

Features of Clay Minerals Supporting Carbon Dioxide Capture

Subjects: Others

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Carbon capture is among the most sustainable strategies to limit carbon dioxide emissions, which account for a large share of human impact on climate change and ecosystem destruction. This growing threat calls for novel solutions to reduce emissions on an industrial level. Carbon capture by amorphous solids is among the most reasonable options as it requires less energy when compared to other techniques and has comparatively lower development and maintenance costs. In this respect, the method of carbon dioxide adsorption by solids can be used in the long-term and on an industrial scale. Furthermore, certain sorbents are reusable, which makes their use for carbon capture economically justified and acquisition of natural resources full and sustainable. Clay minerals, which are a universally available and versatile material, are amidst such sorbents. These materials are capable of interlayer and surface adsorption of carbon dioxide.

Keywords: carbon sequestration ; clay minerals

1. Structural and Property Features of Clay Minerals to Support Carbon Dioxide Capture

The ability of clay minerals to fix CO_2 relies on the structural and property features of a particular clay mineral. While two broad categories of clays can be distinguished (cationic and anionic clays), only one type of these clays can be widely found in nature. Cationic clays are clay minerals found in nature, but anionic clays are LDHs. While cationic clays are widespread in nature, anionic clays are often synthesised due to their rarity and thus their extraction from natural sources cannot be justifiable on a major scale [1]. In addition, the cationic clays often have negatively charged alumina-silicate ($\text{Al}_2\text{O}_3\text{-SiO}_4$) layers, with small cations in the interlayer space to balance the charge. In comparison, the anionic clays have positively charged brucite ($\text{Mg}(\text{OH})_2$) type metal hydroxide layers with balancing ions and water molecules, which are located interstitially [1][2]. Therefore, there are noticeable structural differences between both clay types and therefore also in their support for CO_2 capture.

Cationic clay minerals are hydrous Al^{3+} or Mg^{2+} phyllosilicates with two-dimensional layered structure [3]. In addition, according to the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) nomenclature committee, clay minerals impart plasticity when wet and harden upon drying or firing [4]. This means that clay minerals generally are water-containing compounds with structure in which silicate tetrahedrons are arranged in sheets. Moreover, clay mineral properties change depending on the water content within. Each layer of clay mineral structure consists of a silica tetrahedral sheet and a metal oxide or hydroxide octahedral sheet, which are linked together in certain proportions [5][6][7]. The above-mentioned silica tetrahedral sheet consists of the central silicon (Si^{4+}) cation, which is surrounded by four O_2 atoms (Figure 1). This sheet is formed when three out of four O_2 atoms, known as basal oxygens, are corner-linked with three nearest tetrahedrons; this in turn forms an infinite two-dimensional hexagonal mesh pattern [5][8]. The metal oxide or hydroxide octahedral sheet consists of a central cation, which most often is a Al^{3+} or Mg^{2+} cation that is surrounded by six O_2 or hydroxyl (OH) atoms (Figure 1). This sheet is formed when neighbouring octahedrons edge-share two O_2 atoms with each other and the smallest structural unit contains three such octahedrons and is of a hexagonal or pseudohexagonal symmetry [5][6][8][9].

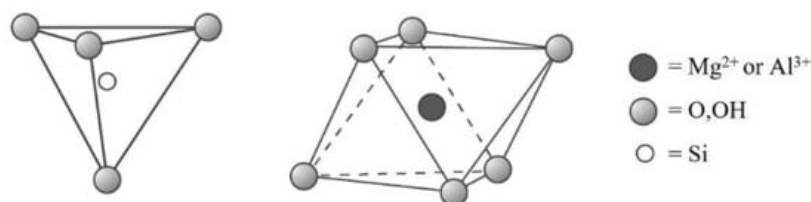


Figure 1. A schematic representation of silica tetrahedron and magnesium or aluminium octahedron.

Cationic clay minerals form due to weathering and decomposition of igneous rocks that are in contact with air, water, or steam, and thus they are very common in soils, sedimentary rocks, metamorphic rocks, and volcanoclastic rocks [10][11][12]. While there are numerous clay minerals, they are generally classified into nine groups, which are based on the variations in the chemical composition and atomic structure of these minerals. These groups are [13][14]:

- Kaolin-serpentine (kaolinite, nacrite, dickite etc.);
- Pyrophyllite-talc;
- Mica;
- Vermiculite;
- Smectite (montmorillonite);
- Chlorite;
- Sepiolite-palygorskite;
- Interstratified clay minerals;
- Allophane-imogolite.

The key factor for determining clay mineral type essentially is the SiO_2 ratio in a formula [11]. In addition, clay minerals are also often classified by layer types or tetrahedral and octahedral sheet combinations, which allows to distinguish three general clay mineral types [15]:

- 1:1 layer type, tetrahedral–octahedral sheet combination;
- 2:1 layer type, tetrahedral–octahedral–tetrahedral sheet combination;
- 2:1:1 layer type, tetrahedral–octahedral–tetrahedral sheet combination.

Yet another clay mineral classification considers the charge per formula unit, dioctahedral, or trioctahedral character and chemical composition of the current clay mineral type. Based on both these criteria, there are 10 main clay mineral groups [16][17][18]:

- Serpentine (e.g., chrysolite, lizardite);
- Kaolin (e.g., kaolinite, dickite, halloysite);
- Talc;
- Pyrophyllite;
- Smectite (e.g., saponite, hectorite, montmorillonite, beidellite);
- Vermiculite;
- True mica (e.g., illite, glauconite, phlogopite, biotite);
- Brittle mica (e.g., clintonite, margarite);
- Chlorite (e.g., clinochlore, chamosite, donbassite);
- Mixed layer group (e.g., chlorite-smectite, chlorite-vermiculite, illite-smectite).

Essentially, clay minerals are constructs of two-dimensional tetrahedral stacks of inorganic layers, where atom substitutions generate a negative charge on each layer surface of clay mineral, which is then balanced by exchangeable interlayer cations [19][20]. These interlayer cations determine clay physicochemical characteristics [21][22][23]. The structural and composition features of particular clay minerals give them different physical and chemical properties, e.g., particle size and shape, specific surface area, CEC, plasticity, hydration, swelling, and surface electric charge [19][20][21][22][23][24]. The overall structural arrangement of clay minerals is simple; however, the complexity arises due to the wide variety of isomorphic substitutions that can occur within the aluminosilicate layers, the disordered nature of the interlayer region, stacking defects in the clay layer sequence, or the variable interlayer separation [20].

