

# Adsorption of Carbon Dioxide for Post-combustion Capture: A Review

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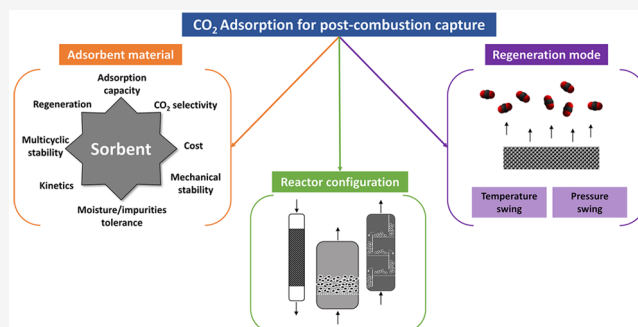
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**ABSTRACT:** Aiming at meeting the global goals established for carbon dioxide (CO<sub>2</sub>) reduction, carbon capture and storage (CCS) plays a key role. In this framework, the adsorption-based CO<sub>2</sub> post-combustion capture is considered one of the most promising approaches because it can provide remarkable energy savings with respect to the standard amine-based absorption capture. To date, most of the research effort has been devoted to the development of novel cutting-edge adsorbent materials with the primary purpose of enhancing the adsorption capacity and lifetime while reducing the heat of adsorption, thus lessening the energetic requirement of the sorbent regeneration. Anyway, other factors, beyond the sorbents, greatly affect the competitiveness of the CO<sub>2</sub> capture based on the adsorption route, namely, the gas–solid contacting system, impacting the sorbent utilization efficiency, and the regeneration strategies, determining most of the global CO<sub>2</sub> capture costs. This review describes the state-of-the-art and most recent progresses of the adsorption-based CO<sub>2</sub> post-combustion capture. In particular, the first section describes the CO<sub>2</sub> adsorption performances of different classes of solid sorbents on the basis of the most important evaluation parameters (equilibrium adsorption capacity, multi-cyclic stability, etc.). In the second section, the two main gas–solid contacting systems, i.e., fixed beds and fluidized beds, have been reviewed, pointing out their strengths and limitations. Finally, the third section provides a review on the different regeneration modes (temperature, pressure, or hybrid swings), with a focus on the possible strategies available to limit the energy penalty.



## 1. INTRODUCTION

According to the Paris Agreement, dangerous climate change will be avoided by limiting global warming to well below 2 °C and pursuing efforts to limit it to 1.5 °C.<sup>1</sup> Therefore, a radical transformation of the way we produce and consume energy will be needed to achieve a rapid reduction in emissions of greenhouse gases (GHGs). In this framework, the International Energy Agency (IEA) has highlighted, in the Energy Technology Perspectives 2020 report,<sup>2</sup> that carbon capture and storage (CCS) will play a major role for the success of the Paris Agreement, being one of four key pillars of global energy transitions, alongside renewable-based electrification, bioenergy, and hydrogen. CCS consists of the separation of fossil CO<sub>2</sub> from industrial and energy-related sources and transport to a storage location, where it can be permanently stored (Figure 1); captured CO<sub>2</sub> can be alternatively used in a variety of ways, including enhanced oil recovery (EOR), improving the growth of plants and algae,<sup>3</sup> or as a raw material in the production of fuels, chemicals, or building materials.<sup>2</sup>

To date, dependent upon the process or plant application in question, there are four main approaches to capture CO<sub>2</sub> generated from a primary fossil fuel (coal, natural gas, or oil), biomass, wastes, or mixtures of these fuels: post-combustion,

pre-combustion, oxyfuel, and chemical looping processes (Figure 1). In post-combustion systems, CO<sub>2</sub> is separated from the flue gases produced by the combustion of the primary fuel in air, thus providing the main advantage of being able to be adapted/retrofitted to any existing plants, many of which were built recently and could operate for decades to come.<sup>4</sup> In pre-combustion systems, the primary fuel is processed in a reactor with steam and air or oxygen to produce a mixture consisting mainly of CO and H<sub>2</sub> ("synthesis gas").<sup>4</sup> Additional H<sub>2</sub>, together with CO<sub>2</sub>, is produced by reacting CO with steam in a second reactor (a "shift reactor"). The resulting mixture of H<sub>2</sub> and CO<sub>2</sub> can then be separated; CO<sub>2</sub> is stored, whereas H<sub>2</sub> is a carbon-free energy carrier that can be combusted to generate power and/or heat or used to produce fuels/chemicals. The high concentrations of CO<sub>2</sub> produced by the

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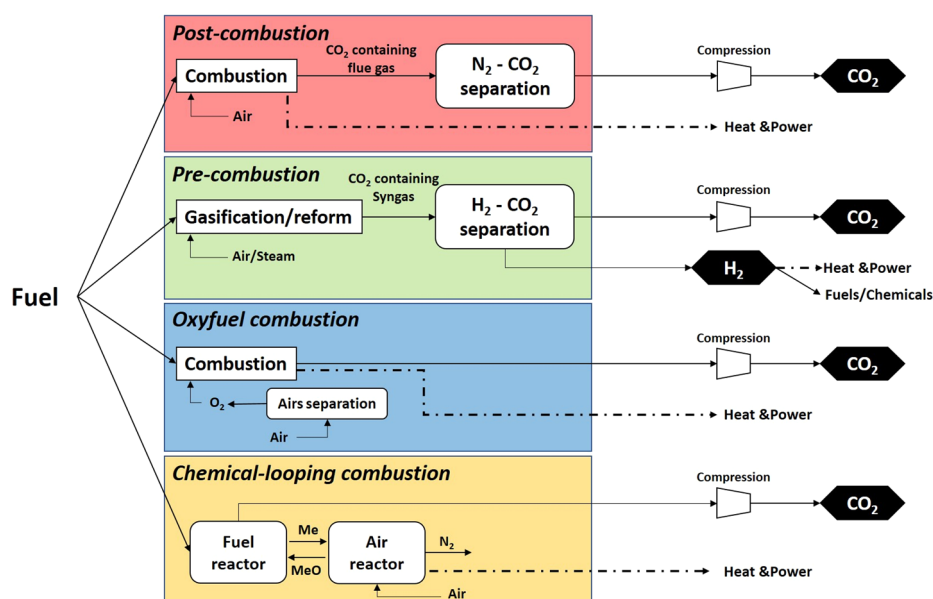


Figure 1. Schematic representation of capture systems.

shift reactor (typically up to 60% by volume on a dry basis) and the high pressures often encountered in these applications make the  $\text{CO}_2$  separation easier than in post-combustion; however, the initial fuel conversion steps are more elaborate and costly than in post-combustion systems.<sup>4</sup> In oxyfuel combustion systems,  $\text{O}_2$  is used instead of air for combustion of the primary fuel to produce a flue gas that is mainly water vapor and  $\text{CO}_2$ .<sup>4</sup> This results in a flue gas with high  $\text{CO}_2$  concentrations (greater than 80% by volume). The water vapor is then removed by cooling and compressing the gas stream. However, oxyfuel combustion requires the upstream separation of oxygen from air, with a purity of 95–99% oxygen assumed in most current designs.<sup>5</sup>

The main idea of chemical looping combustion is to split combustion of a hydrocarbon or carbonaceous fuel into separate oxidation and reduction reactions.<sup>6</sup> In particular, a solid oxygen carrier (generally a metal oxide) is used to transfer oxygen from the air to the fuel. The advantage of this technique compared to normal combustion is that  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are inherently separated from the other components of the flue gas, namely,  $\text{N}_2$  and unreacted  $\text{O}_2$ , and thus no extra energy is needed for  $\text{CO}_2$  separation.<sup>6</sup> However, the development of a suitable oxygen carrier, being able to provide a high fuel conversion ratio, high oxygen transport capacity, and good stability, still represents an open challenge.<sup>7</sup>

Among all of these possible solutions, post-combustion  $\text{CO}_2$  capture is a straightforward approach and forms the basis of the current infrastructure in CCS. Despite distinct advantages of both pre-combustion and oxy-fuel capture, these methods will unlikely replace the post-combustion capture on a global scale.<sup>4,8</sup> On the contrary, post-combustion capture remains the only solution capable of delivering significant emission reductions from existing large stationary sources, essentially power stations and large industrial plants.<sup>8</sup> Moreover, in combination with bioenergy or through direct air capture, it can also generate “negative emissions”, a challenging option for limiting future temperature increases to 2 °C or below. In this framework, the main difficulty of post-combustion capture is represented by the need to produce a highly concentrated  $\text{CO}_2$  stream matching the purity requirement for transportation and

storage from the flue gas stream, where  $\text{CO}_2$  is highly diluted: between 4% for the natural gas combined cycle (NGCC) and 15% for pulverized coal (PC).<sup>9</sup> One more explanation for the slow deployment of fully integrated commercial post-combustion capture schemes is the considerable cost of the capture phase, which represents approximately two-thirds of the total cost for CCS.<sup>9</sup> Therefore, the development of an efficient and cost-effective  $\text{CO}_2$  capture technique is considered to be one of the highest priorities in the field of CCS.<sup>4,8</sup>

Dependent upon the principle of the capture process, there are different types of separation techniques to separate  $\text{CO}_2$  from the flue gas stream: absorption by means of solvents, membranes, cryogenics, adsorption by solid materials, and calcium looping cycle.<sup>10</sup> Among these, amine-based absorption is the most mature option for post-combustion and is actually applied for the separation of  $\text{CO}_2$  in real industrial processes (e.g., natural gas sweetening and production of hydrogen and ammonia).<sup>11,12</sup> However, when applied for post-combustion applications, absorption is characterized by serious shortcomings, such as high energy demands to regenerate the sorbent, corrosion problems, amine losses as a result of evaporation, thermal/chemical degradation of the amines caused by the presence of oxygen, and environmental concerns about amine disposal.<sup>11,12</sup>

In this framework, adsorption, relying on the ability of gases (the adsorbate) to be adsorbed on a solid surface (the adsorbent), which can be subsequently regenerated by acting on either the temperature (temperature swing) or the pressure (pressure swing) of the system, has been receiving great research interest because of its favorable characteristics over all of the other alternative solutions.<sup>13</sup> In particular, it can provide remarkable energy savings with respect to the amine-based absorption approach.<sup>14,15</sup> Besides that, it can be quite easily retrofitted to existing plants also offering a wide flexibility of capturing  $\text{CO}_2$  from different industrial  $\text{CO}_2$  sources as a result of different available sorbent regeneration modes and reactor types.<sup>16</sup> Thus far, research efforts have been focused primarily on the development of the sorbent materials aiming at reducing the energy penalty by minimization of the heat of adsorption and maximization of the adsorption capacity.

