

Review

# CO<sub>2</sub> Adsorption of Materials Synthesized from Clay Minerals: A Review

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**Abstract:** The aim of this work is to make a brief review of the adsorption of  $CO_2$  on modified clay minerals. Previous researchers have used different clay modifications, either by making changes in the structure by a reaction with another product or by the addition of a catalyst to improve their  $CO_2$  adsorption capacity. In order to obtain high values of  $CO_2$  uptake, some researchers have been incorporated amines-speices such as (3-aminopropyl)triethoxysilane (APTES), tetraethylenepentamine (TEPA) and a branched polyethylenimine (PEI) by grafting or impregnation. The synthesis of an adsorbent from mineral clays can generate an increase in its porosity and in its textural properties. These investigations differ in a number of factors such as the kind of clay, the operating conditions, y and the nature of the impregnated compound. The role of these factors in the  $CO_2$  adsorption capacity will be considered in detail in this review.

Keywords: clay mineral; CO<sub>2</sub> adsorption; specific surface area; pore volume; amine incorporation

# 1. Introduction

In the last decades, intensive use of fossil fuels in industrial, transportation and building sectors lead to an increase of damaging emissions into the atmosphere. This ceaseless increase is the main cause of global warming, climate change and acid rain. These effects have harmful consequences on health and the environment [1]. Among all the emissions generated in combustion processes, CO<sub>2</sub> is considered one of the most dangerous pollutants due to the high levels emitted worldwide. Hence, it is necessary to cope with these gaseous pollutants while the scientific community develops alternative sources of energy to replace traditional fossil fuels. Environmental requirements oblige the governments to respect the  $CO_2$  emission by making some regulations to reduce this pollutant's emitted level. These environmental policies pretend to diminish the current energy demand through an improvement in energy efficiency, promoting a low-carbon sustainable economy and at the same time stimulating the economic growth. Taking into account the high energy needs required by the world population, a single measure is not enough to mitigate  $CO_2$  emissions to the atmosphere so it is necessary to take complementary actions. Among them, it has been reported that the  $CO_2$  capture and storage (CCS) is a sustainable strategy to mitigate the  $CO_2$  emissions in short- and mid- terms [2]. Several authors have reported that the first step, i.e., the CO<sub>2</sub> capture, is the most expensive in the CCS process (between 50–90% of the global cost) so the main efforts are directed towards the development of



technologies that allow an efficient capture of  $CO_2$  [2]. The most used technologies applied in the  $CO_2$  capture are cryogenic distillation, membrane purification, and adsorption. Cryogenic distillation is highly used in the  $CO_2$  capture for the separation of small molecules, although its high energy demand rules out its use or larger scale. Despite its easy operation and relatively low energy consumption, the purification through membrane-based processes, is limited when  $CO_2$  is in the minor content [3]. The most mature technology in the  $CO_2$  capture is its absorption using amines with excellent behavior; although this methodology also displays several drawbacks related to its high energy requirements needed in the regeneration step, as well as, the high corrosivity of the amine-species.

The use of adsorbents to capture  $CO_2$  has emerged as an alternative to those technologies indicated previously due to its reduced energetic demands and the easier operation conditions in comparison to the techniques described above. Most efforts are focused on the search and development of adsorbents with high adsorption capacity and selectivity for  $CO_2$ ; however, other parameters such as rapid adsorption/desorption kinetics, good mechanical properties, high hydrothermal and chemical stability, regeneration capacity, and synthesis costs are hardly taken into account in many studies to implement these adsorbents on a large scale [4–8]. Considering these premises, the scientific community is developing porous materials, which can adsorb selectively high levels of  $CO_2$ . These porous structures act as a molecular sieve because  $CO_2$  has a high quadrupole moment, which enhances its interaction with the electrical field gradients of porous materials [2,9].

Several porous materials have been evaluated as potential molecular sieves to the  $CO_2$  capture. In this way, it has been reported in the literature that metal organic frameworks (MOFs) and graphene organic frameworks (GOFs) form 3D ordered structures with narrow and homogenous pore size distribution where the  $CO_2$  molecules are retained [10,11]. However, the main disadvantages of these structures are related to the relatively low thermal stability, which is required in the regeneration step, and the high cost required to prepare these materials in larger scale. The design of homogeneous porous silica has been developed in the last 25 years. Many scientific groups have synthesized several porous silicas with different porosity and morphology such as MCM-41, MCM-48, SBA-15, HMS or mesocellular foams [12-16]. In all cases, the CO<sub>2</sub> adsorption capacity is directly related to the microporosity of the synthesized porous silica, although the CO<sub>2</sub> adsorption capacity is limited compared to the structure of the MOFs [2]. Both zeolites [17,18] and activated carbons [8,19] are other structures with narrow pore size, so these materials also reach higher CO<sub>2</sub> adsorption values. Considering that the  $CO_2$  capture is the most expensive step in the CCS process, it is necessary to develop inexpensive adsorbents to obtain more economic and sustainable processes to be implanted on a larger scale. Thus, clay minerals have become an alternative because of their excellent behavior in adsorption and catalysis [20]. This factor together with their high availability and stability make them potential adsorbents to be used in CO<sub>2</sub> capture processes. Taking into account these premises, the purpose of this review is to give a detailed study of clay minerals as potential adsorbents to the CO<sub>2</sub> capture. In addition, this manuscript evaluates the modification of clay minerals by incorporating amino groups, in order to increase the CO<sub>2</sub> adsorption capacity and to enhance the chemical interaction between the absorbent and the molecules of CO<sub>2</sub>.

# 2. Structure of the Clay Minerals

Among the wide variety of clay minerals, the phyllosilicates have received much attention due to their chemical composition as well as their different morphologies that can naturally acquire. The structure of the phyllosilicates is well described elsewhere [21]. Briefly, the phyllosilicates, denoted as sheet silicates, are formed from consecutive tetrahedral and octahedral sheets. On the one hand, the tetrahedral sheet (T) is generally formed by the  $[SiO_4]^{4-}$  species. In all cases, silicon is located in the center of the tetrahedron while the four oxygen atoms are located in its edges, leading to an interconnected six member rings of the  $[SiO_4]^{4-}$  tetrahedral that extend outward in infinite sheets along the *a*,*b* plane (Figure 1). On the other hand, the octahedral (O) sheets are connected by sharing

edges, leading to sheets with hexagonal symmetry. In this sheet, the main cations are  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$  and  $Mg^{2+}$ .



**Figure 1.** Typical tetrahedral sheet and octahedral sheet in the phyllosilicates.

The extension outward of the *a*,*b* plane of both tetrahedral (T) and octahedral (O) sheets leads to phyllosilicates of the kaolin (dioctahedral) and serpentine (trioctahedral) group (TO) with a basal spacing of 0.7 nm (Figure 2A). In the TOT phyllosilicates, the octahedral sheet is sandwiched by two tetrahedral sheets faced between them forming phyllosilicates of the pyrophyllite group (dioctahedral) and talc group (trioctahedral) with a basal spacing of 0.9 nm (Figure 2B). In both cases, all charges are counterbalanced so the interaction between the adjacent sheets takes place by electrostatic interactions [21].