In regard to the CO_2 capture, minerals such as kaolin, smectite, and brittle mica group have been investigated as prospective materials with necessary properties for carbon capture [25].

The structure of kaolin group minerals (1:1 layer type) is composed of one alumina octahedral sheet and one silica tetrahedral sheet, which are stacked one above other (**Figure 2a,b**) [5][26]. These sheets are kept together by H_2 bridges between O_2 atoms on the tetrahedral sheet and surface hydroxyl groups on the octahedral sheet [5][6]. The sheet has little or no permanent charge due to the low amount of substitution. As a result, kaolinite has rather low CEC and small surface area [5][6]. In addition, kaolinite is a triclinic (three-dimensional geometrical arrangement) mineral with pseudohexagonal crystals that arrange in book-like aggregates, and their particle size ranges from $0.05\ \mu\text{m}$ to $2\ \mu\text{m}$ [6][8].

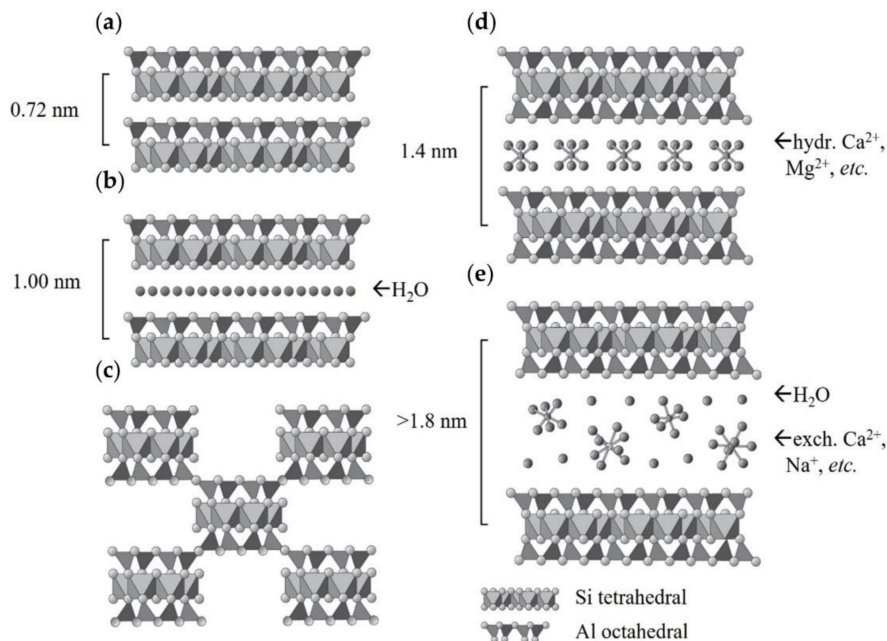


Figure 2. Structural schemes for some of the clay minerals: (a) kaolinite; (b) halloysite; (c) sepiolite; (d) vermiculite, and (e) smectite.

The structure of smectite clay minerals (2:1 layer type) is composed of two silica tetrahedral sheets that encompass one octahedral sheet, which contains Al^{3+} , Fe^{3+} , or Mg^{2+} cations (**Figure 2d,e**) [7][26][27]. One of the characteristic features of smectite minerals is their isomorphous substitution in the octahedral and tetrahedral sheets. There is a substitution of trivalent for tetravalent ions (Al^{3+} for Si^{4+}) in the tetrahedral sheet and of divalent for trivalent ions (Mg^{2+} for Al^{3+}) in the octahedral sheet [17][24][27]. The substitution results in a charge deficiency, which is then balanced by hydrated cations (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) in the interlayer site, which is exchangeable, and thus this leads to high CEC [8][17][26]. The particle size of smectite minerals usually does not exceed 0.5 μm , while the shape varies from subhedral lamellae with irregular outlines to euhedral lamellae with rhombic outlines [8]. The most common smectite minerals are Na^+ and Ca^{2+} montmorillonites, whose layer charge deficiency is balanced by the interlayer cations, such as sodium or calcium, and water molecules [24].

Fibrous clay minerals, such as palygorskite (attapulgite) and sepiolite, have a unique arrangement of the tetrahedral and octahedral sheets that are distinct from the typical 1:1 and 2:1-layer types. Palygorskite and sepiolite are composed of continuous two-dimensional silica tetrahedral sheets and one Mg^{2+} octahedral sheet, which is continuous in only one dimension. As a result, the tetrahedral sheets are split into ribbons and each of these ribbons are linked to the next ribbon by inversion of silica tetrahedral (**Figure 2c**). The dimension of channels between the ribbon strips is ranging from 4 to 6 angstroms for palygorskite and from 4 to 9.5 angstroms for sepiolite [5][7][24]. Both minerals are of fibrous morphology with micropores of around 0.54 nm in diameter; at the same time, mineral crystals are arranged in the bundles in an elongated shape. Notably, these properties are highly varied in clay minerals and even more so within different fibrous clay minerals. The morphology of these clay minerals is the most important physical attribute, which determines a high surface area and provides more active sites and thus also high potential for CO_2 sorption [24][28].

The interaction between CO_2 and clay minerals has attracted the interest of the scientific community as such minerals have proven potential to capture carbon [19][29][30]. In addition, clay minerals are a class of potential adsorbents that also possess good stability and economic viability [31]. Moreover, clay minerals are universally available and versatile materials, and due to their physicochemical properties, they can also be used as ion exchangers or catalysts [2]. Therefore, the use cationic or anionic clay minerals, in addition to liquid and supported amines, are amongst options viewed for trapping CO_2 [32][33][34][35][36][37][38]. In this regard, cationic montmorillonite due to its slight basicity seems to be one of the best options for carbon capture [39][40][41][42][43][44][45][46]. In addition, numerous studies suggest that clay minerals can also be used as support for immobilizing enzymes. These enzymes can be immobilized onto clay minerals through non-covalent adsorption and covalent bonding [3]. The non-covalent adsorption involves van der Waals forces, electrostatic interactions, hydrogen bonding, and hydrophobic interactions. The covalent bonding, in turn, can be used to avoid possible desorption of enzymes [3].