However, it is important to point out that other aspects, affecting the performance/competitiveness and overall cost of the CO<sub>2</sub> adsorption process, must be taken into account for adsorption to become one of the leading capture techniques. Indeed, even though this gas separation technology is mature in a number of large-scale industrial applications, its application to post-combustion CO<sub>2</sub> capture still needs very intense research effort to develop, beyond suitable materials,<sup>17–19</sup> also innovative designs for an improved gas–solid contact system<sup>20–23</sup> and appropriate regeneration strategies.<sup>14,20–22</sup>

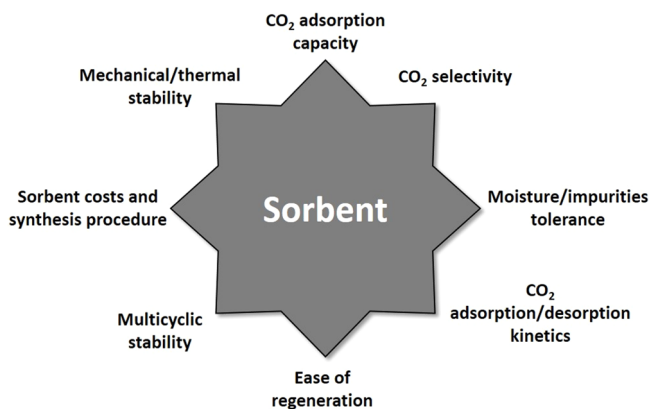
This review provides a critical review of the state-of-the-art adsorption-based systems for post-combustion CO<sub>2</sub> capture. In particular, an in-depth analysis of the literature has been performed, paying attention to the CO<sub>2</sub> adsorbents, regeneration modes, and reactor configuration, thus tracing the main paths currently pursued toward the development of suitable CO<sub>2</sub> adsorption processes.

## 2. ADSORBENT MATERIALS

Adsorption occurs when molecules diffusing in the gaseous phase are held by forces emanating from an adjacent solid surface. On the basis of the nature of the forces involved in the attraction between the adsorbate molecules and the adsorbent, two kinds of adsorption can be defined: physical and chemical adsorption. In physical adsorption, the adsorbate molecules are attracted to the sorbent surface by van der Waals forces and have a low heat of adsorption (i.e., low bond energy on the order of 10 kJ mol<sup>−1</sup>).<sup>13</sup> In such cases, the terms physisorption and physical adsorbents are used to describe the phenomenon and the sorbents, respectively. Because the forces involved are not strong, this adsorption may be easily reversed. On the contrary, in the chemical adsorption, additional forces bind adsorbed molecules to the solid surface (roughly equal to the heat of reaction, 100 kJ mol<sup>−1</sup>), involving the exchange or sharing of electrons or possibly atoms, forming molecules or radicals.<sup>13</sup> In such cases, the terms chemisorption and chemical adsorbents are used to describe the phenomenon and the sorbents, respectively. This is less easily reversed than physical adsorption, and regeneration may be more challenging.

As discussed in the previous paragraph, the selection of suitable sorbents (either physical or chemical) is one of the main points to be addressed and is, indeed, quite complex because the sorbent materials must satisfy several chief criteria to match both the economic and performance requirements under typical post-combustion operating conditions (i.e., low CO<sub>2</sub> pressure up to 0.2 atm) (Figure 2).<sup>4</sup>

- CO<sub>2</sub> adsorption capacity: The equilibrium adsorption capacity of a sorbent, namely, the amount of CO<sub>2</sub> adsorbed at the thermodynamic equilibrium (i.e., achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which they desorb), is of chief importance to the capital cost of the capture system, because it dictates the amount of adsorbent required, thus also fixing the volume of the adsorber vessel. Therefore, a sorbent providing high CO<sub>2</sub> adsorption capacity reduces both the sorbent quantity and size of the process equipment. In this framework, proper adsorbent materials should exhibit a CO<sub>2</sub> adsorption isotherm with a steep slope (favorable CO<sub>2</sub> adsorption isotherm) corresponding to high uptake at low CO<sub>2</sub> partial pressure. Even though the equilibrium



**Figure 2.** Schematic representation of properties of the required adsorbents.

CO<sub>2</sub> adsorption capacity can be actually useful to compare different sorbents, their actual applicability in real cyclic processes cannot be inferred only from this parameter. Indeed, from a practical perspective, it is more significant to evaluate the working in place of the total CO<sub>2</sub> capacity, i.e., the actual amount of CO<sub>2</sub> that can be captured during a full adsorption/desorption cycle.<sup>15,24</sup> This is defined as the difference in the quantity of CO<sub>2</sub> adsorbed during the adsorption (i.e., from a low-temperature and low-purity stream) and desorption (i.e., from a high-temperature and high-purity stream) steps.<sup>25,26</sup> In this framework, it is widely suggested that a CO<sub>2</sub> working capacity in the range of 3–4 mmol g<sup>−1</sup> should be exhibited by an optimum CO<sub>2</sub> adsorbent to be competitive with an existing monoethanolamine (MEA) scrubbing system.<sup>27,28</sup>

- CO<sub>2</sub> selectivity: The selectivity, defined as the ratio of the CO<sub>2</sub> capacity to that of another component (e.g., N<sub>2</sub>) present in the flue gas stream at a given flue gas composition, directly affects the purity of captured CO<sub>2</sub>, which, in turn, impacts both the transportation and sequestration processes and economics. Therefore, proper sorbents should be able to provide high CO<sub>2</sub> selectivity over other components present in the flue gas.
- Tolerance to moisture and other impurities in the flue gas stream: Together with CO<sub>2</sub> and N<sub>2</sub>, flue gas discharged from plants contains water vapor and other species, such as NO<sub>x</sub> and SO<sub>x</sub>; even after being subjected to a denitrification/desulfurization process, NO<sub>x</sub> and SO<sub>x</sub> may still remain (in parts per million amounts) as impurities. Therefore, a suitable adsorbent should be characterized by a proper tolerance to such impurities, so that the capture process is not negatively affected from the economical and operational point of view.<sup>29</sup> Indeed, the main problem concerning the presence of moisture is the reduction in the adsorption capacity of most of the currently well-developed CO<sub>2</sub> adsorbents (such as activated carbons and zeolites). Therefore, the limiting step is the development of sorbents with specific properties, for which adsorption of H<sub>2</sub>O and other impurities would not be competitive with that of CO<sub>2</sub>, to avoid the need of an upstream drying/purification step, which would adversely impact the CO<sub>2</sub> capture economics.
- Adsorption kinetics: Fast adsorption kinetics for CO<sub>2</sub> is essential for a proper CO<sub>2</sub> sorbent because kinetics



controls the cycle time of a dynamic adsorption system; indeed, the faster CO<sub>2</sub> is adsorbed, the more economical the whole capture process will be.<sup>30,31</sup> In this framework, sorbent with fast kinetics provides steep CO<sub>2</sub> breakthrough curves (i.e., CO<sub>2</sub> concentration in the effluent stream as a function of time), while slow kinetics yields expanded breakthrough curves, thus remarkably impacting the amount of sorbent required.<sup>32,33</sup>

- **Easiness in regeneration:** A proper sorbent should be characterized by mild conditions for regeneration to reduce the cost of the capture. In this framework, the required regeneration energy is measured by the heat of adsorption, which should be as low as possible. Clearly, the heats of adsorption are substantially different in the case of physisorbents (20–50 kJ mol<sup>-1</sup>) and chemisorbents (60–100 kJ mol<sup>-1</sup>).<sup>28</sup>
- **Stability to repeated adsorption–desorption cycles:** A proper adsorbent should be able to provide a long lifetime, i.e., low frequency of replacement, to positively affect the economics of a real-scale operation.<sup>28</sup> As a matter of fact, the sorbent recyclability directly affects the overall cost of the post-combustion CO<sub>2</sub> capture process; for example, a sorbent characterized by a higher production cost but with exceptional regenerability may be better than a cheaper sorbent characterized by a poor cyclic stability.
- **Sorbent costs and synthesis procedure:** These represent perhaps the subtlest characteristics. According to the sensitivity analysis presented by Tarka et al.,<sup>34</sup> a cost of approximately \$5 kg<sup>-1</sup> of sorbent would be a good compromise. Besides being cost-effective, the sorbent synthesis approach and manufacturing process should also be environmentally benign and easily scalable.<sup>35</sup>
- **Mechanical/thermal stability:** A proper adsorbent should be characterized by a good microstructure and morphological stability to keep its original CO<sub>2</sub> capture performances (CO<sub>2</sub> adsorption capacity and kinetics) during multi-cyclic operations and, thus, minimize the sorbent makeup rate and CO<sub>2</sub> capture process economics.<sup>4</sup> Indeed, specific operating conditions, such as high volumetric flow rate of flue gas, vibration, and temperature, should not impact the sorbent particles, causing significant disintegration via abrasion or crushing also during handling and storage.

Even though the above-discussed properties are desirable for an ideal adsorbent, hardly will a single adsorbent have all of these attributes.

CO<sub>2</sub> adsorbents can be categorized in several ways based on their chemical composition or structural characteristics (e.g., on the basis of the pore size, they can be classified as micro- and mesoporous adsorbents) or according to the adsorption mechanism involved (i.e., physical versus chemical). Therefore, different class of adsorbents will be revised in the following paragraphs to provide a general overview of the advantages and limitations of each family of adsorbents.

**2.1. Physisorbents.** In physisorption, the mechanism for CO<sub>2</sub> capture consists of the molecules of CO<sub>2</sub> being adsorbed on the sorbent surface as a result of van der Waals attraction between the CO<sub>2</sub> molecules and adsorbent surface as well as pole–ion and pole–pole interactions between the quadruple of CO<sub>2</sub> and the ionic and polar sites of the solid adsorbent surface.

In this section, an overview of the recent progress in CO<sub>2</sub> adsorption by solid physisorbents, i.e., carbon-based sorbents, zeolites, and metal–organic frameworks (MOFs), is provided.

**2.1.1. Carbon-Based Sorbents.** With carbon being the sixth most abundant element in the world,<sup>1</sup> carbonaceous materials are widely available in different classes, such as activated carbons (ACs) and carbon nanomaterials, i.e., carbon nanotubes (CNTs), fullerenes, graphene, and carbon nanofilms or fibers. All of these carbon-based materials are typically cheap and characterized by a high specific surface area and pore volume.<sup>1</sup>

ACs, which are among the most widely used adsorbents in industry, are less expensive compared to other adsorbents<sup>36,37</sup> but are typically characterized by lower adsorption capacity with respect to zeolites under low CO<sub>2</sub> pressure<sup>36</sup> and very low density. As common for physisorbents, ACs are characterized by excellent regenerability, with their capture performances being stable over several adsorption/desorption cycles.<sup>38</sup> ACs, with different micro- and mesoporous structures, can be produced using different raw materials, such as coal, coke pitch, wood, or biomass sources (e.g., spent coffee grounds, olive stones, coconut shells, sawdust, etc.).<sup>39</sup> Regardless of the specific raw materials, ACs are characterized, besides high specific surface area and pore volume, by a peculiar chemical nature giving them either an acidic or basic character.<sup>1,13,40,41</sup> In particular, their chemical nature is defined by the heteroatoms present in their structure, such as nitrogen, hydrogen, oxygen, phosphorus, sulfur, etc., which may come from either the composition of the raw material or the activation process.<sup>4</sup> More specifically, their adsorption capacity and selectivity toward CO<sub>2</sub> depend upon the surface functional groups formed from these heteroatoms and the delocalized electrons of the carbon structure.<sup>4</sup> In particular, the acidic character of ACs is closely related to the presence of functional groups containing oxygen, with the acidity being greater when the oxygen concentration on the AC surface increases.<sup>4</sup> On the contrary, the basic character of ACs is tightly linked to the resonance of  $\pi$  electrons present in carbon aromatic rings, which attract protons and nitrogen-containing groups.<sup>4</sup>

Wide literature is available on the production of ACs using different activation techniques to optimize the capacity for CO<sub>2</sub> sorption.<sup>13,40,42</sup> In this framework, ACs can be prepared either physically or chemically.<sup>43</sup> Summarized CO<sub>2</sub> adsorption properties and performances of different physically and chemically activated carbons are reported in Tables 1 and 2, respectively.