The partial isomorphic substitution of the Si<sup>4+</sup>-species by the Al<sup>3+</sup> or Fe<sup>3+</sup>-species generates a positive charge deficiency in the tetrahedral sheet, which must be counterbalanced by the insertion of alkaline, alkaline-earth cations, or even the H<sup>+</sup>-species in the interlayer sheets of the TOT structure. Thus, a charge deficiency of 0.2–0.6 e-/unit cell leads to phyllosilicates coming from the smectite group while a charge deficiency of 0.6–0.9 e-/unit cell forms phyllosilicates of the vermiculite group (Figure 2D). In both cases, the basal spacing increases until 1.4 nm as a consequence of the hydration sphere that displays the cations located in the interlayer spacing. The existence of these interlayer cations weakens the interaction between adjacent TOT in a such a way that these cations can be replaced by other ones, even bulkier, or by organic molecules, causing an increasing of the basal spacing and subsequent swelling of the clays. This property provides high versatility to these phyllosilicates for a wide range of applications in the adsorption field. By contrast, phyllosilicates whose cations are located in the interlaminar spacing lack the expansion capacity give rise to more rigid structures belonging to the group of micas (Figure 2C). The incorporation of a brucite-like layer between adjacent TOT sheets leads to another phyllosilicate group denoted as chlorites, which presents a basal spacing of 1.4 nm (Figure 2E).

Both the sepiolite and palygorskite are considered phyllosilicates with peculiar characteristics since the T sheet is extended along the *a*,*b* plane (Figure 2F,G), while the octahedral layer is periodically inverted, giving rise to a fibrous structure with nanochannels.



**Figure 2.** Chemical structure of the kaolinite and serpentine group (**A**); talc and pyrophyllite group (**B**); mica groups (**C**); smectite and vermiculite group (**D**); chlorite group (**E**); sepiolite (**F**) and palygorskite (**G**).

## 3. CO<sub>2</sub> Adsorption

#### 3.1. CO<sub>2</sub> Adsorption in Raw Clay Minerals

Several authors have reported the  $CO_2$  adsorption capacity by raw clay minerals (Table 1). In order to compare the  $CO_2$  adsorption capacity of different phyllosilicates, environmental effects should be considered. Thus, clay minerals and the genesis conditions change in such a way each material displays an inherent chemical composition and specific textural properties, which supposes different adsorption capacity. The use of raw kaolinite was hardly reported in the literature owing to its very low adsorption capacity, only 3 mg  $CO_2/g$ . These authors established that the basal spacing does not undergo modifications after the adsorption process. This fact indicates that the  $CO_2$  molecules are adsorbed on the external surface of the kaolinite, discarding the  $CO_2$  adsorption between the TO layers [22,23]. They have supposed that the  $CO_2$  molecules, leading to –the  $HCO_3^-$  species, although its low specific surface area limits its detection [23].

The use of smectites has also been reported to retain  $CO_2$  in the literature. As was indicated previously, smectites display a great capacity to host molecules, even bulky ones. Similar to kaolinite, smectites also display a low  $CO_2$  adsorption capacity (5–6 mg  $CO_2/g$ ) at low temperature (25 °C) and under 1 bar of pressure [24,25]. Similar results were obtained by Gómez-Pozuelo et al. (2019) [26] for bentonite, montmorillonite and saponite, where a  $CO_2$  adsorption capacity between 10–15 mg  $CO_2/g$  at 45 °C and under 1 bar of pressure was indicated. However, these authors were not able to establish a correlation between the textural properties and the  $CO_2$  adsorption capacity [26] while Stevens et al. (2013) [27] have reached an adsorption of 22 mg  $CO_2/g$  for a raw montmorillonite at 100 °C and under 1 bar of pressure. On the other hand, Vilarrasa-García et al. (2017) [28] used solid wastes obtained during the flocculation of a drinking water treatment plant, mainly smectite, which were valorized as absorbent in  $CO_2$  capture processes, reaching a  $CO_2$  adsorption capacity of 7 mg  $CO_2/g$  at 25 °C and 1 bar of pressure. These wastes also showed a high efficiency to retain  $CO_2$  in  $CO_2/N_2$  separation processes.

Several authors have proposed that smectites can adsorb the  $CO_2$  molecules on its interlayer region, causing an increase of its spacing that change depending on the degree of the cation hydration, located in this spacing to counterbalance the charges of the phyllosilicate as well as the adsorption pressure [29,30]. Giesting et al. (2012) [31] have reported that the incorporation of  $CO_2$  in the interlayer space of smectites can expand around 9% with low proportions of  $H_2O$ , which are present in that

spacing (Figure 3). However, the hydration sphere of the located cation must be modulated since a high relative humidity hinders the access of  $CO_2$  molecules within the interlayer spacing [32]. Furthermore, several authors have reported that the interlaminar cation plays an important role in the adsorption of  $CO_2$  since it is directly related to hydration energies of the cation [33,34]. The analysis of  $CH_4/CO_2$  mixtures have revealed that the  $CO_2$  adsorption is selective, due to the strong affinity between the  $CO_2$  molecules and the solvated cations situated in the interlayer spacing [35–37].



Figure 3. CO<sub>2</sub> adsorption on the interlayer spacing of a smectite under supercritical conditions.

The mechanism of the CO<sub>2</sub> adsorption on mica have been also reported in the literature by many authors [38–40]. In all cases, the CO<sub>2</sub> adsorbed through a reaction between the CO<sub>2</sub> molecules and –OH groups of the mica form the –HCO<sub>3</sub><sup>-</sup>-species, which in turn can react with other CO<sub>2</sub> molecules as well as cations located in the layer of the mica [38–40]. Although the CO<sub>2</sub> adsorption is very low, an increase of the pressure can improve the CO<sub>2</sub> adsorption capacity. For fibrous phyllosilicates, such as the sepiolite and palygorskite, the periodic inversion of the tetrahedral sheet generates nanocavities of 0.37 nm × 1.06 nm for sepiolite and 0.37 nm × 0.64 nm for palygorskite. These nanochannels host cations to counterbalance the charge deficiency of the sheets and zeolitic water (Figure 2F,G) [41].Furthermore, these fibrous phyllosilicates can act as a molecular sieve, as takes place in zeolites or in activated carbons, where their channels have appropriate dimensions to retain CO<sub>2</sub> molecules by electrostatic interactions. Thus, Cecilia et al. (2018) [42] have reported a CO<sub>2</sub> adsorption of 65 mg CO<sub>2</sub>/g for sepiolite and 18 mg CO<sub>2</sub>/g for palygorskite at 25 °C and under 1 bar. Similar results were found by Gómez-Pozuelo et al. (2019) [26], where the CO<sub>2</sub> adsorption reached 41 mg CO<sub>2</sub>/g for sepiolite and 12 mg CO<sub>2</sub>/g for palygorskite at 45 °C and 1 bar, or those indicated by Jeon et al. (2014) [43], with a maximum CO<sub>2</sub> adsorption capacity of 137 mg CO<sub>2</sub>/g for the sepiolite under supercritical conditions.

To sum up, temperature plays an important role in the  $CO_2$  adsorption capacity. Thus, it has been reported that the adsorption capacity decreases with temperature, due to the physical interactions of adsorbate-adsorbent, generated by van Der Waals forces, are disfavored with the temperature. Therefore, the adsorption capacity is enhanced at low temperatures [23].

Clay Mineral	CO <sub>2</sub> Adsorption Capacity (mg CO <sub>2</sub> /g) Adsorption Conditio		Ref.
Kaolinite	3	25 °C, 1 bar	[22]
Kaolinite	0	25 °C, 1 bar	[23]
Bentonite	6	25 °C, 1 bar	[24]
Bentonite	5	25 °C, 1 bar	[25]
Bentonite	14	45 °C, 1 bar	[26]
Montmorillonite	10	45 °C, 1 bar	[26]
Montmorillonite	7	25 °C, 1 bar	[28]
Montmorillonite	22	10 °C, 1 bar, 90 min	[27]
Saponite	15	45 °C, 1 bar	[26]
Sepiolite	41	45 °C, 1 bar	[26]
Sepiolite	65	25 °C, 1 bar	[42]
Sepiolite	137	25 °C, 120 bar	[43]
Palygorskite	12	45 °C, 1 bar	[26]
Palygorskite	18	25 °C, 1 bar	[42]

**Table 1.** CO<sub>2</sub> adsorption capacity of raw clay minerals.

## 3.2. CO<sub>2</sub> Adsorption in Clay Minerals Activated by Acid Treatment

With the exception of sepiolite, the phyllosilicates reach a lower  $CO_2$  adsorption capacity than other porous materials such as porous silicas, zeolites or activated carbons. In order to increase the adsorption capacity of these inexpensive materials, the scientific community has developed various strategies to improve the adsorption capacity. Among them, the activation of clay minerals by acid treatment is the easiest and fastest treatment to increase the porosity as a result of partial leaching of the phyllosilicate framework [44]. The activation of phyllosilicates by an acid treatment is a methodology that was first described by Osthaus et al. [45,46] in the 50s. However, this cheap technology had not been applied to  $CO_2$  capture processes until the last decade (Table 2).