In terms of clay mineral parameters with high importance on CO_2 sorption capacity, the moisture may be among the most important ones. This is because there is almost always water in CO_2 containing gas mixtures. Moreover, it is worth noting that the sorption mechanism of CO_2 , for example, on amine containing sorbents differs significantly in humid and in dry

conditions. For example, in humid conditions between one CO₂ and two amine groups, bicarbonates are formed, but in dry conditions carbamates are forming instead. Thus, sorbed amount of CO₂ in humid conditions is comparatively higher than in dry conditions [47]. This was proven by Irani et al. (2015), who reported that the addition of 1 vol% of water could increase CO₂ sorption capacity from 2.2 mmol g⁻¹ in dry conditions to 3.8 mmol g⁻¹ in humid conditions. Yuan et al. (2018) had similar findings, revealing that the adsorption capacity increased from 1.93 mmol g⁻¹ in dry conditions to 2.21 mmol g⁻¹ in humid conditions. At the same time, there were indications that adsorption–desorption cycles show good regenerability in both dry and humid conditions [47][48].

2. Clay Mineral and Carbon Dioxide Interaction Depending on Mineral Type

Studies of CO₂ sorption onto clay minerals started more than 50 years ago with aims to analyse the surface area of clay minerals and to identify the sorption mechanism [49][50]. Nowadays, clay minerals and CO₂ interactions are studied with two main aims: one is the use of clay minerals as sorbents for CO₂ capture, and another is the geological storage of captured CO₂ by clay minerals or in the underground structures containing clay minerals [25][51][52][53]. Additionally, common clay mineral types have been used to study their potential for gas separation and carbon sequestration processes. In fact, by numerous analytical methods, it has also been suggested to characterise CO₂ sorption process, stability of formed complexes, and desorption processes [25][30][54][55][56]. For example, smectite and CO₂ interaction has been investigated by X-ray diffraction experiments while analysing shifts in basal spacing reflections [54]. Smectite and CO₂ interaction has also been investigated with neutron diffraction and infrared measurements [55][56][57]. Smectites are layered nanoporous materials, and it was found that they can sorb CO₂ in their interlayer space due to gaseous CO₂ intercalation into the interlayer nano-space as confirmed using above mentioned techniques [19]. In addition, experiments with smectites have shown that Na-exchanged montmorillonite can swell up to 9% if it is exposed to high purity CO₂, this however depends on the initial hydration state of the interlayers in smectite [30]. CO₂ adsorption within the smectite interlayer region in Na-exchanged montmorillonite is believed to be the reason behind clay swelling up to the accounted 9% [30]. Moreover, recent studies have shown that the pore size, charge, and solvation energies of the interlayer cations in smectite minerals are greatly affecting the structure, dynamics, and energetics of the intercalated CO₂ molecules [58][59]. At the same time, other studies have shown that, for instance, illite and kaolinite minerals are not known for interlayer expansion under any experimental conditions, whilst they are still able to adsorb considerable amounts of CO₂. It is believed that in these clay minerals, CO₂ sorption occurs on clay platelet surface [57]. Accordingly, it can be concluded that CO₂ adsorption mechanisms vary depending on clay mineral type as it can be either CO₂ adsorption in the interlayers, or it can be surface sorption. These regularities must be further addressed in future experiments.

One of the main factors affecting the physical sorption of CO₂ onto clay minerals is the type of exchangeable ion within; for example, Cs-exchanged and tetramethylammonium-exchanged montmorillonite have sorption capacity for CO₂ up to 1.70 mmol g⁻¹ even at ambient pressure and temperature [60]. At the same time, in case of fibrous clay minerals, such as sepiolite, the sorption takes place due to the presence of nanocavities, which are acting as a molecular sieve and therefore the CO₂ uptake can reach up to 1.48 mmol g⁻¹ [61]. In comparison, in saponite (smectite group), CO₂ physical sorption takes place under ambient conditions on the nanosheet surface at the open spaces on clay mineral [62]. Additionally, a number of other clay minerals have also been studied as potential CO₂ adsorbents, for example, hydrotalcite and hectorite, palygorskite, kerolite, and stevensite, thus demonstrating the high potential of clay minerals for carbon capture [61][63][64][65][66].

3. Prospective for Clay Mineral Modification to Improve Carbon Dioxide Capture

Physicochemical characteristics of clay minerals have been widely studied using numerous techniques and approaches, such as neutron and X-ray scattering, nuclear magnetic resonance (NMR) spectroscopy, tracer experiments, numerical modelling, and others [21][22][25][67][68][69][70][71][72][73][74][75]. According to the data obtained from using these approaches, clay mineral properties, in regard to the improvement of CO₂ adsorption, can be optimized by the insertion of organic, inorganic, or organometallic species between adjacent sheets of clay structure, by functionalization or by acid treatment [2][3][66][76][77]. However, before choosing one or another type of clay mineral for carbon capture, it is important to note that the chemical properties of particular minerals, and consequently also the adsorption of gases on or within them, are significantly affected by the structure of the mineral and the charge of clay layers. Mineral structures with all six octahedral sites occupied are known as trioctahedral structures, while structures with four out of six octahedral sites occupied are referred as dioctahedral structures. For example, minerals such as kaolinite, halloysite (1:1 layer structure), and montmorillonite (2:1 layer structure) are dioctahedral, while serpentine (1:1 layer structure) and vermiculite (2:1 layer

structure) are trioctahedral. Furthermore, structures of palygorskite and sepiolite are rather different from above mentioned due to the lack of continuous octahedral sheets; however, there are fibrous clay minerals with dioctahedral and trioctahedral arrangement [78]. At the same time, the structure of a layer, its thickness, and the charge are all interrelated with one another and can therefore affect the particle size and specific surface area of the clay mineral and many other properties [79]. In addition, recent studies indicate that raw clay materials typically show low CO₂ adsorption capacity, and the adsorption properties are generally related to the textural properties of particular minerals [61][80][81][82]. Therefore, clay mineral modification to improve CO₂ capture is a crucial direction of the future research [83][84].

Factors/parameters that are essential for the selection of a potential sorbent material include high CO₂ absorption capacity, high CO₂ selectivity, mechanical, hydrothermal, and chemical stability, rapid adsorption/desorption kinetics, regeneration capacity, low heat capacity, price of raw materials, and costs of synthesis [25][80][85][86]. Therefore, appropriate materials are chosen either based on the highest efficiency within these parameters or materials are modified to improve certain parameters. At the same time, it is important to note that it is almost impossible for a single material to satisfy all of the above-mentioned essential properties of a sorbent. Nonetheless, it is important to assess at least partial compliance and to consider the most important factors.

