MMO on its own. Faria *et al.* [89] studied the results on MgAl LDH wet-impregnated with various loadings of Na or Cs and compared them with the MMO, MMO with K-20 % wt. and commercial MG63. Both the equilibrium sorption capacity and cyclic working capacity were examined. The results were best at low-loading percentage to prevent pore blockage. Even though the K-MMO showed the highest equilibrium sorption capacity (0.67 mmol/g), its lower sorption kinetics may hinder the separation process productivity. In that way, the most promising sample was the MMO with 10 % wt. Cs, as it performed the best (0.32 mmol/g) in cyclic operation (5 cycles, 30 min sorption/30 desorption under vacuum) at CO₂ partial pressure of 0.15 bar and 573 K.

7. Mechanism of adsorption

CO₂ adsorption on MMO at moderate temperatures is a combination of both physisorption and chemisorption processes. The first layer will be chemisorbed while the subsequent deposited layers are physisorbed and have lower binding strength [40]. While at lower temperatures chemical interactions are restricted as higher activation energy is needed, an increment in temperature increases the percentage of chemisorption contribution. On the other hand, physical adsorption capacities decrease as temperature increases, due to the negative enthalpy [13]. Several factors can affect the adsorption mechanisms such as calcination temperature, M²⁺ and M³⁺ cations or their ratio. Calcination of the samples exposes basic sites on the surface of the MMO, which favors physisorption, strongly related to the number of basic sites. Chemisorption, however, is based on the nucleophilic nature of the functional groups, basicity can help improve the nucleophilicity which

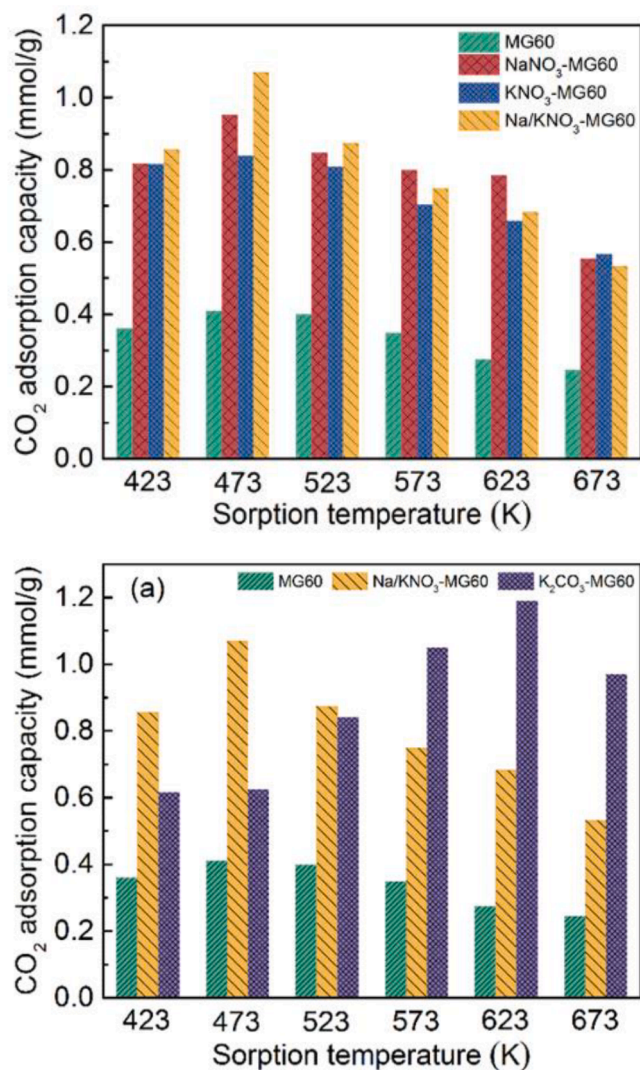


Fig. 6. Difference in behavior of K and Na impregnation on LDH (Reprinted with permission from [86]).

does not directly mean more capture [13,90].