The efficiency of the acid treatment can be improved by using the microwave-assisted radiation, since it is possible to increase the specific surface area of the clay minerals using shorter treatment times and more diluted acid solutions [47,48]. These authors confirmed that the increase of the surface area is ascribed to the partial solution of the octahedral sheet. In this sense, the microwave-assisted acid treatment revealed to be more efficient for the trioctahedral smectites and fibrous silicates, which present a high proportion of Mg-species in the octahedral sheet. However, the dioctahedral smectites, whose octahedral sheet contains a greater proportion of the Al-species, are less prone to its modification due to its partial leaching (Figure 4A) [48]. These conclusions are in agreement with those reported previously by Venaruzzo et al. (2002) [49], where the acid treatment causes a loss of the cations located in the interlayer spacing, as well as the cations located in the octahedral sheet, following the order  $Mg^{2+} > Fe^{2+/3+} > Al^{3+}$  [48]. These authors observed a CO<sub>2</sub> adsorption in the range of 9–24 mg CO<sub>2</sub>/g.



**Figure 4.** Modification of smectites through several treatments: (**A**) Acid treatment; (**B**) intercalation of organic compounds to form organoclays; (**C**) pillared clays (PILCs) and (**D**) porous clay heterostructures (PCHs).

As previously described, the acid treatment increases the textural properties of the clay minerals such as the pore size and the pore volume; however, this process is not always beneficial to improve the  $CO_2$  adsorption capacity. In fact, Cecilia et al. (2018) [42] have reported that 8 min of microwave-assisted acid treatment, rises up the  $S_{BET}$  value from  $182 \text{ m}^2/\text{g}$  to  $326 \text{ m}^2/\text{g}$ , although the  $CO_2$  adsorption capacity reduces from 65 mg  $CO_2/\text{g}$  to 41 mg  $CO_2/\text{g}$  at 25 °C and under 1 bar [41]. This decay is ascribed to the partial digestion of the octahedral layer, which causes an increase in the dimensions of the nanocavities, so that the  $CO_2$  efficiency of these clay minerals impoverishes as a molecular sieve [41]. The decay of the  $CO_2$  adsorption capacity of these clay minerals treated by acid solutions can also be assigned to the loss of the cations located in the nanocavities, which interact with the  $CO_2$  molecules, as was observed previously for smectites [31]. In any case, the growth of the porosity by the acid treatment provides a great potential of these materials to host target molecules, which enhances the chemical interaction between the adsorbent and  $CO_2$  molecules.

Clay Mineral	CO <sub>2</sub> Adsorption Capacity (mg CO <sub>2</sub> /g)	Adsorption Conditions	Ref.
Kaolinite	3	25 °C, 1 bar	[23]
Bentonite	9	25 °C, 1 bar	[47]
Bentonite	24	25 °C, 1 bar	[49]
Sepiolite	41	25 °C, 1 bar	[42]
Palygorskite	43	25 °C, 1 bar	[42]

Table 2. CO<sub>2</sub> adsorption capacity of activated clay through acid treatments.

## 3.3. CO<sub>2</sub> Adsorption in Organoclays

As indicated above, the interaction between of the adjacent TOT structures are too weak to host organic compounds in the interlaminar spacing. This fact implies an increase in the basal spacing and a swelling of the smectites (Figure 4B). The design and synthesis of these organoclays displayed a wide range of applications in adsorption processes [50], and they had also been used for CO<sub>2</sub> adsorption processes in the last years (Table 3). Thus, Azzouz et al. (2009) [51] confirmed the intercalation of several polyol compounds in the interlayer spacing by XRD. These authors also observed an increase of the reversible retention capacity of CO<sub>2</sub> after the intercalation of polyols-species as a consequence of an interaction between the weak base -OH sites and the CO<sub>2</sub> molecules, reaching a maximum adsorption capacity of 110 mg CO<sub>2</sub>/g [51–53].

Other authors have inserted a cationic amine-rich dendrimer in laponite, as polyamidoamine (PAMAM) in the interlayer spacing, obtaining a maximum  $CO_2$  adsorption of 36.4 mg  $CO_2/g$  [54]. These authors have pointed out that the organoclays present three adsorption sites; two of them are attributed to the clay layers (internal binding unit and external binding unit) and the third adsorption site attributed to the availability of the dendrimer sites, which grows directly with the amount of intercalated-dendrimer (Figure 5). These sites are the most determining since the  $CO_2$  adsorption capacity increases directly with the amount of the intercalated-dendrimer as a consequence of the strong affinity between the dendrimer and the  $CO_2$  molecules [54]. In the same way, Shah et al. (2017) [55] have also intercalated the poly (amido amine) dendrimer in a mica and a montmorillonite, being efficient only in the latter case. The presence of the dendrimer and  $CO_2$  also increases, so that the regeneration of the adsorbent requires more severe conditions [55,56].



Figure 5. Scheme of the CO<sub>2</sub> adsorption on the raw smectite and dendrimer-loaded organoclays.

Clay Mineral	Organic Compound Intercalated	CO <sub>2</sub> Adsorption Capacity (mg CO <sub>2</sub> /g)	Adsorption Conditions	Ref.
Montmorillonite	Polyols	110	25 °C, 1 bar	[51]
Laponite	PAMAN	36	25 °C, 1 bar	[54]
Montmorillonite	Polyamido amine	20	40 °C, 1 bar	[56]

**Table 3.** CO<sub>2</sub> adsorption capacity of the activated clay through acid treatments.

#### 3.4. CO<sub>2</sub> Adsorption of Materials Synthesized from Clay Minerals

Clay minerals are inexpensive materials with high potential to synthesize other adsorbents having much  $CO_2$  adsorption capacity than that shown for the raw phyllosilicate. Several studies described the synthesis of zeolites from clay minerals [57]. These materials present a high potential for the  $CO_2$  adsorption since the cage of zeolites can display appropriate dimensions to capture the  $CO_2$  molecules through quadrupole interactions (Table 4). The  $CO_2$  adsorption capacity is directly related to the synthetic parameters, which highly influence the cage dimensions and the crystallinity of the obtained zeolites.