Efficiency-wise, clay minerals are among the materials with the most essential properties required for CO₂ sorption. In addition, porous clay heterostructures have been evaluated as adsorbents for small hydrocarbons, in their separation and in the encapsulation of organic compounds [65][87][88][89]. There have also been experiments on clay structures as the catalytic support in the NO reduction, partial oxidation of H₂S, preferential oxidation of CO₂, and the esterification reactions to obtain bio-lubricants and all of these experiments have shown high potential of clay applications [90][91][92][93].

Strategies to overcome drawbacks for CO₂ sequestration encourages capturing and storing CO₂ using solid adsorbents, which operate through a repetitive adsorption–desorption cycle, thus using sorbents that display base properties [94]. Solid sorbents usually contain a solid with a large specific surface area, and when a layer of such sorbent passes through a mixture of gases, CO₂ is captured by either a physical sorption or a chemisorption process. These sorbents can be regenerated via pressure or temperature change [95][96][97]. For example, pressure changes have been successfully used to induce adsorption–desorption cycle and to separate CO₂ from N₂ at room temperature. In this regard, montmorillonite clay intercalated with dendrimer polyol silica, goes through a pressure-induced adsorption-desorption cycle and shows a potential for reversible CO₂ capture. Moreover, the hydroxyl groups in montmorillonite are found to act as adsorption sites and interact with CO₂ molecules in the gas phase [40][44][63][94][98][99][100][101][102][103]. Numerous clay mineral modifications, such as clay-graphene hybrids, have also been assessed for CO₂ adsorption [104]. Clay minerals are considered suitable for further modifications involving a simultaneous reduction of basicity and an increase in CO₂ sequestration [94].

One of the options for clay mineral modification to improve the CO₂ sorption capacity is their expansion. For instance, smectites are expanded by incorporation of bulky cations in the interlayer space [105]. Additionally, these modified clays are with significantly improved thermal and mechanical resistance when compared to a raw smectite [105][106]. The reactivity of smectite group minerals can be further improved by replacing mobile and exchangeable cations on their surface by higher valence metal ions (e.g., Mg²⁺, Zn²⁺, Cu²⁺, Al³⁺ or Fe³⁺) [107][108][109][110]. Furthermore, the cation exchange with Ni²⁺ ions can promote formation of a carbonaceous residue [111][112][113]. It can be concluded that amongst the most significant properties of clay minerals to support CO₂ adsorption is the ion exchange. The properties of ion exchange allow for isomorphous substitution of metal cations in the lattice by lower-valent ions. The created negative charge can then be balanced by other cations. The cations can be exchanged when they are brought into the contact with other ions in aqueous solution [1]. Considering cation exchange properties and layered structure of clay minerals, it is possible to introduce molecules of other compounds, which then can be used to change and modify clay mineral properties.

References

1. Juzkow, J. Clay Materials Modified with Amino Acids for Purification Processes of Biogas and Natural Gas. Master's Thesis, Technical University of Lisbon, Lisbon, Portugal, 2016.
2. Vaccari, A. Clays and catalysis: A promising future. *Appl. Clay Sci.* 1999, 14, 161–198.
3. An, N.; Zhou, C.H.; Zhuang, X.Y.; Tong, D.S.; Yu, W.H. Immobilization of enzymes on clay minerals for biocatalysts and biosensors. *Appl. Clay Sci.* 2015, 114, 283–296.
4. Guggenheim, S.; Martin, R.T. Definition of clay and clay mineral: Joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clays Clay Miner.* 1995, 43, 255–256.