Isotheric heat is a much useful tool that measures how strongly CO₂ is bound to the adsorbent. The ideal binding energy stands between 35 and 50 kJ/mol [90], values were MMO usually stand [63,88]. Higher values can have strong energy penalty, requiring temperature swing regeneration at high temperature (as with lithium zirconate or calcium oxide) while adsorbents with smaller isotheric heat have lower working capacity when in low partial pressure CO₂ feeds.

8. Adsorption conditions

8.1. Temperature

The general response of the calcined LDH to a rise in the working temperature is a decrease in the adsorption capacity. Several studies have been performed in MgAl MMO [37,74] and this tendency does not change when working with composites [20,33] or changing M²⁺ to lithium [19].

However the impregnation of the samples with potassium carbonate gives thermal stability to the structure of the MMO that allows for an increment in working temperatures to the range of pre-combustion conditions [60]. This translates to a similar adsorption capacity in the range of 200 to 500 °C [13,31,68,85,88,91]. The studies performed with

magnesium [86,92] and lithium [19] showcase the change in behavior of the samples with and without K₂CO₃.

An exception has been found with adamantanecarboxylate intercalated CaAl LDH [75] that have its adsorption peak at 650 °C, something usual in calcium oxide samples [85]. There are, however, outside the pre-combustion working conditions apart from needing regeneration temperatures superior to 900 °C.

8.2. Pressure

There is a considerable need for more research in the adsorption capacities of MMO samples at high pressures. Even though there has been a steady increase of studies on CO₂ adsorption at moderate temperatures, some of the other working conditions such as the presence of steam and, primarily, high pressure are being prorogued. This is probably because of the difficulty in obtaining accurate results due to the displacement effect [93]. Either in water gas shift or steam reforming of methane, operating conditions require pressures around 10 bar [94]. The few studies performed at the required pressure levels are summarized in Table 5. As expected, in all cases an increase of pressure affects adsorption favorably.

Even though almost all the studies performed at around 10 bar used MgAl MMO and, in most of the cases, impregnated with K₂CO₃, the results obtained by Hanif et al. [23] stand out, as their samples double the adsorption capacity of the rest. The key is the synthesis method as a microwave radiation of the gel obtained after co-precipitation was employed (more info can be found in Section 4).

All the studies realized with the use of commercial KMG-30 (Sasol, Germany) collected similar results. Boon et al. [46] developed a SEWGS reactor model to provide information on the competitive adsorption of CO₂ and H₂O. The pure CO₂ adsorption mechanism of the KMG-30 is formed out of two steps: the first is attributed to surface sites and has its maximum at 0.4 mmol/g and the second (partial pressures of over 3 bar) corresponds to nanopore adsorption (see Fig. 7a). A very interesting test was performed by Arstad et al. [95] in which a series of cobalt-magnesium-aluminum LDH were synthesized with various proportion of M²⁺ (cobalt was chosen based on the outcome obtained by Wang et al. [48], see Section 5.1). The results were compared with the performance of KMG-30. The estimated volumetric capacity of Co_{1.5}Mg_{1.5}Al was around 35 % higher than the reference at 375 °C and 21 bar. This sample was tested for long-term stability through 120 adsorption/desorption cycles, showing improved results than the reference case [96].

Garcés-Polo et al. [94] modified commercial LDH with either 5 wt% cobalt, iron or nickel and tested their adsorption capacities at up to 300 °C and 44 bar. The results were compared with four commercial microporous materials: zeolite, MOF, activated carbon and alumina pillared clay. The sample modified with nickel displayed a higher adsorption capacity than the rest which the authors attributed to the presence of a chemisorption mechanism that takes place in basic sites of high strength and density. Results obtained by Ramírez-Moreno et al. [97] give an insight about the importance of research data on high pressure conditions. A comparison of the adsorption of MgAl LDH with a M²⁺/M³⁺ of 3:1 synthesized by coprecipitation method at low supersaturation conditions at several temperatures and pressures is presented. At low pressures (1 bar) the lowest adsorption result was obtained at 300 °C. However, when working at 44 bar, this temperature provided the best results by far which authors attribute to structural and microstructural changes in the interlayer space.