In the former case, the raw material is converted into pyrogenic carbon at relatively low-temperature conditions and in inert atmosphere, and then the carbon is activated with steam, CO<sub>2</sub>, O<sub>2</sub>, or other gases at high-temperature conditions (800–1000 °C).<sup>49–52</sup> Indeed, these high temperatures, in an inert nitrogen or helium atmosphere, induce the decomposition/removal of most of the oxygen functional groups present on carbon surfaces, thus causing an increase of the Lewis basic sites on oxygen-free carbon, i.e., an increase of the hydrophobicity of AC.<sup>4,53</sup> In the latter case, chemicals, such as acid, base, or salt, are used to treat the raw feedstock material to increase the surface area as well as add (or remove) specific surface functional groups.<sup>4,53</sup> In particular, basic nitrogen functionalities are typically introduced to the carbon surfaces<sup>4,54</sup> through the reaction with nitric acid, ammonia, amines, and nitrogen-containing precursors.<sup>55</sup>

**Table 1. CO<sub>2</sub> Adsorption Performances of Physically Activated Carbons<sup>a</sup>**

raw material	atmosphere	surface area (m <sup>2</sup> g <sup>-1</sup> )	P <sub>CO<sub>2</sub></sub> (atm)	adsorption capacity at T = 298 K (mmol g <sup>-1</sup> )	reference
coconut shell	CO <sub>2</sub>	371	0.20	1.80	44
almond shell	CO <sub>2</sub>	862	1.00	2.70	45
olive stone	CO <sub>2</sub>	1215	1.00	3.10	45
coffee residue	CO <sub>2</sub>	593	1.00	2.4	46
dialdehyde cellulose	CO <sub>2</sub>	1241	1.00	5.52	47
<i>Cladophora</i> cellulose	CO <sub>2</sub>	832	1.00	4.97	47
dialdehyde cellulose	N <sub>2</sub>	455	1.00	3.21	47
<i>Cladophora</i> cellulose	N <sub>2</sub>	500	1.00	2.64	47
almond shell	O <sub>2</sub> (3%)	557	1.00	2.10	48
olive stone	O <sub>2</sub> (3%)	697	1.00	2.00	48

<sup>a</sup>Process conditions (P<sub>CO<sub>2</sub></sub> and T) are also provided for a better comparison. P<sub>CO<sub>2</sub></sub>, CO<sub>2</sub> partial pressure; T, temperature.

ACs are typically characterized by important advantages, with respect to other sorbent materials, such as ease of regeneration (i.e., low regeneration energy and temperature), wide availability of the raw materials, and high thermal stability. With regard to their adsorption performances, they can be generally enhanced increasing the CO<sub>2</sub> partial pressure.<sup>13</sup> Even though in a much more limited way than that observed for other adsorbent materials (e.g., zeolites), AC adsorption capacity is also reported to be negatively affected by the presence of moisture and the poisoning of impurities, such as NO<sub>x</sub> and SO<sub>x</sub>; therefore, a decrease in their CO<sub>2</sub> adsorption capacity is often observed with respect to that obtainable under dry conditions.<sup>56,57</sup> With regard to the mechanical stability, ACs are typically friable materials, and therefore, they may undergo severe attrition phenomena during operation.<sup>13</sup> Most of the research efforts are recently focused on the improvement of AC CO<sub>2</sub> adsorption capacity and selectivity at low carbon dioxide partial pressure, also exploring the use of novel raw sources (such as waste materials) to produce sorbents with a tunable active surface area and pore size.<sup>42</sup>

With regard to carbon nanomaterials, including carbon nanotube (CNT) and graphene, whose CO<sub>2</sub> adsorption properties and performances are summarized in Table 3, they are typically characterized by quite good CO<sub>2</sub> adsorption capacity, fast adsorption kinetics, tolerance to moisture, and

**Table 3. CO<sub>2</sub> Adsorption Performances of CNT- and Graphene-Based Adsorbents<sup>a</sup>**

sorbent	surface area (m <sup>2</sup> g <sup>-1</sup> )	T (K)	P <sub>CO<sub>2</sub></sub> (atm)	adsorption capacity (mmol g <sup>-1</sup> )	reference
CNTs	394	298	0.10	0.52	67
MWCNTs		293	0.20	0.84	68
MWCNTs	407	293	0.15	0.64	69
MWCNTs	407	333	0.10	0.34	69
SWCNTs	1587	308	0.10	0.50	70
graphene	477	273	0.15	0.70	71
graphene nanoplates	480	298	0.20	0.35	72

<sup>a</sup>Process conditions (P<sub>CO<sub>2</sub></sub> and T) are also provided for a better comparison. P<sub>CO<sub>2</sub></sub>, CO<sub>2</sub> partial pressure; T, temperature.

low regeneration energy requirement.<sup>36</sup> Besides that, they can typically rely on a well-defined pore size distribution (hierarchical porous structure with both macro- and micropores), high specific surface area, and good chemico-physical stability.<sup>36</sup>

In particular, their peculiar porous structure can be very suitable for CO<sub>2</sub> capture because low-resistance pathways are granted by the macropores, whereas a high surface area is offered by micropores. In this class of materials, great research effort has been focused on the synthesis and characterization of CNTs for CO<sub>2</sub> capture, in particular multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs).<sup>73,74</sup> It has been shown that four main factors greatly impact the CO<sub>2</sub> adsorption of CNTs: the fraction of the opened and unblocked nanotubes, the oxygen content, the available adsorption sites, and the metal/non-metal dopants/eventual impurities.<sup>75</sup> Considering that the CO<sub>2</sub> adsorption capacity of CNTs is greatly influenced by the oxygen content, several works available in the literature focused on the formation of functional oxygen-containing groups, such as -OH, -CO, and -COOH, by means of acids, plasma, and ozone and their removal by heating.<sup>4</sup> Indeed, the variety of functional groups on the surface can be altered by either the thermal or chemical treatments (or combined thermochemical treatments), thus improving the selectivity and CO<sub>2</sub> adsorption capacity of CNTs.

Graphene, which is a flat single layer of sp<sup>2</sup>-hybridized carbon atoms densely packed into an ordered two-dimensional honeycomb network, is another class of carbon nanomaterials with interesting CO<sub>2</sub> adsorption capacity.<sup>76</sup> In light of its large active surface area, in the past decade, great research interest

**Table 2. CO<sub>2</sub> Adsorption Performances of Chemically Activated Carbons<sup>a</sup>**

raw material	activator	surface area (m <sup>2</sup> g <sup>-1</sup> )	T (K)	adsorption capacity at P <sub>CO<sub>2</sub></sub> = 1 atm (mmol g <sup>-1</sup> )	reference
cellulose	KOH	2370	273	5.80	58
starch	KOH	2190	273	5.60	58
algae	KOH	1940	273	7.40	59
yeast	KOH	1348	298	4.80	60
sludge	NaOH	179	298	1.30	61
wood	H <sub>3</sub> PO <sub>4</sub>	1889	303	2.90	62
palm stone	H <sub>3</sub> PO <sub>4</sub>	1320	273	3.10	63
hazelnut shell	NaNH <sub>3</sub>	2318	273	5.91	64
coconut shell	K <sub>2</sub> CO <sub>3</sub>	1082	273	5.12	65
sub-bituminous coal	K <sub>2</sub> CO <sub>3</sub>	1773	273	4.36	66

<sup>a</sup>Process conditions (P<sub>CO<sub>2</sub></sub> and T) are also provided for a better comparison. P<sub>CO<sub>2</sub></sub>, CO<sub>2</sub> partial pressure; T, temperature.

Table 4. CO<sub>2</sub> Adsorption Performances of Zeolites and Zeolite-Like Sorbents<sup>a</sup>

sorbent	nature	type	framework	surface area (m <sup>2</sup> g <sup>-1</sup> )	T (K)	P <sub>CO<sub>2</sub></sub> (atm)	adsorption capacity (mmol g <sup>-1</sup> )	reference
13X	synthetic	Na-exchanged X zeolite	FAU	710	393	0.15	0.70	93
13X	synthetic	Na-exchanged X zeolite	FAU	960	298	0.10	0.38	78
NaY	synthetic	Na-exchanged Y zeolite	FAU		295	1.00	4.06	94
NaY	synthetic	Na-exchanged Y zeolite	FAU	542	323	0.20	0.05	95
NaX	synthetic	Na-exchanged X zeolite	FAU	534	323	0.20	0.60	95
CaA	synthetic	Ca-exchanged A zeolite	LTA	397	323	0.20	0.75	95
CsY	synthetic	Cs-exchanged Y zeolite	FAU	842	333	0.10	0.86	96
APG-II	synthetic	Na-exchanged X zeolite	FAU	710	393	0.15	0.38	93
Naβ	synthetic	Na-exchanged β zeolite	BEA	570	273	0.15	2.30	97
Geopol-G13	synthetic	geopolymer		50	308	0.20	0.38	86
Na-G <sub>12</sub> -Z	synthetic	13X–geopolymer composite		211	308	0.20	1.5	87
ZAPS	natural	erionite		426	290	1	2.80	98
ZNT	natural	mordenite		266	290	1	1.80	98
yellow tuff	natural	tuff		141	298	0.15	0.62	33

<sup>a</sup>Process conditions (P<sub>CO<sub>2</sub></sub> and T) are also provided for a better comparison. P<sub>CO<sub>2</sub></sub>, CO<sub>2</sub> partial pressure; T, temperature; FAU, faujasite; LTA, Linde type A zeolite; and BEA, β zeolite.

has been devoted to the investigation of graphene as a possible CO<sub>2</sub> sorbent. In particular, these studies have been focused on three main aspects: development of new structures, surface modifications, and synthesis of hybrid materials with tunable porosity.<sup>13</sup> Indeed, different functional groups or heteroatoms can be attached to its surface, thus providing quite an easy tailoring of the surface properties without altering the original graphene structure.

**2.1.2. Zeolites and Zeolite-Like Sorbents.** Zeolites are highly ordered microporous crystalline materials made of silicon, aluminum, and oxygen.<sup>4</sup> More specifically, their crystals are TO<sub>4</sub> tetrahedra (with T = Si or Al), forming a matrix of channels and cavities that is able to provide a well-developed porous structure with a very high specific surface area.<sup>4</sup> Among all of the available sorbent materials, zeolites are very promising for post-combustion CO<sub>2</sub> capture because they exhibit high adsorption capacities in combination with fast adsorption kinetics under mild operating conditions (0–100 °C and 0.1–1 atm CO<sub>2</sub>), typical of post-combustion flue gases and biogas. Like ACs, zeolites are also among the best CO<sub>2</sub> adsorbents in terms of regenerability; indeed, their CO<sub>2</sub> adsorption isotherms typically do not show noticeable changes even after extensive adsorption/desorption cycling.<sup>77</sup> Summarized CO<sub>2</sub> adsorption properties and performances of different synthetic and natural zeolites are provided in Table 4.