5. Schulze, D.G. Clay minerals. In *Encyclopaedia of Soils in the Environment*; Hillel, D., Ed.; Elsevier: Boston, MA, USA, 2005; pp. 246–254.
6. Theng, B.K.G. The clay minerals. *Dev. Clay Sci.* 2012, 4, 3–45.
7. Ismadji, S.; Soetaredjo, F.E.; Ayucitra, A. Natural clay minerals as environmental cleaning agents. In *Clay Materials for Environmental Remediation*; Ismadji, S., Soetaredjo, F.E., Ayucitra, A., Eds.; Springer: Copenhagen, Denmark, 2015; pp. 5–37.
8. Christidis, G.E. Industrial clays. In *European Mineralogical Union Notes in Mineralogy. Advances in the Characterization of Industrial Clays*; Christidis, G.E., Ed.; Mineralogical Society of Great Britain and Ireland: London, UK, 2010; Volume 9, pp. 341–414.
9. Schoonheydt, R.A.; Johnston, C.T.; Bergaya, F. Clay minerals and their surfaces. *Dev. Clay Sci.* 2018, 9, 1–21.
10. Nesse, W.D. *Introduction to Mineralogy*, 3rd ed.; Oxford University Press: New York, NY, USA, 2016.
11. Clay Mineral. Available online: <https://www.britannica.com/science/clay-mineral> (accessed on 7 October 2021).
12. Zhou, C.H.; Keeling, J. Fundamental and applied research on clay minerals: From climate and environment to nanotechnology. *App. Clay Sci.* 2013, 74, 3–9.
13. Brigatti, M.F.; Galan, E.; Theng, B.K.H. Structures and mineralogy of clay minerals. *Dev. Clay Sci.* 2006, 1, 19–86.
14. Brigatti, M.F.; Malferrari, D.; Laurora, A.; Elmi, C.; Mottana, A. Structure and mineralogy of layer silicates: Recent perspectives and new trends. Layered mineral structures and their application in advanced technologies. *EMU Notes Mineral.* 2011, 11, 1–71.
15. Martin, R.T.; Bailey, S.W.; Eberl, D.D.; Fanning, D.S.; Guggenheim, S.; Kodama, H.; Pevear, D.R.; Srodon, J.; Wicks, F.J. Report of the Clay Minerals Society Nomenclature Committee: Revised classification of clay materials. *Clays Clay Miner.* 1991, 39, 333–335.
16. Guggenheim, S.; Adams, J.M.; Bain, D.C.; Bergaya, F.; Brigatti, M.F.; Drits, V.A.; Formoso, M.L.L.; Galán, E.; Kogure, T.; Stanjek, H. Summary of recommendations of Nomenclature Committees relevant to clay mineralogy: Report of the association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2006. *Clays Clay Miner.* 2006, 54, 761–772.
17. Schroeder, P. *Clays in the Critical Zone*; Cambridge University Press: Cambridge, UK, 2018; pp. 1–246.
18. Bergaya, F.; Lagaly, G. General introduction: Clays, clay minerals, and clay science. *Dev. Clay Sci.* 2006, 1, 1–18.
19. Michels, L.; Fossum, J.O.; Rozynek, Z.; Hemmen, H.; Rustenberg, K.; Sobas, P.A.; Kalantzopoulos, G.N.; Knudsen, K.D.; Janek, M.; Plivelic, T.S.; et al. Intercalation and retention of carbon dioxide in a smectite clay promoted by interlayer cations. *Sci. Rep.* 2015, 5, 8775.
20. Boulet, P.; Greenwell, H.C.; Stackhouse, S.; Coveney, P.V. Recent advances in understanding the structure and reactivity of clays using electronic structure calculations. *J. Mol. Struct. Theochem* 2006, 762, 33–48.
21. da Silva, G.J.; Fossum, J.O.; DiMasi, E.; Maloy, K.J.; Lutnaes, S.B. Synchrotron x-ray scattering studies of water intercalation in a layered synthetic silicate. *Phys. Rev. E* 2002, 66, 011303.
22. Bordallo, H.N.; Aldridge, L.P.; Churchman, G.J.; Gates, W.P.; Telling, M.T.F.; Kiefer, K.; Fouquet, P.; Seydel, T.; Kimber, S.A.J. Quasi-elastic neutron scattering studies on clay interlayer-space highlighting the effect of the cation in confined water dynamics. *J. Phys. Chem. C* 2008, 112, 13982–13991.
23. Hansen, E.L.; Hemmen, H.; Fonseca, D.M.; Coutant, C.; Knudsen, K.D.; Plivelic, T.S.; Bonn, D.; Fossum, J.O. Swelling transition of a clay induced by heating. *Sci. Rep.* 2012, 2, 618.
24. Murray, H.H. *Applied Clay Mineralogy: Occurrences, Processing and Application of Kaolins, Bentonites, Palygorskite-Sepiolite, and Common Clays*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2006; pp. 1–180.
25. Chouikhi, N.; Cecilia, J.A.; Villarrasa-Garcia, E.; Besghaier, S.; Chlendi, M.; Duro, F.I.F.; Castellon, R.R.; Bagane, M. CO₂ adsorption of materials synthesized from clay minerals: A review. *Minerals* 2019, 9, 514.
26. Yariv, S.; Cross, H. *Organo-Clay Complexes and Interactions*; Marcel Dekker: New York, NY, USA, 2002; pp. 1–688.
27. Stinkule, A. *Clays in the Subterranean of Latvia*; RTU Publishing House: Riga, Latvia, 2014; pp. 1–121.
28. Lan, Y.; Liu, Y.; Li, J.; Chen, D.; He, G.; Parkin, I.P. Natural clay-based materials for energy storage and conversion applications. *Adv. Sci.* 2021, 8, 2004036.
29. Cole, D.R.; Chialvo, A.A.; Rother, G.; Vlcek, L.; Cummings, P.T. Supercritical fluid behaviour at nanoscale interfaces: Implications for CO₂ sequestration in geologic formations. *Phil. Mag.* 2010, 90, 2339–2363.

30. de Jong, S.M.; Spiers, C.J.; Busch, A. Development of swelling strain in smectite clays through exposure to carbon dioxide. *Int. J. Greenh. Gas Control* 2014, 24, 149–161.
31. Chen, Y.; Lu, D. CO₂ capture by kaolinite and its adsorption mechanism. *Appl. Clay Sci.* 2015, 104, 221–228.
32. Soares, J.L.; Moreira, R.F.P.M.; Jose, H.J.; Grande, C.A.; Rodrigues, A.E. Hydrotalcite materials for carbon dioxide adsorption at high temperatures: Characterization and diffusivity measurements. *Sep. Sci. Technol.* 2004, 39, 1989–2010.
33. Birbara, P.J.; Nalette, T.A. Regenerable Supported Amine-Polyol Sorbent. US Patent 5,376,614, 27 December 1994.
34. Yong, Z.; Rodrigues, A.E. Hydrotalcite-like compounds as adsorbents for carbon dioxide. *Energy Convers. Manag.* 2002, 43, 1865–1876.
35. Gray, M.L.; Soong, Y.; Champagne, K.J.; Baltrus, J.; Stevens, R.W.; Toochinda, P.; Chuang, S.S.C. CO₂ capture by amine-enriched fly ash carbon sorbents. *Sep. Purif. Technol.* 2004, 35, 31–36.
36. Santos-Costa, A.; Imae, T.; Takagi, K.; Kikuta, K. Intercalation of dendrimers in the interlayer of hydrotalcite clay sheets. In *Surface and Colloid Science*; Springer: Berlin/Heidelberg, Germany, 2004; Volume 128, pp. 113–119.
37. Sirwardane, R.V. Solid sorbents for removal of carbon dioxide from gas streams at low temperatures. US Patent 6908497, 21 June 2005.
38. Chaffee, A.L.; Knowles, G.P.; Liang, Z.; Zhang, J.; Xiao, P.; Webley, P.A. CO₂ capture by adsorption: Materials and process development. *Int. J. Greenh. Gas Control* 2007, 1, 11–18.
39. Thomas, J.; Bohor, B.F. Surface area of vermiculite with nitrogen and carbon dioxide as adsorbates. *Clays Clay Miner.* 1969, 17, 205–209.
40. Aylmore, L.A.G. Gas sorption in clay mineral systems. *Clays Clay Miner.* 1974, 22, 175–183.
41. Azzouz, A. *Physicochimie des Tamis Moléculaires*; Office des Publications Universitaires: Algiers, France, 1994.
42. Rodlert, M.; Plummer, C.J.G.; Leterrier, Y.; Manson, J.-A.E.; Grunbauer, H.J.M. Rheological behaviour of hyperbranched polymer/montmorillonite clay nanocomposites. *J. Rheol.* 2004, 48, 1049–1065.
43. Lingaiah, S.; Shivakumar, K.N.; Sadler, R.; Sharpe, M. A method of visualization of dispersion of nanoplatelets in nanocomposites. *Compos. Sci. Technol.* 2005, 65, 2276–2280.
44. Azzouz, A.; Nistor, D.; Miron, D.; Ursu, A.-V.; Sajin, T.; Monette, F.; Niquette, P.; Hausler, R. Assessment of the acid–base strength distribution of ion-exchanged montmorillonites through NH₃ and CO₂-TPD measurements. *Thermochim. Acta* 2006, 449, 27–34.
45. Liu, P. Hyperbranched aliphatic polyester grafted attapulgite via a melt polycondensation process. *Appl. Clay Sci.* 2007, 35, 11–16.
46. Azzouz, A.; Assaad, E.; Ursu, A.-V.; Sajin, T.; Nistor, D.; Roy, R. Carbon dioxide retention over montmorillonite-dendrimer materials. *Appl. Clay Sci.* 2010, 48, 133–137.
47. Irani, M.; Fan, M.; Ismail, H.; Tuwafi, A.; Dutcher, B.; Russell, A.G. Modified nanosepiolite as an inexpensive support of tetraethylenepentamine for CO₂ sorption. *Nano Energy* 2015, 15, 235–246.
48. Yuan, M.; Gao, G.; Hu, X.; Luo, X.; Huang, Y.; Jin, B.; Liang, Z. Pre-modified sepiolite functionalized with triethylenetetramine as an effective and inexpensive adsorbent for CO₂ capture. *Ind. Eng. Chem. Res.* 2018, 57, 6189–6200.
49. Thomas, J.; Bohor, B.F. Surface area of montmorillonite from the dynamic sorption of nitrogen and carbon dioxide. *Clays Clay Miner.* 1968, 16, 83–91.
50. Fripiat, J.J.; Cruz, M.I.; Bohor, B.F.; Thomas, J. Interlamellar adsorption of carbon dioxide by smectites. *Clays Clay Miner.* 1974, 22, 23–30.
51. Wang, Q.; Huang, L. Molecular insight into competitive adsorption of methane and carbon dioxide in montmorillonite: Effect of clay structure and water content. *Fuel* 2019, 239, 32–43.
52. Chan, W.H.; Mazlee, M.N.; Ahmad, Z.A.; Ishak, M.A.M.; Shamsul, J.B. The development of low-cost adsorbents from clay and waste materials: A review. *J. Mater. Cycles Waste Manag.* 2017, 19, 293–301.
53. Jeon, P.R.; Choi, J.; Yun, T.S.; Lee, C.H. Sorption equilibrium and kinetics of CO₂ on clay minerals from subcritical to supercritical conditions: CO₂ sequestration at nanoscale interfaces. *Chem. Eng. J.* 2014, 255, 705–715.
54. Giesting, P.; Guggenheim, S.; Koster van Groos, A.F.; Busch, A. Interaction of carbon dioxide with Na-exchanged montmorillonite at pressures to 640 bars: Implications for CO₂ sequestration. *Int. J. Greenh. Gas Control* 2012, 8, 73–81.