In all cases, the zeolites require Al-rich clays, which are treated in a strong basic medium, under hydrothermal conditions. Thus, the kaolinite and bentonite were chosen to synthesize 13X zeolites under hydrothermal conditions in a basic medium [58,59]. Authors observed an increase of the surface area, with a maximum  $S_{BET}$  value of 876 m<sup>2</sup>/g, being highly microporous in all cases, which provides excellent properties as a molecular sieve to capture CO<sub>2</sub>, obtaining an adsorption close to 211 mg CO<sub>2</sub>/g at 25 °C and under 1 bar [58]. In the same way, clay minerals have also been used as starting materials to synthesize zeolites type A from kaolinite, obtaining a CO<sub>2</sub> adsorption capacity of 0.46 mg CO<sub>2</sub>/g zeolite after only 77 s [60]. Pour et al. (2016) [61] also synthesized A-zeolite, using a montmorillonite as a starting clay, reaching an excellent CO<sub>2</sub> adsorption of about 220 mg CO<sub>2</sub>/g, with a high selectivity in mixtures of CO<sub>2</sub>/CH<sub>4</sub> at 1 bar of pressure, although an increase of the pressure causes a decrease of the selective adsorption. On the other hand, kaolinite has been also used as a starting material to obtain a microporous Y-zeolite, obtaining zeolite with a high CO<sub>2</sub> adsorption capacity (138 mg CO<sub>2</sub>/g at 0 °C and a pressure of 1 bar) [62]. In the same way, Thakkar et al. (2017) [63] synthesized several zeolites from kaolinite, reaching a CO<sub>2</sub> adsorption of 13 mg CO<sub>2</sub>/g for ZSM-5, 40 mg CO<sub>2</sub>/g for Y-zeolite and 26 mg CO<sub>2</sub>/g for SAPO-34.

In another study, a kaolinite was mixed with limestone, and then it was undergone to a strong basic medium under hydrothermal conditions, obtaining a mixture of gehlenite (Ca<sub>2</sub> Al(Al<sub>1.22</sub>Si<sub>0.78</sub>O<sub>6.78</sub>)OH<sub>0.22</sub>) and stilbite (Na<sub>5.76</sub>Ca<sub>4.96</sub>(Al<sub>15.68</sub>Si<sub>56.32</sub>O<sub>144</sub>)). This adsorbent displays a low S<sub>BET</sub> value, in spite of its high microporisity and its interesting CO<sub>2</sub> adsorption capacity of 245 mg CO<sub>2</sub>/g at 150 °C and under 45 bar [64].

The smectites can also insert pillars between adjacent sheets, causing an increase of the pore volume and pore size. The synthesis of the pillared clays was first described by Barrer and MacLeod in 1955 [65], by the insertion of a bulky polyoxocation and subsequent calcination (Figure 4C). Since these pillared clays (PILCs) have been highly studied in catalytic and adsorption processes. With regard to its application in CO<sub>2</sub> adsorption processes, Gil et al. (2007) [66], inserted the Keggin polycation,  $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ , in the interlayer spacing of the montmorillonite and saponite, which leads to Al<sub>2</sub>O<sub>3</sub> pillars after its calcination and an increase of the surface area and porosity in both cases. The analysis of the  $CO_2$  adsorption capacity of these materials reveals a value of 57 mg  $CO_2$ /g for the pillared saponite and 48 mg  $CO_2/g$  for the pillared montmorillonite at 0 °C and under 1 bar of pressure. Wang et al. (2018) [67] incorporated pillars of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub>/SiO<sub>2</sub> between adjacent layers of montmorillonte, generating an increase of the SBET value in comparison to the raw bentonite, reaching a highest surface area of 437  $m^2/g$  for the montmorillonite with TiO<sub>2</sub>/SiO<sub>2</sub> pillars. These authors reported that the CO<sub>2</sub> adsorption capacity is directly related with the S<sub>BET</sub> values and mainly with the pore volume, attaining a maximum  $CO_2$  adsorption of 52 mg  $CO_2/g$  at 25 °C and under 1 bar of pressure in the case of the montmorillonite with TiO<sub>2</sub>/SiO<sub>2</sub>. The increase of the CO<sub>2</sub> adsorption is due to an increase of the microporosity of the material since the formation of pillars causes a random displacement of the sheets, which supposes the formation of a "house of cards" structure with a high microporisity after the pillar formation.

Porous clay heterostructures (PCHs) have also emerged as potential materials for the  $CO_2$  adsorption due to their high specific surface area, pore volume and high thermochemical stability. The synthesis of the PCH was firstly described by Galarneau et al. (1995) [68], using smectites as starting materials. In a first step, the cation, located in the interlayer space, is exchanged by a bulkier

one (alkylammonium cation). Then, silicon alkoxide is hydrolized to form SiO<sub>2</sub> around the bulky cation. Finally, the material is calcined to remove the organic cation, forming a material with a high micro and meso-porosity (Figure 4D). Thereby, the high microporosity provides to these materials interesting applications as a molecular sieve to adsorb and separate small molecules as CO<sub>2</sub>. In this regard, Vilarrasa-García et al. (2017) [25] synthesized a PCH with a S<sub>BET</sub> value of 640 m<sup>2</sup>/g and a high microporosity, as indicated in the *t*-plot data (376 m<sup>2</sup>/g). These textural properties supposed a CO<sub>2</sub> adsorption capacity of 28 mg CO<sub>2</sub>/g at 25 °C and under 1 bar of pressure. In addition, the presence of mesoporosity allows hosting target molecules, which can favor a chemical interaction between the adsorbent and the CO<sub>2</sub> molecules, leading to an increase of the CO<sub>2</sub> adsorption capacity [25]. In the same way, these authors pointed out that the pillaring of the wastes obtained from the flocculation of the drink water treatment with SiO<sub>2</sub> also enhances the CO<sub>2</sub> adsorption from 7 mg CO<sub>2</sub>/g to 22 mg CO<sub>2</sub>/g, as a consequence of an increase of the microporosity of the adsorbent [28].

Clay Mineral	Porous Material Synthesized	CO <sub>2</sub> Adsorption Capacity (mg CO <sub>2</sub> /g)	Adsorption Conditions	Ref.
Bentonite	Zeolite 13X	211	25 °C, 1 bar	[58]
Kaolinite	Zeolite A	0.46	25 °C, 1 bar, 77 s	[60]
Kaolinite	ZSM-5	13	25 °C, 1 bar	[63]
Kaolinite	Zeolite A	40	25 °C, 1 bar	[63]
Kaolinite	SAPO-34	26	25 °C, 1 bar	[63]
Kaolinite	Zeolite Y	130	0 °C, 1 bar	[62]
Kaolinite/limestone	Gehlenite/Stilbite	295	100 °C, 45 bar	[64]
Montmorillonite	Zeolite A	220	25 °C, 1 bar	[61]
Montmorillonite	Pillared clays (PILCs)	57	0 °C, 1 bar	[66]
Saponite	Pillared clays (PILCs)	48	0 °C, 1 bar	[66]
Montmorillonite	Pillared clays (PILCs)	52	25 °C, 1 bar	[67]
Montmorillonite	Porous clay heterostructure (PCH)	28	25 °C, 1 bar	[25]
Montmorillonite	Porous clay heterostructure (PCH)	22	25 °C, 1 bar	[28]

Table 4. CO<sub>2</sub> adsorption of the porous materials synthesized from clay minerals.

# 3.5. Clay Minerals Modified with Amino Groups Applied in CO<sub>2</sub> Adsorption Processes

Generally, clay minerals reach low CO<sub>2</sub> adsorption values in comparison to other adsorbents as activated carbon or zeolites; however, the high availability and low price of the clays provide a great potential to be used as an adsorbent in  $CO_2$  capture processes. The  $CO_2$  adsorption capacity can be improved by the incorporation of amine-species on its surface, which favors the chemical interactions with the  $CO_2$  molecules. Several methodologies have been described to incorporate the amine-species such as the functionalization by grafting and the impregnation with an amine-rich polymer. The most common mechanism for the  $CO_2$  capture in adsorbents functionalized with amino groups involves the formation of a zwitterion [69,70] through the interaction of CO<sub>2</sub> with an amine (primary or secondary), followed by deprotonation of zwitterion by a base to produce a carbamate (Reaction (1)) [71–74]. The tertiary amines react with the  $CO_2$ , giving rise to the bicarbonate, but it's not possible to form carbamate [75,76]. The efficiency, defined as the mol of  $CO_2$  captured per mol of nitrogen in the material, is a useful measure to quantify the effectiveness of the N-species of adsorbents for the  $CO_2$ capture. In the "zwitterionic" mechanism, under anhydrous conditions, a second amine acts as a base to produce an ammonium carbamate (Reactions (2) and (3)), giving a theoretical maximum efficiency of 0.5. This suggests that obtaining materials with a high density of amines, close to each other, can improve the efficiency of the capture.