A very interesting feature of zeolites is that their distinctive properties, such as chemical composition, pore size, and architecture, affect their CO<sub>2</sub> adsorption performance.<sup>77</sup> With regard to the chemical compositions, a negative charge in the framework is induced by the cations present in the silicate structure (e.g., Na<sup>+</sup> and Li<sup>+</sup>), which provide the zeolites with the ability to adsorb CO<sub>2</sub> with an extent depending upon the amount and nature of the cations.<sup>78</sup> Likewise, the Si/Al ratio is also reported to play a major role in controlling the CO<sub>2</sub> adsorption performances. In particular, it is widely accepted that the best performing zeolites for CO<sub>2</sub> capture are those having a low Si/Al ratio, which corresponds to a higher number of extra-framework cations in the lattice.<sup>79</sup> Indeed, the aluminum atoms present in the framework induce negative charges in the framework that are compensated by more exchangeable cations.

In this framework, several works are focused on the substitution of the cations originally present in the zeolite framework with alkali cations, such as Na, Rb, Li, Cs, and K, to further enhance the CO<sub>2</sub> adsorption capacity.<sup>80</sup> Even though zeolites with a low silica content can provide high CO<sub>2</sub> adsorption capacity and selectivity at a low pressure, they have a poor tolerance to the presence of moisture, thus remarkably hindering the CO<sub>2</sub> capture because H<sub>2</sub>O is preferentially adsorbed instead of CO<sub>2</sub>.<sup>81</sup> This issue encouraged several research activities investigating the CO<sub>2</sub> adsorption performances of hydrophobic zeolites with a high silica content, such as MWW zeotype<sup>82</sup> and NaZSM-5.<sup>83</sup> In analogy to carbon-based adsorbents, zeolites can also be poisoned by a trace amount of NO<sub>x</sub> or SO<sub>x</sub>, thus resulting in a decreased CO<sub>2</sub> adsorption capacity. With reference to the porous structure (pore size) of the zeolite, it controls the CO<sub>2</sub> diffusion rate and selectivity. In particular, zeolites with large pore sizes are characterized by enhanced CO<sub>2</sub> diffusion, whereas zeolites with small pore sizes (i.e., similar to the kinetic diameter of CO<sub>2</sub>) can provide an enhanced kinetic selectivity (separation of CO<sub>2</sub> and other gases).<sup>84</sup>

Also, in the framework of synthetic zeolites, geopolymers, being synthetic aluminosilicates with intrinsic and tunable porosity,<sup>85</sup> have also been investigated alone or in combination with 13X zeolite as CO<sub>2</sub> sorbents.<sup>86</sup> They exhibit interesting CO<sub>2</sub> adsorption capacity and selectivity in the low to medium range of carbon dioxide partial pressure (up to 20 vol %) as a result of a synergy in the composite material, where both 13X and NaA zeolite phases are present.<sup>86</sup> Furthermore, the geopolymer synthesis, operated at a low temperature with green materials, represents an easy protocol to produce monoliths or granules with improved mechanical resistance and limited impact on gas diffusion.

A viable alternative to synthetic zeolites, whose high synthesis cost and environmental footprint adversely influence their sustainability,<sup>87,88</sup> is represented by natural occurring zeolites. Natural zeolites are, indeed, largely available in different regions in the composition of different types of rocks.<sup>89,90</sup> Therefore, their variable composition that may change even in a single deposit, low purity, and likely inferior separation performance compared to the more performant synthetic zeolites are somehow counterbalanced by their



abundance and low or null price.<sup>89</sup> In this framework, natural zeolites have been promisingly tested for both CO<sub>2</sub> capture from flue gas<sup>33</sup> and biogas purification.<sup>91,92</sup>

**2.1.3. Metal–Organic Frameworks (MOFs).** MOFs are porous crystalline materials made of metallic species and organic ligands and have held great promise for CO<sub>2</sub> post-combustion capture,<sup>99</sup> in terms of CO<sub>2</sub> adsorption capacity and outstanding recycling stability with negligible reduction in their capture performances over repeated adsorption/desorption cycles.<sup>99</sup> Summarized CO<sub>2</sub> adsorption properties and performances of different MOFs are provided in Table 5.

**Table 5. CO<sub>2</sub> Adsorption Performances of MOFs<sup>a</sup>**

sorbent	surface area (m <sup>2</sup> g <sup>−1</sup> )	T (K)	P <sub>CO<sub>2</sub></sub> (atm)	adsorption capacity (mmol g <sup>−1</sup> )	reference
HKUST-1	680	298	0.15	1.14	105
MOF-508	323	323	0.10	0.10	106
HKUST-1		295	0.10	0.62	107
IRMOF-1	1892	298	0.10	0.08	107
Ni/DOBDC	936	298	0.10	4.07	107
Co/DOBDC	957	298	0.10	2.81	107
ZIF-8	1135	298	0.10	0.12	107
MIL-47	600	298	0.10	0.18	107
UMCM-1	4034	298	0.10	0.09	107

<sup>a</sup>Process conditions (P<sub>CO<sub>2</sub></sub> and T) are also provided for a better comparison. P<sub>CO<sub>2</sub></sub>, CO<sub>2</sub> partial pressure; T, temperature.

Because almost all metals and a wide variety of organic species can be adopted, a very large number of MOFs can be synthesized with different properties, such as pore size and structure;<sup>100</sup> indeed, by properly selecting the organic ligands and the metallic species, these features can be easily tuned to have high surface areas (up to 3000 m<sup>2</sup> g<sup>−1</sup>) and specific pore sizes.<sup>101</sup> In particular, MOFs with pore dimension compatible with the kinetic diameter of the CO<sub>2</sub> molecules and with polar functional groups inside the pores [−OH, −N=N−, −NH<sub>2</sub>, and −N=C(R)−], able to interact with the quadrupole moments of CO<sub>2</sub> molecules, have a higher CO<sub>2</sub> adsorption capacity.<sup>101</sup> MOFs can be divided into two main groups, rigid and flexible (dynamic). In the former case, they are characterized by a robust framework with permanent pores, like zeolites. In the latter case, they exhibit a soft (dynamic) framework that can change by means of external stimuli, such as the introduction of guest molecules, temperature, and pressure.<sup>102</sup>

It has been reported also that the pressure and temperature play a major role on the CO<sub>2</sub> adsorption on MOFs.<sup>101</sup> In particular, under low-pressure conditions, the CO<sub>2</sub> adsorption capacity depends upon the heat of adsorption, whereas under high-pressure conditions, the CO<sub>2</sub> adsorption capacity depends upon the specific surface area.

With regard to the thermal stability of MOFs, it can be enhanced by increasing the number of linkers connected to each node as a result of the superior strength of the bond between the node and linker.<sup>99</sup> In this concern, the use of oxyanion-terminated trivalent linker cations, like Al(3), Zr(3), and Ti(3), characterized by high bond enthalpy and bond dissociation energy, in place of commonly used linkers, such as the carboxylate group and divalent cations, also enhances the thermal stability.<sup>103</sup> Likewise, the hydrothermal stability of MOFs is also remarkably affected by the strength of the bond

between the node and the linker. In particular, MOFs in which the node–linker bond has a high heat of formation are more stable to the presence of moisture. Clearly, the hydrothermal stability can also be improved by modifying the MOF surface, i.e., introducing hydrophobic functionalities, for example, replacing H atoms in the ligands with F.<sup>104</sup> With regard to mechanical stability, in terms of elastic moduli, rigidity, and compressibility, it is influenced by the physical structure of MOFs rather than their chemical functionality. In this framework, increasing values of porosity yield a lower mechanical stability, despite porosity being beneficial to CO<sub>2</sub> adsorption.<sup>99,101</sup> Possible solutions to increase the mechanical stability of MOFs are reported to be filling MOFs with solvent, increasing of the coordination number of the metal, and shortening of the linker.<sup>99,101</sup>

With regard to the CO<sub>2</sub> adsorption capacity and selectivity, they can be enhanced using different strategies, such as fixing the pore size and shape, functionalization of the pore surface, and introduction of heterocyclic ligands, amino groups, phenolic hydroxyl groups, alkaline carbonates, and nitro groups.<sup>108</sup> Likewise, the hybridization of MOFs with carbon-based materials, like graphene-related materials (GRMs), has also been reported to be beneficial.<sup>109</sup> Despite their beneficial CO<sub>2</sub> adsorption characteristics, MOFs are, unfortunately, easily poisoned by H<sub>2</sub>S, SO<sub>x</sub>, and NO<sub>x</sub> (even at the trace level).<sup>4</sup> They exhibit, indeed, a great affinity toward these species that are preferentially adsorbed on the available adsorption sites, thus requiring their complete removal from the flue gas before introduction in the adsorption bed to avoid a drastic reduction in CO<sub>2</sub> adsorption capacity.

Even though MOFs hold great promise for post-combustion capture, the cost of their production and utilization is still high if compared to commercially available sorbents.<sup>99</sup> As a matter of fact, the synthesis/characterization of MOFs with expensive linkers has been tested only at the lab scale (milligram scale).<sup>35</sup> Moreover, as a result of the use of expensive and often toxic solvents, the currently available MOF synthesis routes can be hardly scaled up for large-scale applications in an environmentally friendly manner.<sup>35</sup> Therefore, the possibility to tune their characteristics at the molecular level must be combined with the need to limit their synthesis costs and environmental impact.<sup>99</sup>

**2.2. Chemisorbents.** The chemical adsorption of CO<sub>2</sub> exploits the fact that CO<sub>2</sub> is a nonpolar, linear molecule containing an electropositive C atom and two electronegative O atoms. Therefore, the adsorption of CO<sub>2</sub> on chemisorbents relies on the nucleophilic character of the chemical functional groups present on the sorbent surface and being able to chemically interact with the CO<sub>2</sub> molecule. Hence, the chemical functionalization of adsorbent materials, for example, by means of the introduction of different types of amines, has been proposed as a possible solution to overcome the main drawbacks of adsorption, i.e., the low CO<sub>2</sub> adsorption capacity and selectivity at low CO<sub>2</sub> partial pressure, which is also negatively affected by the presence of moisture in the feed, with the H<sub>2</sub>O adsorption being competitive with that of CO<sub>2</sub>.<sup>41,110</sup>

Amine-functionalized adsorbents can be classified according to the type of interactions between the amine groups and the support: amine-impregnated sorbents, characterized by weakly bonded polymeric amines, are synthesized by means of the quite simple impregnation method, consisting of physically mixing the support with amines and solvents; amine-grafted

**Table 6. CO<sub>2</sub> Adsorption Performances of Amine-Impregnated Sorbents<sup>a</sup>**

support	amine (loading wt %)	T (K)	P <sub>CO<sub>2</sub></sub> (atm)	adsorption capacity (mmol g <sup>-1</sup> )	reference
MCM-41	PEI (50)	348	0.10	2.10	112
MCM-41	PEI (50)	348	0.13	2.84	113
SBA-15	PEI (50)	348	0.15	1.95	114
β zeolite	TEPA (38)	303	0.10	2.08	115
zeolite 13X	MEA (25)	348	0.15	0.45	116
activated carbon	PEI (40)	298	1.00	1.98	117
PE-MCM-41	DEA (76)	298	0.05	3.00	118
Al <sub>2</sub> O <sub>3</sub>	DETA (40)	330	1.00	1.50	119
PMMA beads	DBU (30)	338	0.10	2.34	120
SBA-15	TEPA (30) + DEA (20)	348	0.05	3.77	121

<sup>a</sup>Process conditions (P<sub>CO<sub>2</sub></sub> and T) are also provided for a better comparison. P<sub>CO<sub>2</sub></sub>, CO<sub>2</sub> partial pressure; T, temperature.