8.3. Steam

The effect that the presence of water vapor has in the adsorption of CO₂ is extremely important as H₂O is present in H₂ production processes (pre-combustion) but also in exhaust streams from coal-fired power stations (post-combustion) were neither pressure or, to an extent, temperature are an issue. Steam has been proven to improve the working

Table 5
MMO performances at high pressure.

LDH	Modification	Temperature (°C)	CO ₂ adsorption (mmol/g) at		Ref.
			atmospheric pressure	high pressure	
MgAl ₂ -CO ₃ (KMG-30)	20 % K ₂ CO ₃	400	0.27	0.47, 8 bar	[39]
MgAl ₂ -CO ₃ (KMG-30)	25 % K ₂ CO ₃	450	0.38	0.64, 10 bar	[93]
MgAl ₂ -CO ₃ (KMG-30)	20 % K ₂ CO ₃	400	0.3	1.25, 18 bar	[46]
Mg ₃ Al-CO ₃	20 % K ₂ CO ₃	300	0.4	5.7, 43.5 bar	[97]
Mg ₂ Al-CO ₃	20 % K ₂ CO ₃	300	1.5	2.4, 10 bar	[23]
CO _{1.5} Mg _{1.5} Al	22 % K ₂ CO ₃	375	–	2.0, 20 bar	[95]
Mg ₆ Al ₂ -CO ₃	–	300	0.22	0.59, 10 bar	[94]
	5 % Ni	300	0.57	1.03, 10 bar	