55. Schaef, H.T.; Ilton, E.S.; Qafoku, O.; Martin, P.F.; Felmy, A.R.; Rosso, K.M. In situ XRD study of Ca²⁺ saturated montmorillonite (STX-1) exposed to anhydrous and wet supercritical carbon dioxide. *Int. J. Greenh. Gas Control* 2012, 6, 220–229.
56. Rother, G.; Ilton, E.S.; Wallacher, D.; HauB, T.; Schaef, H.T.; Qafoku, O.; Rosso, K.M.; Felmy, A.R.; Krukowski, E.G.; Stack, A.G.; et al. CO₂ sorption to sub-single hydration layer montmorillonite clay studied by excess sorption and neutron diffraction measurements. *Env. Sci. Technol.* 2013, 47, 205–211.
57. Busch, A.; Alles, S.; Gensterblum, Y.; Prinz, D.; Dewhurst, D.N.; Raven, M.D.; Stanjek, H.; Krooss, B.M. Carbon dioxide storage potential of shales. *Int. J. Greenh. Gas Control* 2008, 2, 297–308.
58. Maruthi Sena, M.; Krishnan, M. Role of cations in adsorption of supercritical carbon dioxide at smectite mineral-water interfaces: Molecular dynamics and adaptive biasing force simulation studies. *J. Phys. Chem. C* 2018, 123, 1170–1184.
59. Narayanan Nair, A.K.; Cui, R.; Sun, S. Overview of the adsorption and transport properties of water, ions, carbon dioxide, and methane in swelling clays. *ACS Earth Space Chem.* 2021, 5, 2599–2611.
60. Mendel, N.; Sîretanu, D.; Sîretanu, I.; Brilman, D.W.; Mugele, F. Interlayer Cation-Controlled Adsorption of Carbon Dioxide in Anhydrous Montmorillonite Clay. *J. Phys. Chem. C* 2021, 125, 27159–27169.
61. Cecilia, J.A.; Vilarrasa-García, E.; Cavalcante, C.L.; Azevedo, D.C.S.; Franco, F.; Rodríguez-Castellón, E. Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO₂ Capture. *J. Environ. Chem. Eng.* 2018, 6, 4573–4587.
62. Sato, K.; Hunger, M. Carbon dioxide adsorption in open nanospaces formed by overlap of saponite clay nanosheets. *Comm. Chem.* 2020, 3, 91.
63. Azzouz, A.; Nousir, S.; Platon, N.; Ghomari, K.; Shiao, T.C.; Hersant, G.; Bergron, J.-Y.; Roy, R. Truly reversible capture of CO₂ by montmorillonite intercalated with soya oil-derived polyglycerols. *Int. J. Greenh. Gas Control* 2013, 17, 140–147.
64. Delgado, J.A.; Uguina, M.A.; Sotelo, J.L.; Rui'z, B.; Rosa'rio, M. Carbon dioxide/methane separation by adsorption on sepiolite. *J. Nat. Gas. Chem.* 2007, 16, 235–243.
65. Pires, J.; Bestilleiro, M.; Pinto, M.; Gil, A. Selective adsorption of carbon dioxide, methane, and ethane by porous clays heterostructures. *Sep. Purif. Technol.* 2008, 61, 161–167.
66. Franco, F.; Cecilia, J.A.; Pozo, M.; Pardo, L.; Bellido, E.; Garcia-Sancho, C. Microwave assisted acid treatment of kerolitic clays from the Neogene Madrid Basin (Spain) and its use in CO₂ capture processes. *Microporous Mesoporous Mater.* 2020, 292, 109749.
67. Dazas, B.; Lanson, B.; Breu, J.; Robert, J.-L.; Pelletier, M.; Ferrage, E. Smectite fluorination and its impact on interlayer water content and structure: A way to fine tune the hydrophilicity of clay surfaces? *Microporous Mesoporous Mater.* 2013, 181, 233–247.
68. da Silva, G.J.; Fossum, J.O.; DiMasi, E.; Maloy, K.J. Hydration transitions in a nanolayered synthetic silicate: A synchrotron x-ray scattering study. *Phys. Rev. B* 2003, 67, 094114.
69. Jansson, M.; Eriksen, T.E. In situ anion diffusion experiments using radiotracers. *J. Contam. Hydrol.* 2004, 68, 183–192.
70. Tambach, T.J.; Hensen, E.J.M.; Smit, B. Molecular simulations of swelling clay minerals. *J. Phys. Chem. B* 2004, 108, 7586–7596.
71. Malikova, N.; Cadene, A.; Dubois, E.; Marry, C.; Durand-Vidal, S.; Turq, P.; Breu, J.; Longeville, S.; Zanotti, J.-M. Water diffusion in a synthetic hectorite clay studied by quasi-elastic neutron scattering. *J. Phys. Chem. C* 2007, 111, 17603–17611.
72. Porion, P.; Michot, L.J.; Faugere, A.M.; Delville, A. Structural and dynamical properties of the water molecules confined in dense clay sediments: A study combining 2H NMR spectroscopy and multiscale numerical modelling. *J. Phys. Chem. C* 2007, 111, 5441–5453.
73. Tenorio, R.P.; Alme, L.R.; Engelsberg, M.; Fossum, J.O.; Hallwass, F. Geometry and dynamics of intercalated water in Na-fluorhectorite clay hydrates. *J. Phys. Chem. C* 2008, 112, 575–580.
74. Tenorio, R.P.; Engelsberg, M.; Fossum, J.O.; da Silva, G.J. Intercalated water in synthetic fluorhectorite clay. *Langmuir* 2010, 26, 9703–9709.
75. Jimenez-Ruiz, M.; Ferrage, E.; Delville, A.; Michot, L.J. Anisotropy on the collective dynamics of water confined in swelling clay minerals. *J. Phys. Chem. A* 2012, 116, 2379–2387.
76. Kloppe, J.T. Synthesis of smectites and porous pillared clay catalysts: A review. *J. Porous Mater.* 1998, 5, 5–41.
77. Franco, F.; Pozo, M.; Cecilia, J.A.; Benitez-Guerrero, M.; Pozo, E.; Rubi, J.A.M. Microwave assisted acid treatment of sepiolite: The role of composition and “crystallinity”. *Appl. Clay Sci.* 2014, 102, 15–27.