**Table 7. CO<sub>2</sub> Adsorption Performances of Amine-Grafted Sorbents<sup>a</sup>**

support	amine (loading mmol g <sup>-1</sup> )	T (K)	P <sub>CO<sub>2</sub></sub> (atm)	adsorption capacity (mmol g <sup>-1</sup> )	reference
silica gel	AP (1.26)	323	1.00	0.89	125
PE-MCM-41	TRI (7.90)	323	0.10	1.59	126
SBA-16	AEAPS (3.06)	333	0.15	0.73	127
SBA-15	APTES (2.56)	338	0.10	0.45	128
silica spheres	EDA (0.99)	333	0.10	0.73	129
zeolite ITQ-6	AP (1.26)	293	0.12	0.67	130
SBA-15	aziridine polymer (9.78)	348	0.10	4.00	131

<sup>a</sup>Process conditions (P<sub>CO<sub>2</sub></sub> and T) are also provided for a better comparison. P<sub>CO<sub>2</sub></sub>, CO<sub>2</sub> partial pressure; T, temperature.

sorbents, characterized by covalently bonded small amine molecules or *in situ* formed polymeric amines, are synthesized by means of chemical tethering of amines to support surface upon synthesis (*in situ*) or post-synthesis modification.<sup>111</sup> Summarized CO<sub>2</sub> adsorption properties and performances of different amine-impregnated and amine-grafted sorbents are provided in Tables 6 and 7, respectively.

Amine-impregnated sorbents can typically rely on higher capture capacity than amine-grafted sorbents. However, they suffer from poor multi-cyclic stability, caused by the leaking of amines over repeated adsorption/desorption cycles, and diffusion limitations, i.e., CO<sub>2</sub> transport resistance to adsorption sites, caused by the higher amine loading achievable with impregnation.<sup>41</sup> On the contrary, amine-grafted sorbents can provide a better stability over extensive adsorption/desorption cycling, also typically exhibiting a higher rate of adsorption, sometimes even higher than commercial adsorbents, such as zeolite 13X, and cyclic stability.<sup>122</sup>

In this framework, great attention is focused on the use of polymeric amines [e.g., polyethylenimine (PEI), polypropylenimine (PPI), polyallylamine (PAA), amino dendrimers, polyaniline, hyperbranched polyamines, etc.] for the synthesis of amine-functionalized sorbents, namely, polymers with amine moieties in their backbone or side chains, as a result of their large content of amine groups.<sup>123</sup> Polymeric amines containing more primary and secondary amine moieties are preferentially used as a result of their capability to effectively adsorb CO<sub>2</sub> in both dry and wet conditions.<sup>124</sup> In particular, as a result of the high amine density, amount of primary amine moieties, relatively low cost, wide availability, and adequate thermal stability up to 90 °C, PEI-based systems have been extensively investigated.<sup>41</sup>

Moreover, PEI is compatible with a large number of supports, such as siliceous materials (fumed silica, precipitated silica, SBA-15, MCM-41, mesoporous siliceous foams, silica gels, etc.), carbonaceous materials (ACs, CNTs, fullerenes,

graphene, etc.), aluminosilicates (geopolymers), clays, MOFs, alumina, porous polymers, and zeolites.<sup>41</sup> PPI, being structurally similar to PEI, is able to enhance the CO<sub>2</sub> adsorption performances. However, its commercialization potential is limited by issues related to monomer synthesis and polymerization duration.<sup>41</sup> PAA-supported sorbents are also often reported to exhibit better performances with respect to PEI-supported sorbents as a result of improved oxidative and thermal resistance and larger amine/support binding strength.<sup>41</sup> Likewise, polyaniline has shown similar benefits, also in combination with a rather facile synthesis, availability in high-surface nanostructured forms, and high thermal stability.<sup>41</sup> Very positive results have also been obtained using dendritic polymers, such as amino dendrimers and hyperbranched polyamines, as a result of their exceptional morphological features and high amine/nitrogen density.<sup>41</sup>

As observed for all other families of CO<sub>2</sub> adsorbents, flue gas impurities also have great impact on the CO<sub>2</sub> adsorption performances of amine-functionalized materials. Indeed, both NO<sub>x</sub> and SO<sub>x</sub> can react with the amines to form stable salts, thus remarkably reducing the CO<sub>2</sub> adsorption capacity.<sup>4</sup> Besides that, before amine-functionalized adsorbents may actually be used in real post-combustion CO<sub>2</sub> capture processes, the issue related to the environmental impact of their large-scale manufacturing and deploying must be carefully assessed.<sup>35</sup>

**2.3. Summary of Adsorbent Materials.** In summary, different types of sorbent materials can be used to capture CO<sub>2</sub>, and the selection of the most proper sorbent material depends upon a complex set of features: adsorption capacity, selectivity, adsorption/desorption rate, adsorption/desorption temperatures, thermal and mechanical stability, cycling stability, tolerance to moisture and other impurities in the flue gas, and production cost (Table 8).

Among all of the reviewed adsorbents, both zeolites and carbon-based materials (e.g., ACs) can rely on the widest



**Table 8. Pros and Cons of Different Classes of Sorbents**

adsorbent	advantages	disadvantages
activated carbons	wide precursor availability	limited values of CO <sub>2</sub> adsorption capacity
	low cost	friability
	high specific surface area	low selectivity
	high thermal stability	
	rather good tolerance to moisture	
carbon nanomaterials	easy regeneration	
	well-defined pore size distribution	complex/expensive synthesis
	high specific surface	limited selectivity
	high CO <sub>2</sub> adsorption capacity	
	good chemico-physical stability	
synthetic zeolites	fast adsorption kinetics	
	tolerance to moisture	
	tunable pore size and surface properties	expensive synthesis
	high surface area and porosity	low tolerance to moisture/impurities
	high CO <sub>2</sub> adsorption capacity	low selectivity
natural zeolites	high thermal stability	
	large availability	low purity as a result of variable chemical composition
	low cost	limited separation performances
MOFs	tunable pore size and surface properties	complex/expensive synthesis
	high surface area and porosity	low tolerance to moisture/impurities
	high CO <sub>2</sub> adsorption capacity	limited thermal stability
amine-functionalized materials	large number of supports	low thermal/oxidative stability (amine degradation)
	high CO <sub>2</sub> capacity	pore blockage
	low production cost	
	good regeneration ability	

industrial maturity. With regard to zeolites, both natural and synthetic types can be applied for post-combustion CO<sub>2</sub> capture. Their CO<sub>2</sub> adsorption mechanism is governed by the structure of their framework (i.e., Si/Al ratio) as well as the composition/location of the extra-framework cations. While natural zeolites (such as tuff, kaolinite, etc.) are cheap but characterized by limited CO<sub>2</sub> adsorption capacity, synthetic zeolites can typically provide quite high CO<sub>2</sub> adsorption capacity (zeolite 13X is often taken as the benchmark of CO<sub>2</sub> adsorbents) but at the price of a much more expensive synthesis procedure. As for zeolite shortcomings, they greatly suffer from a dramatic sensitivity to moisture, which thus hinders their CO<sub>2</sub> uptake and makes their actual utilization subordinated to an upstream drying step.

With regard to the carbon-based adsorbents, except for carbon nanomaterials (e.g., CNTs and graphene), they are usually inexpensive and can be quite easily manufactured in large scale. Even though their CO<sub>2</sub> adsorption behavior is typically physical in nature, with porosity (especially micropores) playing a major role in the global CO<sub>2</sub> uptake, the presence of heteroatoms (i.e., O-containing groups) in their internal structure, as a consequence of the peculiar synthesis/

activation procedure, may also provide them with desirable chemisorption interactions. As a result of their typical hydrophobic character, they are less affected by moisture than zeolites. However, without any type of functionalization, their CO<sub>2</sub> adsorption capacity and selectivity are typically lower than those of zeolites.

MOFs can rely on tunable pore size and chemistry, exceptionally a high surface area and porosity, which yield remarkable CO<sub>2</sub> adsorption capacity. Their CO<sub>2</sub> adsorption mechanism takes place by means of a sieving effect, but also chemisorption can occur through CO<sub>2</sub> molecules/open metal sites and CO<sub>2</sub> molecules/functional groups (located on the MOF ligands) interactions. Like zeolites, they exhibit a rather strong instability to the presence in the feed of moisture, whose adsorption becomes competitive with that of CO<sub>2</sub>, and other impurities (e.g., NO<sub>x</sub>, SO<sub>x</sub>, etc.), which cause a poisoning issue, thus needing a previous drying/purification of the flue gas before the adsorption step. Unlike zeolites and ACs, most of the MOFs are still synthesized only at the lab scale, and those few that are manufactured at a larger scale are synthesized only in the form of quite fine powders.

Amine-functionalized sorbents are capable of combining the benefits of porous solid adsorbents (large specific surface area) and solvents (high numbers of adsorption sites). Therefore, they can provide quite a high CO<sub>2</sub> adsorption capacity, owing to the incorporation of N-containing functionalities, with relatively low production costs. The mechanism of CO<sub>2</sub> adsorption of amine-functionalized adsorbents is not univocal, depending upon the type of amines as well as the type of support material. Even though amine functionalization enhances the CO<sub>2</sub> uptake, the uniform distribution of liquid amines onto the porous substrate without blocking the pores and the improvement of the thermal/oxidative stability still constitute open challenges.