Under moisture conditions, water or hydroxide ions can act as a base, leading to theoretical amine efficiencies approaching to the unity. Currently, it has been proposed a second mechanism [74], where an ammonium bicarbonate specie is formed under moist conditions, which also display a

theoretical amine efficiency of one. In all cases, it is expected that amine efficiency values are lower than the theoretical ones at low partial pressures of  $CO_2$ , as a consequence of kinetic limitations and equilibrium conditions.

$$R_1 R_2 NH + CO_2 \rightarrow R_1 R_2 NH^+ COO^- (Zwitterion)$$
(1)

$$R_1 R_2 NH^+ COO^- \rightarrow R_1 R_2 NCOO^- \text{ (Carbamate)} R_1 R_2 NH_2^+ \tag{2}$$

The overall reaction is:

$$R_1R_2NH + CO_2 \rightarrow R_1R_2NCOO^- + R_1R_2NH_2^+$$
 (3)

Under the presence of water, the overall reaction is:

$$R_1R_2NH + CO_2 + H_2O \rightarrow R_1R_2NH_2^+HCO_3^- (Bicarbonate) \rightarrow R_1R_2NH_2^+HCO_3^{2-} (Carbonate)$$
(4)

It can be observed how the  $CO_2$  adsorption leads to the formation of a zwitterion. A deprotonation may take place, due to a base to produce a carbamate (Reaction (4)) [69,72].

The efficiency of the  $CO_2$  adsorption with the N-species is defined as the molar ration between the  $CO_2$  adsorbed and the N-species of the adsorbent. Under anhydrous conditions, a second amine typically acts as the base to produce an ammonium carbamate, with a theoretical N-efficiency of 0.5.

## 3.5.1. Functionalization of Clay Minerals by Grafting

The functionalization with the amine-species by grafting, is carried out through a chemical reaction between the available silanol groups and an amine-alkoxisilane compound. The incorporation of the amine-species on the surface of the adsorbent by a chemical interaction, provides a high thermochemical stability for these amine-based materials. The methodology used for the grafting was widely described to functionalize porous silica [12], although, in recent years, the functionalization by grafting was also employed by the incorporation of the amine-species on clay minerals due to the presence of silanol groups in the sheets as well as in the pillared structures (Figure 6). These data are compiled in Table 5.



Figure 6. Mechanism proposed for the  $CO_2$  adsorption in clay minerals grafted with APTES.

The first study was performed by Stevens et al. (2013) [27], which exfoliated a montmorillonite by the cationic exchange of Na<sup>+</sup> by hexadecyltrimethylammonium cations (HDM–NH<sub>4</sub><sup>+</sup>). This fact implied an increase of the availability of the silanol groups to increase the efficiency of the grafting process. Then, the exfoliated montmorillonite was grafted with N-2-aminoethyl-3- aminopropyltrimethoxysilane (AEAPTS). The CO<sub>2</sub> adsorption increases from 22 mg CO<sub>2</sub>/g for the raw montmorillonite to 77 mg CO<sub>2</sub>/g for the unexfoliated montmorillonite grafted with AEAPTS. The exfoliation improved the efficiency of the adsorption process since the N-content is similar with and without the exfoliation, although the CO<sub>2</sub> adsorption increased to 105 mg CO<sub>2</sub>/g at after 90 min at 100 °C and 1 bar of

pressure [27]. Later, Vilarrasa-García et al. (2017) [25] enhanced the CO<sub>2</sub> adsorption of a raw bentonite from 5 mg CO<sub>2</sub>/g to 11 mg CO<sub>2</sub>/g after the pillaring process to form the PCH. This grafting with 3-aminopropyltriethoxysilane (APTES) raised noticeably led to materials with an N content between 1.5% to 3.6% of N. This fact supposed a noticeable increase of the CO<sub>2</sub> adsorption capacity up to 50 mg CO<sub>2</sub>/g at 25 °C and 1 bar of pressure [25]. These data were similar to those reported for solid wastes obtained in the flocculation step of a drinking water treatment plant, where they were used as starting materials and then were pillared to form their respective PCH [28].

In the case of the fibrous clay minerals (sepiolite and palygorskite), the grafting with APTES does not improve the CO<sub>2</sub> capacity of the sepiolite, because of the nanochannels that are partially occluded in the grafting steps, in such a way that the CO<sub>2</sub> adsorption only reaches a value of 44 mg CO<sub>2</sub>/g at 25 °C and under 1 bar of pressure [26,42]. However, the grafting seems to enhance the adsorption of the palygorskite, since the CO<sub>2</sub> adsorption increases from 18 mg CO<sub>2</sub>/g to 33 mg CO<sub>2</sub>/g at 25 °C and under a pressure of 1 bar [42]. Similar results were recently reported by Gómez-Pozuelo et al. (2019) [26] in bentonite, montmorillonite, saponite, palygorkite and sepiolite functionalized by grafting with the 3-aminopropyltriethoxysilane and N1-(3-trimethoxysilylpropyl) diethylenetriamine) (TMSPDEA) [26], reaching a CO<sub>2</sub> adsorption between 32 mg CO<sub>2</sub>/g and 61 mg CO<sub>2</sub>/g at 45 °C and under 1 bar. While Ouyang et al. (2018) [77] have undergone a sepiolite to acid treatment to raise its porosity, and then they grafted APTES through a similar synthetic procedure, obtaining a CO<sub>2</sub> adsorption of 121 mg CO<sub>2</sub>/g after 120 min at 70 °C and 1 bar.

Halloysite is a cylindrical phyllosilicate structure, whose wall thickness is 10–15 atomic alumosilicate sheets with an outer diameter of 50–60 nm, an inner diameter of 12–15 nm, and a length of 0.5–10 m [21]. As occurs in other clay minerals, the presence of silanol groups in the cylindrical structure favors the grafting of the APTES molecules. Thus, Jana et al., (2015) [78] grafted APTES on the surface of the halloysite to obtain a material, with an adsorption amount of 5 mg  $CO_2/g$  at 85 °C and under 1 bar.

The  $CO_2$  adsorption in clay minerals takes place by physical interaction. These clays act as molecular sieves. However, the incorporation of amine species by a grafting process causes a decrease of the surface area and pore volume, although these materials can still act as molecular sieves. Thus, the coexistence of porosity and available N-sites leads to adsorbents where the physical and chemical interaction sites coexist. In this sense, Vilarrasa-García et al. (2017) [25] considered the existence of two adsorption sites (physical and chemical interactions) in clays, following the same methodology that was described for porous silicas previously [9]. The isotherms confirmed the coexistence of both adsorption sites. In fact, the modification of the adsorption temperature barely modifies the  $CO_2$  uptakes as a consequence of the antagonistic response of both adsorption sites. Thus, the efficiency of physical adsorption diminishes when the adsorption temperature increases, while the efficiency of the chemical sites improve with the adsorption temperature. However, Stevens et al. (2013) [27] observed a different behavior when the temperature was modified, the  $CO_2$  adsorption remarkably raised for higher adsorption temperatures probably due to the chemical sites are predominant in comparison to the physical sites since the N content was higher (10.9%) while the N-content shown by Vilarrasa-García et al. (2017) [25] did not exceed 5% in any case.