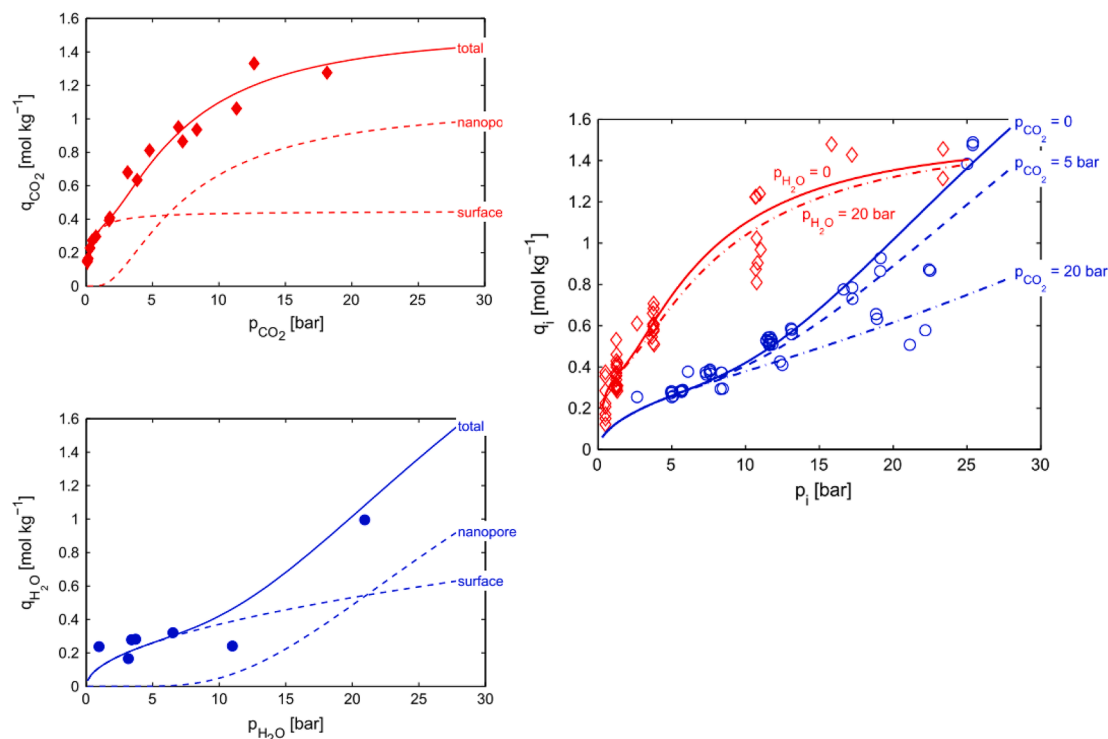


Fig. 7. Breakthrough capacities of pure CO₂ (a), pure H₂O (b) and CO₂-H₂O mixture (c) (Reprinted with permission from [46]).

capacity of the MMO: not only in the adsorption process itself [54,98–101] but also in the desorption which implies a better performance throughout consecutive cycles. Water molecules react with the metal oxides to produce hydroxides that work with the CO₂ and form bicarbonates [102]. Analysis performed by *Salomé Macedo et al.* [8] with XRD found that the MMO were able to partially recover its LDH structure when in dry conditions and totally recover their interlayer space in the presence in wet conditions due to the bicarbonate species formed. Depending on the sample textural properties, an excess of steam can be counterproductive, causing a reduction of the pore apertures and, thus, an increment in the diffusion resistance of the adsorbate [103]. When at higher pressures (10 bar), XRD diffractograms obtained by *Walspurger et al.* [82] showed the immediate formation of potassium carbonate when changing from dry to wet conditions and a progressive appearance of magnesium carbonate with the subsequent disappearance of periclase (MgO).

Coenen et al. [45] used TGA cycles together with experiments in a packed bed reactor to study the various mechanisms that drive the combined adsorption of CO₂ and H₂O at several composition and temperatures on a commercial hydrotalcite (KMG30, Sasol). The description of the process is fulfilled with the existence of four types of adsorption sites: one for H₂O and another for CO₂, easily regenerated, the first one decreases with the increment of temperature and the second increases

with it and the other two sites are a combine both components and not so easy to regenerate. The presence of H₂O increases the working capacity of the adsorbent as it makes possible the regeneration of one of the latter. The efficiency of the process was optimized by increasing the CO₂ partial pressure and decreasing that of H₂O at once. *Boon et al.* [46] developed a SEWGS reactor model to predict the breakthrough and the regeneration behavior of the competitive adsorption of CO₂ and H₂O at pressures up to 24 bar and 400 °C. The surface adsorption appears at lower partial pressures and occurs at various sites for CO₂ and H₂O. Nanopore adsorption mechanism that appears at over 5 bar is competitive and H₂O is more affected in the presence of CO₂ than vice versa (Fig. 7b). All these studies were performed with MMO that had an LDH with carbonate anion as precursor. The use of various anions can have counterproductive effects in the adsorption mechanism if steam is present. This was proven by *Rocha et al.* [57] when using MgAlGa LDH with either carbonate or triacetoxymethylborohydride as anion, on the latter the presence of steam had a negative effect on its performance. Other anions such as stearate in a K-MgAl MMO had good response to the presence of minor steam content [72].

8.3.1. H₂O for regeneration

The use of steam on the desorption step of the cycle has been proven to have multiple benefits: quicker and better removal of the adsorbate

and a better performance on the next cycle. The steam produced in multifunctional reactors for CO₂ capture and conversion following the reaction $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$, gave synergistic effect to the process [91]. The formation of methane is favored by the presence of steam, that also makes it faster and more efficient to desorb CO₂ than in dry conditions, making next cycle more productive. Halabi et al. [104] used a calcined commercial MgAl LDH (MG61 Sasol) loaded with 22 wt% K₂CO₃ as CO₂ adsorbent for high purity H₂ production at moderate temperatures (400–500 °C) by steam reforming process. The use of 20 vol% water content was found to reduce the desorption time by a factor of 7. Two steps appeared: a fast desorption step, associated with physisorption on the monolayer surface of the MMO and a slower step, linked to multilayer reversible chemisorption. Martunus et al. [105] studied the effects of steam in the adsorption and desorption process which was proven to be effective up to a point (32.5 % and a 30 % concentration of CO₂), as larger concentrations reduced the working capacity of the reactor.