### 3. GAS–SOLID REACTOR CONFIGURATION

As discussed in the [Introduction](#), the research and development of sorbent materials should proceed in tight connection with the gas–solid reactor configuration and regeneration mode.<sup>6,132</sup> Therefore, for the selected sorbent to be efficiently used, research efforts are needed to develop a suitable gas–solid contacting system, which has a great impact on the process efficiency, footprint, and overall capture costs.<sup>10</sup>

In this framework, different kinds of gas–solid reactors have been proposed for adsorption-based CO<sub>2</sub> capture processes, such as fixed,<sup>32,33,133–136</sup> moving,<sup>10,137,138</sup> and fluidized<sup>23,139–151</sup> beds. As a result of the easy and basic design, the fixed bed configuration is by far the most extensively studied at the laboratory scale, with a wide number of papers reporting the assessment of several types of sorbents also using different regeneration modes.<sup>10</sup> However, in light of the growing awareness on the importance of the gas–solid contacting system in the wider and more complex scenario represented by a post-combustion capture process, other reactor configurations have been recently investigated. Indeed, the global technology effectiveness and affordability strongly depend upon the simplicity of retrofitting to existing plants, ease of operation, and total footprint.<sup>10</sup> For example, only two reactors, envisaging the circulation of the sorbent between them, are needed in some configurations, whereas trains of multiple reactors, involving complex operating systems, are required in other configurations. In general, complex process schemes (e.g., involving multiple stages) are required when

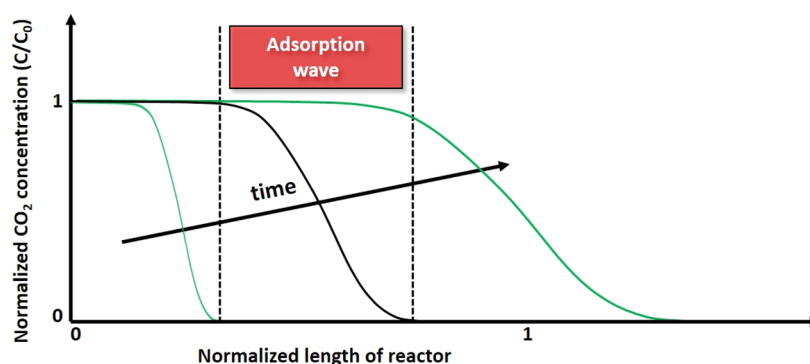


Figure 3. Normalized CO<sub>2</sub> concentration profile along the length of the reactor and as a function of the time.

poor performances of the sorbent or kinetic/thermodynamic constraints occur.

Therefore, different types of gas–solid reactor configurations will be reviewed in the following paragraphs to provide a detailed overview of their working principles, benefits, and drawbacks.

**3.1. Fixed Bed Reactors.** The fixed bed reactor is by far the simplest gas–solid configuration, in which the flue gas is passed through a packed bed of relatively large sorbent particles. The main feature of the fixed bed reactor is its plug-flow nature, provided that the axial dispersion is negligible: the bed is saturated along its length, starting from the feeding point up to the exit point, thus maximizing the CO<sub>2</sub> adsorption until the bed is almost saturated. A typical CO<sub>2</sub> concentration profile along the length of the reactor is reported in Figure 3. Clearly, no CO<sub>2</sub> is adsorbed on the sorbent on the right of the adsorption wavefront because the sorbent is completely saturated ( $C/C_0 = 1$ , with  $C_0$  being the CO<sub>2</sub> concentration in the feed) and on the left side because the CO<sub>2</sub> front has not yet arrived ( $C/C_0 = 0$ ). On the contrary, in the adsorption wave, CO<sub>2</sub> adsorption occurs. Upon bed saturation, the system is switched by feeding a purging gas or vapor for sorbent regeneration.

The main drawback of this reactor configuration, when used to carry out adsorption-based processes for CO<sub>2</sub> post-combustion capture, is represented by the rather high values of pressure drops, even at moderate flow rates, thus resulting in a remarkably high footprint caused by the impossibility to use high gas velocities in both adsorption and regeneration steps.<sup>152</sup> Indeed, as thoroughly discussed by Yang et al.,<sup>23</sup> the major restrictions for CO<sub>2</sub> capture from conventional power plants are as follows: (i) Large volumetric flue gas flow rate (e.g., about  $3.4 \times 10^4 \text{ m}^3 \text{ min}^{-1}$  for a 500 MW power plant). The final reactor design needs to result in a reasonable number of modules and reactor size. (ii) Low available pressure drop for the design of the adsorption/desorption reactor. The flue gas of a typical power plant has a pressure close to the atmospheric pressure. It can be estimated that, after appropriate integration, the pressure drop that can be available at the CO<sub>2</sub> adsorption reactor is around 0.21 atm. Obviously, any increase of the pressure drop requirement above this value will involve additional fan costs to increase the flue gas pressure, thus causing a remarkable energy penalty for the global plant efficiency.

Therefore, aiming at minimizing the pressure drop in fixed bed reactors for post-combustion CO<sub>2</sub> capture, only relatively coarse sorbent particles can be used (e.g., it can be estimated that, for a bed height of 3 m and a superficial gas velocity of

about  $1 \text{ m s}^{-1}$ , the sorbent particles must have a size of at least  $2000 \mu\text{m}$  to keep the total pressure drop below the critical value of 0.21 bar; at  $1.5 \text{ m/s}$  and larger, they must be coarser than  $5000 \mu\text{m}$ ); of course, this causes an increase of heat and mass transfer resistances, which, in turn, hinders the CO<sub>2</sub> working adsorption capacity. As a matter of fact, fixed beds are intrinsically characterized by poor heat transfer coefficients. The consequence of such mass/heat transfer limitations is the dispersion of the reaction front traveling through the bed, i.e., a wide adsorption wave causing CO<sub>2</sub> to break through at the reactor outlet with a large fraction of the bed still unsaturated (high values of length of the unused bed).<sup>10</sup> More specifically, as a result of the exothermicity of the adsorption process, the heat generated during CO<sub>2</sub> adsorption causes a heat front traveling through the bed in analogy to the reaction front.<sup>153</sup> The adsorption equilibrium is, then, negatively affected by the resulting increase in the bed temperature; i.e., the adsorption capacity is decreased, and as a consequence, more frequent switching of the inlet and outlet valves are required because a lower amount of CO<sub>2</sub> can be captured in each cycle. Clearly, the amplitude of this heat front depends upon the heat of adsorption, the sorbent specific heat capacity and thermal conductivity, the adsorption kinetics, and the CO<sub>2</sub> partial pressure in the feed.<sup>6,154</sup> Several solutions have been proposed to overcome this intrinsic thermal limitation of fixed bed reactors. A viable approach is represented by the insertion of a heat exchanger in the reactor to remove the released heat.<sup>10</sup> However, this solution may cause increased heating/cooling time as a result of the poor heat transfer coefficients of fixed bed reactors.<sup>10</sup> Another viable approach is represented by the development of sorbent particles embedded with phase change materials (PCMs), thus being able to absorb the heat released during the CO<sub>2</sub> adsorption with minimal temperature change.<sup>155</sup> Clearly, the dilution of the active phase (i.e., the adsorbent material) with the PCMs causes an unavoidable reduction of the volumetric CO<sub>2</sub> adsorption capacity (i.e., amount of CO<sub>2</sub> adsorbed per volume of reactor), thus still constituting a major challenge for this approach. Obviously, an increase of the volume and costs of the reactor is caused by both of these approaches.

In this framework, special structured reactor configurations have also been investigated as viable alternatives to standard fixed bed reactors. Indeed, even though the most obvious way of decreasing the mass transfer resistances (which vary as the square of the particle size<sup>156</sup>) would be reducing the particle size, an alternate approach has also been investigated, consisting of developing novel non-particulate adsorbent structures. Different types of structures with tunable shape,

cell density, and wall thickness have been investigated for CO<sub>2</sub> capture, being characterized by a reduced pressure drop and heat transfer resistance and fast mass transfer kinetics (as a result of a shorter diffusion path) with respect to standard fixed bed reactors.<sup>156</sup> In light of these benefits, the cycle time may be remarkably reduced and productivity increased, thus making the use of more expensive and sophisticated sorbents possible but still keeping the competitiveness of the CO<sub>2</sub> capture process. However, when dealing with structured adsorbents, different trade-off behaviors should be taken into account.<sup>156</sup> Indeed, on the one hand, aiming at maximizing the external surface area per unit volume of adsorbent and, thus, enhancing the kinetic properties, the wall thickness and spacing should be as small as possible. On the other hand, a thinner wall thickness, meaning a shorter diffusion path, also leads to a lower adsorbent loading, thus resulting in a low effective sorbent bulk density (i.e., the inert support structure occupies a large fraction of the reactor volume). Therefore, a high voidage is associated with faster kinetics, but at the same time, it yields a lower working capacity as a result of the reduced bed density. Likewise, small spacing between adjacent sheets or small channels cause an increase of the pressure drop.

In this context, the monoliths, where a thin film of the sorbent is coated on the wall of a support material (in monolithic form), have been proven to be one of the most efficient solutions to pack a high adsorbent surface area into a fixed volume, allowing also the use of higher flow rates with a remarkably lower pressure drop in comparison to standard configurations.<sup>157,158</sup> More specifically, the performances of monoliths depend upon three main geometrical parameters: cell density [the number of cells per unit of cross-sectional area, expressed as cells per square inch (cpsi)], cell spacing, and wall thickness. Clearly, the pressure drop increases with increasing cell density, at a fixed value of gas viscosity, monolith length, and open frontal area. Likewise, at a fixed cell density, the pressure drop decreases with a decreasing wall thickness. The mass transfer in monoliths has two major resistances: external film resistance and pore diffusion within the walls. Therefore, using a thinner adsorbent wall makes it possible to reduce the characteristic diffusion length. Laminate structures and foams have also been investigated.<sup>159–161</sup> Considering that the residence time in structured adsorbents is typically shorter than in a standard fixed bed, the time scales of diffusion and transport through the channels may often be comparable. Therefore, the low pressure drop of this system must be exploited using longer beds to increase the gas residence time. In this framework, a formal optimization approach to identify the optimum conditions for different structured adsorbents has been proposed by Razei and Webley.<sup>162</sup> On the basis of their simulation results, monolithic adsorbents can be successfully employed provided that they have sufficiently high cell densities (>1000 cpsi), whereas laminate structures should be manufactured with small enough spacing (<0.2 mm) and sheet widths (0.2 mm).

In conclusion, fixed bed reactors are typically most suitable for pressure swing processes, i.e., regeneration based on the reduction of the pressure (see section 4.2), rather than temperature swing processes, i.e., regeneration based on the increase of the temperature (see section 4.1), with physisorbents having low reaction enthalpy and being not very sensitive to the temperature.

**3.2. Moving Bed Reactors.** An alternative gas–solid system to carry out an adsorption-based CO<sub>2</sub> capture process

is represented by the moving bed reactors. In this configuration, the adsorbent particles are moved through different sections/reactors, which are always operated at the same fixed conditions required for their precise purpose (adsorption, desorption, or cooling), thus reducing the pressure drop with respect to an equivalent fixed bed. However, at the same time, the plug-flow nature, which is typical of a fixed bed reactor, is preserved and a steady-state operation is also possible. Moreover, an additional advantage of this configuration is that the reaction front can be located in a fixed position, provided that the rate of the movement of the particles in one direction is the same as that of the reaction front in the opposite direction. The main shortcoming of this configuration is, however, the higher complexity, related to the necessity to move particles between different reactors, which should be interconnected, thus limiting the possibility of carrying out pressure swing processes. On the contrary, the moving bed configuration makes it possible to overcome one of the main drawbacks of the temperature swing processes carried out in fixed bed reactors (with the sorbent packed in large columns); namely, a long cycle time is connected to the heating/cooling steps, thus remarkably improving the efficiency of the separation process.<sup>163</sup>

In this framework, the first moving bed concept is the “hypersorption” process proposed by Berg,<sup>164</sup> in which the sorbent particles flow through an adsorption tower and a stripping section. More recently, aiming at reducing the energy penalty of post-combustion CO<sub>2</sub> capture, a new integrated moving bed adsorber–stripper scheme was developed by SRI International,<sup>165</sup> in which advanced water-resistant carbon sorbent granules move, by gravity, from the adsorber to the stripper (where steam is used as purging gas), in a single vertical column in counter-current with the rising flue gas. Then, after regeneration and cooling, the carbon granules are cycled back to the absorber. This integrated design makes it possible to limit the pressure drop and obtain quite a good heat transfer efficiency as a result of the direct contact with steam in the stripping section.