In the case of the montmorillonite or PCHs grafted with amine species, the N-efficiency is mainly in the range of 0.35-0.45 in anhydrous conditions [26,42], so it is slightly lower than the theoretical values (0.5), probably due to the side condensation reactions in the grafting step, which generate secondary and ternary amines, which are less prone to capture CO<sub>2</sub> molecules.

In order to simulate the flue gas conditions, several authors have worked with  $CO_2/N_2$  mixtures to evaluate the efficiency of the separation. It has been reported that the incorporation of the amine-species by grafting enhances the  $CO_2$  adsorption selectivity, since the  $N_2$  molecules present a low quadrupole moment. This fact supposes that the N<sub>2</sub>-adsorption can be considered negligible in comparison with the one of the  $CO_2$  [27,28].

Clay Mineral	Amine Grafted	CO <sub>2</sub> Adsorption Capacity (mg CO <sub>2</sub> /g)	Adsorption Conditions	Ref.
Bentonite	APTES	43	45 °C, 1 bar	[26]
Bentonite	TMSPDEA	32	45 °C, 1 bar	[26]
Montmorillonite	APTES	33	45 °C, 1 bar	[64]
Montmorillonite	TMSPDEA	50	45 °C, 1 bar	[26]
Montmorillonite	AEAPTS	77	100 °C, 1 bar, 90 min	[27]
Exfoliated-montmorillonite	AEAPTS	105	100 °C, 1 bar, 90 min	[27]
Saponite	APTES	35	45 °C, 1 bar	[26]
Saponite	TMSPDEA	39	45 °C, 1 bar	[26]
Porous clay heterostructure from montmorillonite	APTES	50	25 °C, 1 bar	[25]
Porous clay heterostructure from montmorillonite	APTES	48	25 °C, 1 bar	[28]
Sepiolite	APTES	44	25 °C, 1 bar	[42]
Sepiolite	APTES	121	70 °C, 1 bar, 120 min	[77]
Sepiolite	APTES	44	45 °C, 1 bar	[26]
Sepiolite	TMSPDEA	61	45 °C, 1 bar	[26]
Palygorskite	APTES	33	25 °C, 1 bar	[42]
Palygorskite	APTES	38	45 °C, 1 bar	[26]
Palygorskite	TMSPDEA	57	45 °C, 1 bar	[26]
Halloysite	APTES	5	85 °C, 1 bar	[33]

**Table 5.** CO<sub>2</sub> adsorption capacity of clay minerals functionalized with amine groups by grafting.

## 3.5.2. Functionalization of Clay Minerals by Impregnation

The impregnation of clay mineral with an amine-rich polymer is another alternative to disperse a high amount of the amine-species on the surface of adsorbents. This methodology has been widely described for porous silicas or zeolites and, in recent years, clay minerals have also been used as supports to disperse these amine-rich polymers (Table 6). In all cases, a large amount of the amine-rich polymer is impregnated and stabilized by the support through electrostatic interactions, mainly hydrogen bonds (Figure 7).



Increase of the amine loading

**Figure 7.** Scheme of the pore blocking process in a clay mineral by an amine-rich polymer. (I) Surface area reduction due to micropores blocking; (II) surface area reduction due to pore necks blocking; (III) multiple-layer amine-rich polymer film and (IV) clay mineral particle covered by the amine-rich polymer.

An untreated kaolinite has been used as support to disperse monoethanolamine (MEA), ethylenediamine (EDA) and a mixture of both (4MEA + 1EDA) [22], obtaining a composite similar to the one indicated below.

$$Si-OH + R-NH_2 \rightarrow SiO^- N^+H_3-R \tag{5}$$

The impregnation of a large amount of these amine-compounds (50 wt.%) improves the CO<sub>2</sub> adsorption capacity in comparison to the raw kaolinite as a consequence of a chemical interaction on the surface of the adsorbent, reaching a maximum value of 60 mg CO<sub>2</sub>/g for the EDA-kaolinite, 129 mg CO<sub>2</sub>/g for the MEA-kaolinite and 149 mg CO<sub>2</sub>/g, for the 4MEA + 1EDA-kaolinite, which is the highest one. In order to increase the CO<sub>2</sub> adsorption capacity, a kaolinite was treated to synthesize several zeolites (ZSM-5, Y-zeolite and SAPO-34), that were later impregnated with tetraethylenepentamine (TEPA), between 5–20 wt.%. The adsorption data revealed that the CO<sub>2</sub> capture diminished for those zeolites with lower pore volume after their impregnation (ZSM-5 and SAPO-34). However, zeolites with bigger channels increased the CO<sub>2</sub> adsorption from 40 mg CO<sub>2</sub>/g to 50 mg CO<sub>2</sub>/g [63].

Several bentonites were treated with several cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup>) to obtain the homoionic cation. Then, they were impregnated with monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). The Mg-bentonite impregnated with amine reaches the maximum CO<sub>2</sub> adsorption values, increasing from 37mg CO<sub>2</sub>/g for the raw bentonite to 129 mg CO<sub>2</sub>/g for the MEA<sup>+</sup>-Mg-bentonite, 125 mg CO<sub>2</sub>/g for the DEA<sup>+</sup>-Mg-bentonite and 114 mg CO<sub>2</sub>/g for the TEA<sup>+</sup>-Mg-bentonite [79]. In addition, these authors reported that the MEA<sup>+</sup>-Mg-bentonite composite displays a high affinity to adsorb the CO<sub>2</sub> molecules over the N<sub>2</sub> and CH<sub>4</sub> due to its higher quadrupolar moment in comparison with other molecules, which favors an electrostatic interaction between CO<sub>2</sub> and the MEA<sup>+</sup>-Mg-bentonite [80]. In another research, Atilhan et al. (2016) [81] impregnated the montmorillonite K-10 with dimethyl dialkyl (C14C18) amine (35–45 wt.%) (DMDAA), obtaining a CO<sub>2</sub> capture of 211 mg CO<sub>2</sub>/g at 25 °C and under 50 bar of pressure.

Chen et al. (2013) [24] modified a bentonite with a branched polyethylenimine (PEI), obtaining a composite that increased the CO<sub>2</sub> adsorption from 6 mg CO<sub>2</sub>/g to 47 mg CO<sub>2</sub>/g at 75  $^{\circ}$ C and under atmospheric pressure owing to a chemical interaction between the amine species and CO<sub>2</sub> molecules. Similar results were obtained by Gómez-Pozuelo et al. (2019) [26]. These authors impregnated bentonite, montmorillonite and saponite with 37 wt.% of PEI, obtaining 46 mg CO<sub>2</sub>/g for the Bent-PEI, 60 mg CO<sub>2</sub>/g for the Mont-PEI and 67 mg CO<sub>2</sub>/g for the Sap-PEI as a value of the CO<sub>2</sub> adsorption at 45 °C and under 1 bar [26]. In order to increase the dispersion of the amine-species, Wang et al. (2018) [82] modify a montmorillonite wit acid treatment to obtain materials with an important value of the S<sub>BET</sub> and pore volume, to be impregnated later, with a large amount of PEI, between 30–65 wt.%. The rise of the porosity of the montmorillonite favored the dispersion of the amine-rich polymer enhancing the amount of the available N-sites. This fact supposed an increase of the  $CO_2$  adsorption capacity, obtaining a maximum amount of 112 mg CO<sub>2</sub>/g at 75 °C and under atmospheric pressure, when the montmorillonite treated with acid was impregnated with 50 wt.% of PEI. Another study suggested to replace TEPA by PEI in a similar research, reaching a  $CO_2$  breakthrough sorption capacity of 130 mg CO<sub>2</sub>/g at 75 °C under dry conditions; however, these values were improved to 190 mg  $CO_2/g$  under wet conditions (18 vol% of moisture addition) [67] due to the formation of the bicarbonate species  $CO_2/N$ , as was indicated previously (Reactions (1)–(4)).