Water can be also used as a previous step to the adsorption process. Hanif et al. [34] used a 30-minute pre-treatment with steam in exfoliated NiAl LDH that were only treated at 200 °C in order to prevent the interlayer water from totally disappearing. This moisture treatment led to an increase on the adsorbance of almost 85 %.

9. Stability and adsorption kinetics

The durability of the adsorbents is one of the crucial aspects to consider for industrial implementation. As the initial adsorption capacity of the MMO is frequently not steady in time and a change in adsorbent for each cycle is not cost effective, the most adequate measurement to analyze when selecting adsorbents is the working capacity of a sample. Both the thermal and the chemical stability of a sample can be tested by subjecting the sample to several adsorption/desorption cycles. On the other hand, only the samples with fast kinetics are considered interesting as candidates for large-scale applications.

There are several adsorption/desorption strategies, the most common being the pressure swing (PSA) and the thermal swing approaches (TSA). The PSA is faster and saves the energy costs of thermal regeneration and that is why is heavily extended [35,44]. Some examples are Salomé Macedo et al. [8] which brought the pressure from 4.7 to 1 bar or Faria et al. (2022) who thought of an application in post-combustion conditions (adsorption at $p\text{CO}_2 \leq 0.15$ bar and 300 °C) and desorbed the adsorbate at $p\text{CO}_2 < 0.001$ bar. Other studies examine the application of the TSA [19,38,43,74].

MMO have fast adsorption kinetics [88,106]. An extensive study performed by Coenen et al. [39] with a variation of adsorption and desorption times and temperatures concluded that the working capacity for both CO₂ and H₂O of a potassium-promoted hydrotalcite (KMG30, Sasol) can be determined by its desorption kinetics. The adsorption of CO₂ of the samples showed a very fast adsorption kinetics at first followed by a slower adsorption rate that did not seem dependent of temperature or time. However, desorption kinetics were significantly slower although could be increased with a rise in the temperature, thus proving that TSA was required in this case. Wu et al. [13] studied the response of MG30 (Sasol) impregnated with 20 wt% KNO₃ to both thermal swing and isothermal regeneration. Even though the decrease of the adsorption capacity was similar after 10 cycles (only ~7%) in both cases, the time required for the desorption can be reduced to 60 min if performing the TSA. The strategy of an isothermal regeneration was also approached by Rocha et al. [57] with the change of the feed gas from CO₂ to N₂. Although there are advantages in using pressure swing strategy, such as minor required desorption time, sometimes its recovery rate is not as effective. The study of a comparison of PSA vs TSA [40] on Mg₃Al MMO shows that after minor losses of CO₂ adsorbed on consecutive operation cycles with PSA a regeneration step at 400 °C brings back the initial adsorption capacity.

The change in the initial adsorption capacity of the samples, usually

for the worse, shows the presence of an irreversible adsorption of the CO₂ taking place. As studied by Miguel et al. [56], this irreversible chemisorbed CO₂ is pressure dependent, an increment in pressure up to 1.1 bar led to an increase of more than 50 % of the permanently chemisorbed CO₂. The preparation method also affects, an increment on the surface basicity of the samples will yield unidentate carbonates [104], which remain after a desorption temperature of 400 °C (TSA) and correspond to strong adsorption sites that will ultimately cause irreversible adsorbed CO₂. There are examples [37,68] of calcined MMO where the initial adsorption capacity increases with every following cycle. It is called self-reactivation and the former study, with LDH/GO composite and a 30 % alkaline metal impregnation, describes the effect of both the presence of GO in the prevention of the surface's reduction and the changes in the smoothness of surface area.