A moving bed system for CO<sub>2</sub> capture, named the Kawasaki CO<sub>2</sub> capture system (KCC), suitable for large-scale plants has also been developed by Kawasaki Heavy Industries.<sup>166</sup> The KCC scheme, in which gas and solids move in counter-current, consists of three main components: (i) an adsorber, in which CO<sub>2</sub> is captured by an amine-impregnated porous material, (ii) a desorber, in which low-grade steam (<100 °C) is used as purging gas, and (iii) a sorbent dryer, in which warm air is used to remove the water accumulated in the sorbent.

Aiming at avoiding the direct contact with the steam, Knaebel<sup>167</sup> proposed an indirectly heated scheme, in which the hot flue is used as heat transfer fluid in an indirect-contact heat exchanger, through which the heat is indirectly transferred to the sorbent (a zeolite) during the regeneration step. Recently, the feasibility of this type of configuration, integrated with some heat recovery from the hot regenerated sorbent (leaving the desorption section) for preheating the cold spent sorbent (leaving the adsorption section), has been positively assessed by Mondino et al.<sup>163</sup> with a detailed mathematical model.

**3.3. Fluidized Bed Reactors.** In a fluidized bed reactor, a gas is passed through a solid granular material with a high enough flow rate to suspend the solid and cause it to behave as though it was a fluid. Owing to their intrinsic fluid dynamics, fluidized bed reactors can quite easily manage the pressure drop limit (about 0.21 atm<sup>23</sup>) imposed by the pressure of a



typical power plant flue gas, because the pressure drop across the bed ceases to increase once the minimum fluidization velocity is reached. Moreover, ideal solid mixing can be achieved, thus leading to excellent mass and heat transfer coefficients with immersed walls, especially in the bubbling fluidization regime (as high as  $300 \text{ W m}^{-2} \text{ K}^{-1}$ ),<sup>10,168</sup> which might, however, be detrimental for the  $\text{CO}_2$  adsorption as a result of  $\text{CO}_2$  bypassing the bed through the bubbles. Moreover, the already good temperature homogeneity can be further enhanced by simply immersing heat transfer surfaces (e.g., immersed exchanger tubes) in the bed to remove/add heat.<sup>169,170</sup> Therefore, this configuration is inherently able to overcome the heat transfer limitations of fixed bed reactors and is particularly suitable to perform temperature swing adsorption processes.<sup>139,145,171</sup>

In this framework, most of the works investigating the  $\text{CO}_2$  adsorption in fluidized bed reactors deal with the use of two interconnected fluidized bed reactors, i.e., involving the circulation of sorbent particles between the two reactors, one acting as adsorber and the other as desorber, and operating at steady conditions.<sup>150,172,173</sup> Considering the high flue gas velocities applicable in this configuration, a limited footprint can be envisaged, on the one hand, and attrition issues, on the other hand. More specifically, regarding the attrition issues, it must be considered that, even though fluidized beds are generally characterized by a much greater extent of this phenomenon with respect to fixed bed reactors, the possibility to use sorbents with a relatively small particle size (with respect to those employable in fixed beds) and with appropriate mechanical stability<sup>172,173</sup> can remarkably limit the attrition rate.<sup>23</sup> Likewise, a sound-assisted fluidized bed have also been proven to improve adsorption/desorption performances, in terms of the adsorption capacity and adsorption/desorption rate, of different types of fine/ultrafine solid sorbents.<sup>20–22,105,140,174</sup> Indeed, fine/ultrafine powdered sorbents have been receiving growing research interest thanks to their special size/shape; their surface can be tailored and/or functionalized quite easily to improve their  $\text{CO}_2$  adsorption performances,<sup>175,176</sup> and they can provide reduced intraparticle diffusion resistance with respect to pelletized sorbents.<sup>30</sup>

Nonetheless, if, on one hand, the ideal solid mixing represents a benefit from the heat transfer and gas–solid contact efficiency, on the other hand, it also causes a key drawback of fluidized bed reactors, namely, the adsorption equilibrium limitations, leading to fast  $\text{CO}_2$  breakthrough, resulting, in turn, in either poor  $\text{CO}_2$  recovery or low sorbent utilization as a result of the internal back mixing. In particular, while, in a fixed bed (which may be considered in first approximation as a plug-flow reactor), most of the bed is in equilibrium with the feed, in a fluidized bed (which may be considered in first approximation as a perfectly stirred tank reactor), the sorbent is in equilibrium with the purified feed, namely, with a much smaller  $\text{CO}_2$  partial pressure.<sup>146</sup> For example, in the case of two interconnected fluidized bed configurations, the loading of the sorbent material leaving the adsorber determines the minimum  $\text{CO}_2$  partial pressure achievable in the adsorber off-gas. Likewise, with regard to the desorber, the equilibrium partial pressure of the lean sorbent leaving the desorber limits the maximum  $\text{CO}_2$  concentration in the off-gas. As a consequence, fluidized beds can provide only a very low cycle working capacity, which means, in turn, that very high solid circulation rates and stripping flow rates are required with high expected

regeneration energy demand. In light of the above-reported considerations, an effective reactor configuration should be able to combine the absence of solid back-mixing (which can be easily achievable in fixed bed reactors), i.e., approaching a counter-current flow between gas and solid, and excellent heat transfer (which is typical of fluidized bed reactors);<sup>147</sup> in other words, the positive aspects of fixed bed reactors, i.e., better thermodynamics, should be combined with those of fluidized beds, i.e., greater heat/mass transfer coefficient.

In this framework, the multi-stage fluidized bed configuration has been proposed as a promising solution. In particular, a large number of works have been focused on a multi-stage fluidized bed with a gas–solid counter-current arrangement.<sup>146,170,177,178</sup> In this configuration, the sorbent particles flow downward through a series of fluidized bed stages, while the flue gas is fed at the bottom and acts as a fluidizing agent in the different stages (Figure 4). In particular,

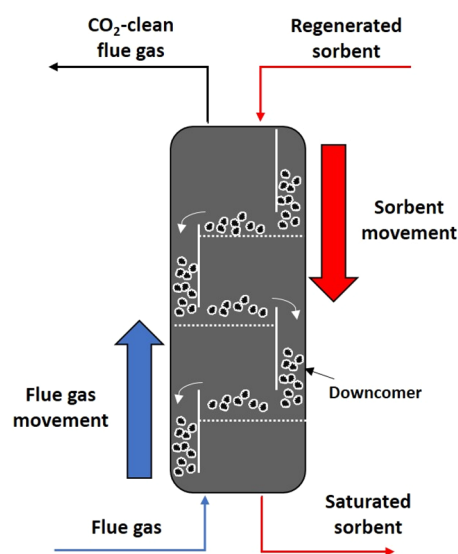


Figure 4. Multi-stage fluidized bed.

each of the individual stages is provided with a gas distributor, a downcomer controlling the flow of adsorbent from stage to stage, and an immersed heat exchanger for heat supply/removal. With regard to the fluidization regime, a bubbling fluidization regime has been selected to exploit the highest heat transfer coefficients between the immersed heat exchangers and the sorbent material. Noticeably, the advantage of this configuration for an adsorption-based post-combustion capture process is associated with counter-current arrangement rather than a different fluid dynamic behavior with respect to a standard single-stage fluidized bed reactor. Indeed, as thoroughly discussed by Shony et al.,<sup>147</sup> the fluid dynamic behavior of a multi-stage fluidized bed column, in terms of pressure drop, can be easily expressed considering it as a series of single-stage fluidized beds. Obviously, the height of the fluidized bed in each stage is strictly related to the downcomer, whose design is essential for the stable operation of the multi-stage column. In particular, the pressure drop caused by the fluidized bed within an individual stage of the multi-stage column is the same as that of a conventional single-stage fluidized bed, with the height of the bed considered equal to the downcomer weir. Clearly, for stable operation, the condition that the pressure drop across the downcomer is

Table 9. Pros and Cons of Different Reactor Configurations

	advantages	disadvantages
conventional fixed bed	simple configuration	relatively high pressure drop, with respect to all of the other configurations, resulting in a larger energy penalty
	plug-flow nature, which increases the achievable working adsorption capacity	poor heat transfer coefficients; i.e., heat fronts limit the working adsorption capacity
	more suited for pressure swing processes	relatively high pressure drop limits the gas velocities, thus increasing the footprint
structured fixed bed	reduced heat/mass transfer limitations and pressure drop with respect to conventional fixed beds	low effective sorbent bulk density; i.e., the inert support monolith occupies a large fraction of the reactor volume
	relatively lower pressure drop, with respect to conventional fixed beds; i.e., faster gas flows can be employed, thus resulting in a smaller footprints	
moving bed	counter-current mode increases the working adsorption capacity	relatively lower heat transfer coefficients, with respect to fluidized beds
	simple steady-state operation achievable by means of the solid circulation through the different sections	counter-current mode limits the gas velocity to avoid fluidization of the sorbent particles moving downward, thus resulting in a larger footprint
	more suited for temperature swing processes, in both direct and indirect heating modes	high operational difficulties for pressure swing processes as a result of the interconnected system design
conventional fluidized bed	ideal solid mixing, thus leading to excellent mass and heat transfer coefficients with immersed walls	high mixing rate resulting in fast CO <sub>2</sub> breakthrough and low working adsorption capacity, thus requiring large sorbent recirculation rates to achieve acceptable CO <sub>2</sub> recovery
	possibility to use both direct and indirect heating modes	relatively higher flue gas velocities are allowed, with respect to the other configurations, thus resulting in a smaller footprint
	simple steady-state operation achievable using only two interconnected reactors with the sorbent circulating between them	sorbent attrition issues
	excellent for temperature swing processes as a result of the high heat transfer rates in both direct and indirect heating modes	
multi-stage fluidized bed	possible counter-current mode, which increases the working adsorption capacity but preserving the good heat transfer of conventional fluidized beds	increased footprint, with respect to conventional fluidized beds, as a result of the counter-current operation, which somehow limits the gas velocities to keep the sorbent flowing downward
	excellent for temperature swing processes as a result of the high heat transfer rates	high operational difficulties for pressure swing processes as a result of the interconnected system design

equal to the pressure drop as a result of the upper bed and upper distributor must be satisfied.<sup>179</sup>

This configuration, in contrast to the single-stage fluidized bed configuration, is able to remarkably limit the overall back mixing, thus approaching the plug-flow behavior and the high CO<sub>2</sub> working capacity of fixed bed reactors, just after 3–5 stages. Indeed, a high driving force and improved capture efficiency can be achieved at each stage, because fresher adsorbent particles (i.e., with small loading of CO<sub>2</sub>), which flow downward, are contacted with a gas stream, flowing upward, with decreasing CO<sub>2</sub> partial pressure. In particular, it has been shown that additional energy saving of about 20% can be achieved using a lean–rich solid–solid heat exchanger: the sensible heat from the hot lean solid material (i.e., the regenerated sorbent) leaving the desorber is recovered and used to preheat the cold rich sorbent (i.e., the saturated sorbent) leaving the adsorber.<sup>149</sup> Clearly, it must be considered that the cost of the multi-stage fluidized bed configuration is significantly higher than that of the single-stage fluidized bed.