Vilarrasa-García et al. (2017) [25] synthesized a PCH from bentonite, in order to be impregnated with a different amount of PEI or TEPA. The textural properties revealed a drastic decrease of the  $S_{BET}$  and pore volume, although the CO<sub>2</sub> adsorption capacity raised remarkably, obtaining a 64 mg CO<sub>2</sub>/g for the PCH impregnated with 60 wt.% of PEI and 72 mg CO<sub>2</sub>/g for the PCH impregnated with 60 wt.% of TEPA at 25 °C and under atmospheric pressure. By applying the Dualsite Langmuir model, these authors also reported that the CO<sub>2</sub> adsorption predominantly takes place on the surface of the composite through chemical interactions between the amine groups and CO<sub>2</sub> molecules [25]. These authors obtained higher adsorption values when they synthesized a PCH from solid wastes, obtained in the flocculation step of a drinking water treatment plant (110 mg CO<sub>2</sub>/g at 25 °C and 1 bar), due to the presence of the montmorillonite, displaying a low crystallinity, which increases the macroporosity between adjacent particles. This fact favors the dispersion of the amine-rich polymer and the amount of the available N-sites [28].

In spite of the fibrous phyllosilicates, sepiolite has the highest  $CO_2$  adsorption capacity. These fibrous clay minerals were also impregnated with a large amount of the amine-rich polymer. Thus, both sepiolite and palygorskite were impregnated with 36 wt.% of PEI, reaching a CO<sub>2</sub> adsorption of 67 mg CO<sub>2</sub>/g and 56 mg CO<sub>2</sub>/g for Pal-PEI and Sep-PEI, respectively at 45 °C and atmospheric pressure [26]. In this sense, it is noticeable that the  $CO_2$  adsorption by the Sep-PEI is below than that data obtained for the raw sepiolite. Similar results were shown by Cecilia et al. (2018) [42], obtaining a CO<sub>2</sub> adsorption of 45 mg CO<sub>2</sub>/g for the sepiolite impregnated with 40 wt.% of PEI at 25 °C and under atmospheric pressure, while the  $CO_2$  adsorption for the raw sepiolite was 65 mg  $CO_2/g$ . The decrease of the adsorption capacity is attributed to the occlusion of nanocavities, which act as molecular sieves, by a large amount of amine-species. This fact supposes that the amine species are on the surface of the fibrous minerals and the adsorption only takes places chemically. Similar results were obtained by Irani et al. (2015) [83] for a sepiolite impregnated with TEPA, which reached the maximum  $CO_2$ capacity of 165 mg  $CO_2/g$  at 60 °C and under atmospheric pressure for the sepiolite impregnated with 60 wt.% of TEPA, maintaining its CO<sub>2</sub> adsorption capacity after 10 cycles. Generally, both the Sep-PEI and Sep-TEPA improved their CO<sub>2</sub> adsorption capacity with the increase of temperature. This fact is ascribed to a reordering of the stacked amine-rich polymer at a high temperature, which facilitates the diffusion of the  $CO_2$  molecules along the amino-rich polymer and also increases the amount of available amino groups involved in the  $CO_2$  adsorption [42,83]. In addition, it was reported that the presence of a small amount of water improved the  $CO_2$  adsorption capacity owing to the formation a bicarbonate-species, which enhance the CO<sub>2</sub>/N efficiency [83].

The acid treatment of the fibrous phyllosilicates causes a partial digestion of the Mg-species located in the octahedral sheet in sepiolite and palygorskite. This fact implies an increase of the porosity in this fibrous phyllosilicates and favors the dispersion of larger amount of amine-rich polymer. The impregnation of these modified enhanced the  $CO_2$  adsorption up to 109 mg  $CO_2/g$  at 75 °C and under atmospheric pressure [84]. However, other authors have reported that the acid treatment does not improve those data reported by the raw sepiolite and palygorskite due to chemical interaction is less favored at lower adsorption temperature [42]. On the other hand, other authors have pointed out that the sepiolite treated with an acid solution and then impregnated with 30 wt.% of triethylenetetramine (TETA) also exhibits an excellent  $CO_2$  adsorption capacity with a value of 85 mg  $CO_2/g$  at 50 °C and under atmospheric pressure [85]. These authors did not observe an improvement of the CO<sub>2</sub> adsorption with the temperature as a consequence of the amine lost from the composite during the vacuum degassing step [85]. Diethylenetriamine (DETA) has been another "basket molecule" incorporated to a sepiolite modified by acid treatment [86]. In all cases, the  $CO_2$  adsorption was higher than that obtained for the raw sepiolite, attaining a maximum adsorption value of 73 mg CO<sub>2</sub>/g. As takes place in other clay minerals impregnated with amine-rich polymers, this adsorbent can be easily regenerated and reused for several runs. An increase of the adsorption temperature improves its CO<sub>2</sub> adsorption capacity; however, a further increase in the temperature up to 80 °C causes a decrease of the  $CO_2$  capture, suggesting that the diffusion has less influence than the thermodynamic effects at higher adsorption temperatures, being the  $CO_2$  adsorption unfavorable under more severe adsorption conditions [86]. Ouyang et al. (2018) [77] reported a higher  $CO_2$  adsorption when TEPA was used (160 mg CO<sub>2</sub>/g after 120 min at 70 °C and under atmospheric pressure) instead of PEI. It has been reported that the TEPA molecule is less bulky than the PEI so the dispersion and reordering to enhance the amount of the available N-sites and facilitate the diffusion of the CO<sub>2</sub> molecules is easier when TEPA is impregnated due to its lower viscosity and the presence of a lower electrostatic interaction between these molecules and the support in comparison to the PEI [85]. In addition, the CO<sub>2</sub> adsorption of the sepiolite treated with acid and then impregnated with PEI or TEPA was highly selective to retain the  $CO_2$  molecules in  $CO_2/N_2$  mixtures [84].

Palygorskite was also modified by an acid treatment to increase its porosity and then it has been impregnated with amine-rich polymers. In this sense, Cecilia et al. (2018) [42] have observed a slight increase of the CO<sub>2</sub> adsorption capacity, attaining a maximum value of 32 mg CO<sub>2</sub>/g at 25 °C and

under atmospheric pressure for a palygorskite modified by microwave-assisted acid treatment and impregnated with PEI. However, Ouyang et al. (2018) [87] have reached higher adsorption values using a palygorskite treated with an acid solution and impregnated with TEPA reaching a  $CO_2$  adsorption capacity of 110 mg  $CO_2/g$  at 70 °C and under atmospheric pressure.

Halloysite nanotubes were also treated with an acid solution to improve its textural properties to then favor the dispersion of PEI, obtaining a nanocomposite whose  $CO_2$  adsorption capacity reaches 121 mg  $CO_2/g$  at 85 °C for 2 h [88]. The influence of the adsorption temperature follows the same trend to that observed for other clay minerals. Thus, the  $CO_2$  adsorption in clay-PEI is favored when the temperature increases, attaining a maximum value between 70–85 °C.