78. Silva, V.C.; Araujo, M.E.B.; Rodrigues, A.M.; Cartazo, J.M.; Menezes, R.R.; Neves, G.A. adsorption behaviour of acid-treated Brazilian palygorskite for cationic and anionic dyes removal from water. *Sustainability* 2021, 13, 3954.
79. Wal, K.; Rutkowski, P.; Stawinski, W. Application of clay minerals and their derivatives in adsorption from gaseous phase. *Appl. Clay Sci.* 2021, 215, 106323.
80. Gomez-Pozuelo, G.; Sanz-Perez, E.S.; Arencibia, A.; Pizarro, P.; Sanz, R.; Serrano, D.P. CO₂ adsorption on amine-functionalized clays. *Microporous Mesoporous Mater.* 2019, 282, 38–47.
81. Chen, Y.H.; Lu, D.L. Amine modification on kaolinites to enhance CO₂ adsorption. *J. Colloid Interface Sci.* 2014, 436, 47–51.
82. Horri, N.; Sanz-Pérez, E.S.; Arencibia, A.; Sanz, R.; Frini-Srasra, N. Amine grafting of acid-activated bentonite for carbon dioxide capture. *Appl. Clay Sci.* 2019, 180, 105195.
83. Ramadass, K.; Sathish, C.I.; Singh, G.; Ruban, S.J.; Ruban, A.M.; Bahadur, R.; Vinu, A. Morphologically tuneable nano architectonics of mixed kaolin-halloysite derived nitrogen-doped activated nanoporous carbons for supercapacitor and CO₂ capture applications. *Carbon* 2022, 192, 133–144.
84. Bo Hunvik, K.W.; Loch, P.; Wallacher, D.; Kirch, A.; Cavalcanti, L.P.; Riess, M.; Fossum, J.O. CO₂ adsorption enhanced by tuning the layer charge in a clay mineral. *Langmuir* 2021, 37, 14491–14499.
85. Niu, M.; Yang, H.; Zhang, X.; Wang, Y.; Tang, A. Amine-impregnated mesoporous silica nanotube as an emerging nanocomposite for CO₂ capture. *ACS Appl. Mater. Interface* 2016, 8, 17312–17320.
86. Roth, E.A.; Agarwal, S.; Gupta, R.K. Nanoclay-based solid sorbents for CO₂. *Energy Fuels* 2013, 27, 4129–4136.
87. Pinto, M.L.; Mafra, L.; Guil, J.M.; Pires, J.; Rocha, J. Adsorption and activation of CO₂ by amine-modified nanoporous materials studied by solid-state NMR and ¹³CO₂ adsorption. *Chem. Mater.* 2011, 23, 1387–1395.
88. Pinto, M.L.; Pires, J. Porous and hybrid clay-based materials for separation of hydrocarbons. *Microporous Mesoporous Mater.* 2012, 151, 403–410.
89. Garea, S.A.; Mihai, A.J.; Ghebaur, A.; Nistor, C.; Sarbu, A. Porous clay heterostructures: A new inorganic host for 5-fluorouracil encapsulation. *Int. J. Pharm.* 2015, 492, 299–309.
90. Chmielarz, L.; Piwowarska, Z.; Kustrowski, P.; Wegrzyn, A.; Gil, B.; Kowalczyk, A.; Dudek, B.; Dziembaj, R.; Michalik, M. Comparison study of titania pillared interlayered clay and porous clay heterostructures modified with copper and iron as catalysts of the DeNO_x process. *Appl. Clay Sci.* 2011, 53, 164–173.
91. Cecilia, J.A.; Arango-Diaz, A.; Jimenez-Jimenez, J.; Storaro, L.; Moretti, E.; Rodriguez-Castellon, E. CuO-CeO₂ supported on montmorillonite-derived porous clay heterostructures (PCH) for preferential CO oxidation in H₂-rich stream. *Catal. Today* 2015, 253, 126–136.
92. Soriano, M.D.; Cecilia, J.A.; Natoli, A.; Jimenez-Jimenez, J.; Nieto, J.M.L.; Rodriguez-Castellon, E. Vanadium oxide supported on porous clay heterostructure for the partial oxidation of hydrogen sulphide to sulphur. *Catal. Today* 2015, 254, 36–42.
93. Saboya, R.M.A.; Cecilia, J.A.; Garcia-Sancho, C.; Luna, F.M.T.; Rodriguez-Castellon, E.; Cavalcante, C.L. WO₃-based catalysts supported on porous clay heterostructures (PCH) with Si–Zr pillars for synthetic esters production. *Appl. Clay Sci.* 2016, 124–125, 69–78.
94. Azzouz, A.; Platon, N.; Nousir, S.; Ghomari, K.; Nistor, D.; Shiao, T.C.; Roy, R. OH-enriched organo montmorillonites for potential applications in carbon dioxide separation and concentration. *Sep. Purif. Technol.* 2013, 108, 181–188.
95. Cavenati, S.; Grande, C.A.; Rodrigues, A.E. Separation of CH₄/CO₂/N₂ mixtures by layered pressure swing adsorption for upgrade of natural gas. *Chem. Eng. Sci.* 2006, 61, 3893–3906.
96. Grande, C.A.; Rodrigues, A.E. Electric swing adsorption for CO₂ removal from flue gas. *Int. J. Greenh. Gas Control* 2008, 2, 194–202.
97. Zhang, J.; Webley, P.A.; Xiao, P. Effect of process parameters on power requirements of vacuum swing adsorption technology for CO₂ capture from flue gas. *Energy Convers. Manag.* 2008, 49, 346–356.
98. Gupta, S.K.; Lesslie, R.D.; King, A.D. Solubility of alcohols in compressed gases. A comparison of vapor-phase interactions of alcohols and homomorphic compounds with various gases I. Ethanol in compressed helium, hydrogen, argon, methane, ethylene, ethane, carbon dioxide, and nitrous oxide. *J. Phys. Chem.* 1973, 77, 2011–2015.
99. Massoudi, R.; King, A.D. Solubility of alcohols in compressed gases. A comparison of vapor-phase interactions of alcohols and homomorphic compounds with various gases II. 1-Butanol, diethyl ether, and n-pentane in compressed nitrogen, argon, methane, ethane, and carbon dioxide at 25.deg. *J. Phys. Chem.* 1973, 77, 2016–2018.
100. Saharay, M.; Balasubramanian, S. Electron donor–acceptor interactions in ethanol–CO₂ mixtures: An ab initio molecular dynamics study of supercritical carbon dioxide. *J. Phys. Chem. B* 2006, 110, 3782–3790.