The use of LDH-composites in other works [78,79] with MWCNT, and [33] with GO revealed that the presence of the supports made the adsorption capacity of the samples more stable throughout the cycles, something that did not happen when AC was chosen as support [20].

There are studies performed with CaAl MMO [70,75] that display fast kinetics and very steady results up to 60 adsorption–desorption cycles and work at several percentage of CO₂ in the feed. However, both have chosen a high adsorption temperature (600–700 °C) that may not have interest for pre-combustion working conditions, and the latter study shows a 50 % reduction in the initial adsorption capacity when working at 400–500 °C.

10. Techno-economic feasibility

Although sometimes overlooked, the cost of production of the sorbent should be considered as it is one of the critical aspects that can “make or break” a candidate. Several requirements have to be met: sorbents should have greatly abundant metals but also the amount of waste generated in the sorbent production must be limited to the minimum. Patel et al. [90] argues that metals such as magnesium or calcium are preferable and that even aluminum could pose a problem because, even though it is abundant, it is not in the required pure form. One possible solution can be the collection of aluminum from non-conventional sources such as saline slags, a non-desired hazardous waste generated in the recycling of aluminum, to be later employed in the synthesis of LDH as validated by Gil et al. [47]. Cost of production should be never neglected as a slight improvement on the adsorption capacity of MMO can be proven counterproductive if the materials employed are in short supply/expensive.

Even though much research is needed in this area, life cycle assessments is a powerful tool that can help with the comparison of different systems/sorbents. Petrescu et al. among others [107] evaluated the performance of a calcined LDH in a SEWGS process integrated to steel plants with the post-combustion capture of CO₂ using monoethanolamine (MEA), concluding that CCS of CO₂ in the former had much lower overall environmental impact.

11. Conclusions and future perspectives

This review gives a general insight on the state-of-art of MMO adsorbents of CO₂ at moderate temperatures (200–450 °C). MMO were chosen as they are the best positioned candidates to be used for this purpose: they are cheap, easy to synthesize, stable and respond well to both the presence of steam and high pressures. Their greatest weakness lies in their adsorption capacity, which, as seen throughout this review, can be improved with a finely-tuned control of both the adsorption and synthesis conditions. Any change in the adsorbent composition must be carefully chosen considering its cost and environmental impact.

Although numerous analysis have been performed, there is still an astonishing lack of results when it comes to the adsorption capacity of the samples at elevated pressures, even though both the presence of steam and high pressures improve the adsorption capacity of the MMO.

Of the synthesis and amelioration techniques employed, some clues can be considered for further research:

- While there is a general consensus on the choice of MgAl samples, the chosen anion is still on debate. Carbonate results exceeds that of other even larger molecules although, when the number of carbons is larger than 10, it is outperformed. These larger anions can however be not as effective in the presence of steam, in general stearate seems like a good place to start.
- The exfoliating process of the LDH might be effective, although it needs to be consistent for several cycles.
- Choosing a M^{2+}/M^{3+} ratio larger than 4 can work although its structure might not be entirely that of LDH.
- The use of composites has been proven to function, especially the combination GO/LDH that, apart from increasing the adsorption capacity of the samples, confers the structure with a mechanical stability that lasts throughout several cycles.
- The impregnation of the samples with potassium carbonate works, even though the mechanism of action is not clear, and the use of various solvents when impregnating should be further studied.
- Two proposals have been suggested when trying to explain the general lack of uniformity in the results: the presence of sodium remaining after the synthesis process or the lack of calcination prior to adsorbance tests as the memory effect of the LDH can alter the results. These should be also considered for clarification.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Research ethics

We further confirm that any aspect of the work covered in this manuscript that has involved human patients has been conducted with the ethical approval of all relevant bodies and that such approvals are acknowledged within the manuscript.

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