Clay Mineral	Amine-Rich Polymer	CO <sub>2</sub> Adsorption Capacity (mg CO <sub>2</sub> /g)	Adsorption Conditions	Ref.
Kaolinite	MEA + DEA	144	25 °C, 1 bar	[22]
ZSM-5 from kaolinite	TEPA	7	25 °C, 1 bar	[63]
Zeolite-Y from kaolinite	TEPA	50	25 °C, 1 bar	[63]
SAPO-34 from kaolinite	TEPA	23	25 °C, 1 bar	[63]
Bentonite	MEA	129	25 °C, 1 bar	[79]
Bentonite	DEA	125	25 °C, 1 bar	[79]
Bentonite	TEA	114	25 °C, 1 bar	[79]
Bentonite	PEI	46	45 °C, 1 bar	[26]
Bentonite modified by acid treatment	PEI	47	75 °C, 1 bar	[24]
Montmorillonite	PEI	60	45 °C, 1 bar	[26]
Montmorillonite	DMDAA	211	25 °C, 50 bar	[81]
Montmorillonite modified by acid treatment	PEI	112	70 °C, 1 bar	[67]
Montmorillonite modified by acid treatment	TEPA	136	70 °C, 1 bar	[67]
Montmorillonite modified by acid treatment	TEPA	190	70 °C, 1 bar, 18% moisture	[67]
Saponite	PEI	67	45 °C, 1 bar	[26]
Porous clay heterostructure from montmorillonite	PEI	64	25 °C, 1 bar	[25]
Porous clay heterostructure from montmorillonite	TEPA	72	25 °C, 1 bar	[25]
Porous clay heterostructure from montmorillonite	PEI	110	25 °C, 1 bar	[28]
Sepiolite	TEPA	165	60 °C, 1 bar	[83]
Sepiolite	PEI	56	45 °C, 1 bar	[26]
Sepiolite	PEI	45	25 °C, 1 bar	[42]
Sepiolite modified by acid treatment	DETA	73	70 °C, 1 bar	[86]
Sepiolite modified by acid treatment	TEPA	160	70 °C, 1 bar	[77]
Sepiolite modified by acid treatment	PEI	109	75 °C, 1 bar	[84]
Sepiolite modified by acid treatment	TETA	85	50 °C, 1 bar	[85]
Palygorskite	PEI	67	45 °C, 1 bar	[26]
Palygorskite	PEI	32	25 °C, 1 bar	[42]
Palygorskite modified by acid treatment	PEI	34	25 °C, 1 bar	[42]
Palygorskite modified by acid treatment	TEPA	110	25 °C, 1 bar	[87]
Halloysite	PEI	121	85 °C, 1 bar, 2 h	[88]

Table 6. CO<sub>2</sub> adsorption capacity of clay minerals functionalized with amine groups by impregnation.

In all cases, the efficiency ( $CO_2/N$  molar ratio) is below that shown by the same porous materials functionalized by grafting. In this sense, several authors have reported that the incorporation of a large amount of the amine-rich polymer by impregnation causes a stacking of the N-species, which are not

available for the  $CO_2$  adsorption. However, the reordering of the polymer when the temperature was increased improves the efficiency, although these values do not usually reach those values obtained for the adsorbent that the amine species were incorporated by grafting [25,26,42]. In most cases, the highest adsorption capacity of the impregnated samples is attributed to the greater amount of the nitrogen species on the surface of the adsorbent, although its efficiency is lower. Generally, the incorporation of a large amount of the amine species causes a blockage of the cavities so these impregnated-materials hardly act as molecular sieves. Thus, the adsorption process mainly occurs on the surface of the adsorbent through chemical interactions between the amine species and the  $CO_2$  molecules, while the physical interactions can be considered as negligible.

## 3.5.3. Double Functionalization of Clay Minerals (Grafting + Impregnation)

Recently, Sanz et al. (2013) [89] have reported that the double functionalization of the amine species achieves a higher  $CO_2$  adsorption value in porous silicas due to amino groups successively incorporated by grafting and impregnation interact more easily with the  $CO_2$  molecules in comparison to the one-step procedures. Considering these satisfactory results, this methodology was extrapolated to the minerals of the clay. In this sense, Gómez-Pozuelo et al. (2019) [26] have hardly improved the adsorption capacity of the non-functionalized montmorillonite while sepiolite worsens its adsorption values probably due to the narrow interlayer space of the montmorillonite or the nanocavities of sepiolite causes a stacking of the amine-rich polymer, which implies a decrease of the available N-sites for the  $CO_2$  adsorption. In the same way, Altilhan et al. (2016) [81] employed a montmorillonite, which was treated by grafting with APTES and then impregnated with octadecylamine, attained similar results to that obtained for the untreated montmorillonite. On the contrary, Cecilia et al. (2018) [42] treated a sepiolite by grafting with APTES and then was impregnated with PEI, achieving a higher  $CO_2$  adsorption capacity in comparison to its respective raw sepiolite (91 mg  $CO_2/g$  at 65 °C and under 1 bar of pressure), although it required a higher adsorption temperature to improve the chemical adsorption.

If the efficiency of the N-species is evaluated from the  $CO_2/N$  ratio, it can be observed how the obtained values are between those obtained for the adsorbents grafted and those impregnated with a large amount of the amine-rich polymer. This fact suggests that the functionalization by grafting in the first step seems to show a beneficial effect in the dispersion of the polymer, enhancing the amount of available amine-species. In addition, as takes place in the adsorbents functionalized by impregnation, an increase of the adsorption temperature improves the  $CO_2$  adsorption capacity in most cases [42] by the reordering of the amine-rich polymer incorporated in the second step of the functionalization (Table 7).

Clay Mineral	Grafted Amine/Amine-Rich Polymer	CO <sub>2</sub> Adsorption Capacity (mg CO <sub>2</sub> /g)	Adsorption Conditions	Ref.
Montmorillonite	APTES/PEI	18	45 °C, 1 bar	[26]
Montmorillonite	TMSPDEA/PEI	11	45 °C, 1 bar	[26]
Sepiolite	APTES/PEI	37	45 °C, 1 bar	[26]
Sepiolite	TMSPDEA/PEI	33	45 °C, 1 bar	[26]
Sepiolite	APTES/PEI	62	25 °C, 1 bar	[42]
Sepiolite	APTES/PEI	91	65 °C, 1 bar	[42]
Sepiolite	APTES/Octadecylamine	185	25 °C, 50 bar	[81]
Sepiolite modified by acid treatment	APTES/PEI	48	25 °C, 1 bar	[42]
Palygorskite	APTES/PEI	46	25 °C, 1 bar	[42]
Paygorskite modified by acid treatment	APTES/PEI	34	25 °C, 1 bar	[42]

**Table 7.** CO<sub>2</sub> adsorption capacity of the clay minerals functionalized with amine groups in two steps (1st grafting, 2nd impregnation).

#### 4. Conclusions

Clay minerals are inexpensive materials, with an abundant availability around the world. Clay is efficient for several applications such as the adsorption of  $CO_2$ , thanks to its chemical and morphological variety. The clay mineral are prone to suffer chemical modification in such a way the textural properties can be improved, increasing the microporosity as well as the  $CO_2$  adsorption capacity in most cases. Thus, the acid treatment of clay increases the microporosity by a partial solution of its sheets favoring that these structures can act as a molecular sieve trapping the  $CO_2$  molecules. The impregnation of the amine in the natural clays increases the  $CO_2$  adsorption capacity, as a consequence of an increase of the chemical interactions between the formed composite and the  $CO_2$  molecules. This process mainly takes place in the surface since the incorporation of the amine clays blocks the cavities of the clay minerals.

Pillared clays and clays modified by the hydrothermal treatment show an important specific surface area and pore volume. The improvement of the textural properties also leads to an improvement in the  $CO_2$  capture capacity. The clay minerals can also be used as an inexpensive source to synthesize economically competitive zeolites, which present a high microporosity and high  $CO_2$  adsorption capacity.

In summary, the main challenge for the use of clay minerals as starting materials to synthesize competitive adsorbents for the  $CO_2$  capture processes is related to its modification to obtain microporous adsorbents through inexpensive methods. This challenge is difficult considering that the clay mineral is a raw material where a large number of physicochemical and environmental parameters affect in its genesis and therefore in its textural properties, being key parameters for its  $CO_2$  adsorption capacity.

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