101. Azzouz, A.; Ursu, A.-V.; Nistor, D.; Sajin, T.; Assaad, E.; Roy, R. TPD study of the reversible retention of carbon dioxide over montmorillonite intercalated with polyol dendrimers. *Thermochim. Acta* 2009, 496, 45–49.
102. Calderon, M.; Quadir, M.A.; Sharma, S.K.; Haag, R. Dendritic polyglycerols for biomedical applications. *Adv. Mater.* 2010, 22, 190–218.
103. Gassensmith, J.J.; Furukawa, H.; Smaldone, R.A.; Forgan, R.S.; Botros, Y.Y.; Yaghi, O.M.; Stoddart, J.F. Strong and reversible binding of carbon dioxide in a green metal–organic framework. *J. Am. Chem. Soc.* 2011, 133, 15312–15315.
104. Garcia-Gallastegui, A.; Iruretagoyena, D.; Gouvea, V.; Mokhtar, M.; Asiri, A.M.; Basahel, S.N.; Al-Thabaiti, S.A.; Alyoubi, A.O.; Chadwick, D.; Sha, M.S.P. Graphene oxide as support for layered double hydroxides: Enhancing the CO₂ adsorption capacity. *Chem. Mater.* 2012, 24, 4531–4539.
105. Galarneau, A.; Barodawalla, A.; Pinnavaia, T.J. Porous clay heterostructures formed by gallery-templated synthesis. *Nature* 1995, 374, 529–531.
106. Cecilia, J.A.; Garcia-Sancho, C.; Franco, F. Montmorillonite based porous clay heterostructures: Influence of Zr in the structure and acidic properties. *Microporous Mesoporous Mater.* 2013, 176, 95–102.
107. Humphrey, J.; Boyd, D. *Clay: Types, Properties and Uses*; Nova Science Publishers, Inc.: New York, NY, USA, 2011.
108. Nawani, P.; Gelfer, M.Y.; Hsiao, B.S.; Frenkel, A.; Gilman, J.W.; Khalid, S. Surface Modification of nanoclays by catalytically active transition metal ions. *Langmuir* 2007, 23, 9808–9815.
109. Zope, I.S.; Dasari, A.; Camino, G. Elucidating the catalytic effect of metal ions in montmorillonite on thermal degradation of organic modifier. *Mater. Chem. Phys.* 2015, 157, 69–79.
110. Reddy, C.R.; Bhat, Y.S.; Nagendrappa, G.; Jai Prakash, B.S. Brønsted and Lewis acidity of modified montmorillonite clay catalysts determined by FT-IR spectroscopy. *Catal. Today* 2009, 141, 157–160.
111. Tang, T.; Chen, X.; Meng, X.; Chen, H.; Ding, Y. Synthesis of multiwalled carbon nanotubes by catalytic combustion of polypropylene. *Angew. Chem. Int. Ed.* 2005, 44, 1517–1520.
112. Tang, T.; Chen, X.; Chen, H.; Meng, X.; Jiang, Z.; Bi, W. Catalyzing carbonization of polypropylene itself by supported nickel catalyst during combustion of polypropylene/clay nanocomposite for improving fire retardancy. *Chem. Mater.* 2005, 17, 2799–2802.
113. Hu, Y.; Wang, X.; Li, J. Regulating effect of exfoliated clay on intumescent char structure and flame retardancy of polypropylene composites. *Ind. Eng. Chem. Res.* 2016, 55, 5892–5901.