**3.4. Summary of Reactor Configurations.** In summary, different types of reactor configurations can be used to capture CO<sub>2</sub> (Table 9).

The conventional configuration of both fixed bed reactors and fluidized bed reactors is not suitable to fully exploit the potential of the technology when applied to post-combustion capture applications.

Fixed bed reactors suffer from high pressure drops, which cause a high energy penalty and footprint as a result of the limited adoptable gas velocities. As a matter of fact, a suitable balance must be struck between the need to keep the sorbent particle size small, to improve the intraparticle diffusion kinetics, and the need to use coarser sorbent particles, to limit the pressure drop. In this framework, structured packings have been proposed to reduce both heat transfer limitations and pressure drop, thus allowing for the use larger gas flow rates

and, in turn, decreasing the footprint with respect to standard fixed bed reactors. However, the use of sorbents characterized by fast adsorption/desorption must be envisaged in such reactors. This issue represents a big challenge especially for the practical utilization of novel adsorbent materials (such as MOFs) that are still manufactured only in the form of quite fine powders.

The fluidized bed, on the contrary, is able to provide a smaller footprint as a result of the possibility to employ larger gas velocities than in fixed bed reactors and can rely on ideal mixing, which leads, on the one hand, to high heat/mass transfer rates and, on the other hand, to strong thermodynamic limitations, which cause fast CO<sub>2</sub> breakthrough and, in turn, poor CO<sub>2</sub> working capacity (i.e., need for a large sorbent recirculation rate). In this framework, multi-staged fluidized beds have been proposed to solve the back-mixing issue, thus improving the CO<sub>2</sub> working capacity and recovery but still keeping all of the advantages of the high heat transfer rates of fluidized beds.

Clearly, the scale-up of both structured fixed beds and multi-stage fluidized beds is more complex with respect to their conventional configurations, but nonetheless, they are the most promising solutions for post-combustion adsorption-based CO<sub>2</sub> capture.

In this framework, the moving bed configuration is conceptually similar to the multi-stage fluidized bed configuration. The sorbent working capacity is further increased, but at the same time, challenges arise regarding the heat transfer efficiency, because the mixing in moving beds is not as effective as in fluidized beds. Besides, another major challenge associated with large-scale moving beds is that the gas velocity must be kept small enough to prevent the solids from becoming fluidized, thus increasing the footprint.

## 4. REGENERATION STRATEGIES

The different gas–solid contacting systems available for CO<sub>2</sub> adsorption-based capture processes have been reviewed in the previous section. However, the choice of the most proper reactor configuration is also greatly affected by the regeneration mode, which should be efficient and, at the same time, cost-effective. In this framework, the CO<sub>2</sub> desorption process and, in turn, the regeneration of the sorbent can be induced by acting on either the temperature or the pressure, thus having temperature swing adsorption (TSA) and pressure/vacuum swing adsorption (PSA/VSA), respectively. It is also possible to combine the two modes, i.e., acting on both temperature and pressure, thus having a hybrid regeneration mode (VTSA/PTSA).

**4.1. Temperature Swing Adsorption (TSA).** In TSA, CO<sub>2</sub> adsorption is performed at a relatively low temperature (about 50–60 °C to capture CO<sub>2</sub> efficiently<sup>4</sup>), whereas the regeneration of the sorbent and, hence, the CO<sub>2</sub> desorption are induced by heating the system (about 150–200 °C<sup>4</sup>). It is evident that, in TSA, the operating temperature and gas flow rate have a great impact on the global performances, measured in terms of CO<sub>2</sub> purity and recovery and energy consumption. Indeed, higher values of CO<sub>2</sub> purity and recovery will be obtained at higher desorption temperatures, which will obviously increase the energy consumption.

In a conventional TSA regeneration process, the spent sorbent is regenerated by purging the bed with a hot gas (typically N<sub>2</sub>), namely, by directly contacting the sorbent particles with the hot purging gas (direct heating).<sup>170,180–183</sup> Clearly, in the case of CO<sub>2</sub> capture application, the use of a large volume of a purging gas would cause an unavoidable and remarkable dilution of the desorbed CO<sub>2</sub> stream, which is indeed the desired product of the whole capture process and must, actually, satisfy very strict purity specifications for the transportation.<sup>20,22,174</sup> For this reason, different technological solutions have been proposed to address this issue, consisting in modifying either the purging gas or the heating mode.

With regard to the former approach, a gas that may be separated by captured CO<sub>2</sub> in a relatively facile way is needed and a viable option is represented by steam. Anyway, the use of steam also poses some issues, which represent the main drawback of TSA with direct heating.<sup>10</sup> First, even though water can be easily separated by condensation, an additional unit for water removal must be envisaged before compressing CO<sub>2</sub> for the subsequent transportation and storage. Second, it is of utmost importance that the sorbent is tolerant to the presence of water from both the reactive and mechanical point of view.<sup>22</sup> Indeed, most of the investigated CO<sub>2</sub> sorbents (especially physisorbents) suffer from a dramatic reduction of their CO<sub>2</sub> adsorption capacity when water is present and would, therefore, require an additional drying step before they can be used in a new cycle.<sup>22</sup> Besides that, even in the case of sorbents exceptionally tolerant to the presence of water from the reactive point of view (i.e., sorbents whose CO<sub>2</sub> adsorption capacity is not affected by water because water adsorption is not competitive with CO<sub>2</sub> adsorption), the mechanical stability of the sorbent as a result of high sorbent attrition rates may become an issue.<sup>184</sup> Clearly, these additional operations cause an increase of the global process complexity, energy penalty, and economics. A further possible alternative is represented by the adoption of CO<sub>2</sub> instead of steam as hot purging gas, thus avoiding the necessity for the above-mentioned additional

units linked to the use of steam.<sup>184</sup> However, it must be considered that the use of CO<sub>2</sub> as purging gas will decrease the desorption driving force, thus resulting in the need to apply a higher regeneration temperature and, in turn, a higher global thermal energy consumption, provided that the sorbent can stand the required temperatures.<sup>184</sup> In this framework, Ntiamoah et al.<sup>184</sup> proposed a TSA process, using NaUSY zeolite as the sorbent material, in which recovered CO<sub>2</sub> is heated (at 250 °C) and used as purging gas obtaining a CO<sub>2</sub> purity larger than 91% and CO<sub>2</sub> recovery of 83.6% with a thermal energy consumption of 4.5 MJ kg<sup>−1</sup> of CO<sub>2</sub>.

With regard to the latter approach, namely, the modification of the heating mode, a possible solution is represented by indirectly heating the sorbent with a heat exchanger inserted in the reactor (indirect heating).<sup>180</sup> With this heating mode, no purging gas is used, thus eliminating the cause of both dilution and/or additional operation units, and CO<sub>2</sub> is desorbed by thermal expansion with 100% purity, only requiring limited energy for evacuation.<sup>181</sup> For its simplicity and the possibility to recover CO<sub>2</sub> with very high purity, deriving from the absence of purging gas, this heating mode has been proposed for fixed bed reactors. In this framework, Clausse et al.<sup>182</sup> proposed an indirect TSA process, with an internal heat exchanger, using 13X and 5A, obtaining a CO<sub>2</sub> purity larger than 95%, a CO<sub>2</sub> recovery level of 81%, and a specific energy consumption of 3.23 GJ/tonne of CO<sub>2</sub>. However, as largely discussed in the previous section, fixed bed reactors suffer from poor heat transfer coefficients, which also applies to tube-to-particle heat transfer coefficients, and, therefore, the indirect heating mode is not the best option.<sup>10</sup> On the contrary, the potential of the indirect heating mode can be fully exploited in the fluidized bed configuration, which can rely on the intrinsically high heat transfer coefficients, which maximize the heat supply during the regeneration step but also the temperature control during the adsorption step (by removing the heat released by the adsorption process) and, in turn, the adsorption working capacity and capture efficiency.<sup>146</sup>

Also, in the framework of the modification of the heating mode, electric swing adsorption (ESA) can be a viable solution. In ESA, the heat required to perform the regeneration is generated passing electric current through the sorbent, i.e., exploiting the Joule effect.<sup>185,186</sup> In comparison to standard TSA, ESA can ensure a faster heat transfer rate and desorption kinetics.<sup>185,186</sup> Clearly, this regeneration mode has a strict requirement; namely, the sorbent must be provided with electric conductivity in combination with all of the other required features (Figure 2), such as high CO<sub>2</sub> capacity and selectivity. In this framework, ACs, as a result of their relevant electrical conductivity, are considered the most suitable candidates for ESA.<sup>185,186</sup> Besides the limitation in the sorbent selection, another major drawback of ESA is the remarkably high electrical energy consumption. Indeed, electrical energy is way more expensive than the low-grade heat (and in most cases also waste heat) typically employed for sorbent regeneration in TSA.<sup>185,186</sup> In this framework, Grande et al.<sup>187</sup> investigated the performance of ESA for CO<sub>2</sub> capture from flue gases with a CO<sub>2</sub> content of 3.5% (as typical of flue gases deriving from natural gas power stations) obtaining a CO<sub>2</sub> purity of 16% with a recovery of 89% (adsorption temperature = 293 K and desorption temperature = 423 K). More recently, Zhao et al.<sup>186</sup> studied an ESA process for a feed stream with 15% CO<sub>2</sub> balanced with N<sub>2</sub> using a carbon monolith as the sorbent, obtaining that CO<sub>2</sub> purity and energy



Table 10. Comparison of the Performances of Different Regeneration Strategies<sup>a</sup>

regeneration mode	adsorbent	reactor	$y_{\text{feed},\text{CO}_2}$	purity (vol %)	recovery (%)	productivity ( $\text{g}_{\text{CO}_2} \text{kg}^{-1} \text{sorb} \text{h}^{-1}$ )	energy consumption ( $\text{MJ kg}^{-1} \text{CO}_2$ )	reference
TSA (direct: hot product gas purge)	NaUSY zeolite	fixed	0.15	>91	55.5–83.6	24–41	3.40–4.5	184
TSA (indirect + N <sub>2</sub> purge)	13X zeolite	fixed	0.10	95.0	81.0	58	3.23	182
TSA (indirect)	13X zeolite	moving	0.05	95.1	96.0	121	2.21	163
TSA (indirect + steam purge)	carbon honeycomb monoliths	fixed monolith	0.14	95.6	85.4	40	3.59	199
TSA (indirect + vacuum + CO <sub>2</sub> purge)	amine-functionalized	multi-stage fluidized	0.13	96.0	90.0	68	2.80	170 and 200
VPSA (two stages)	13X zeolite–activated carbon	fixed	0.16	95.6	90.2	65	2.44	201
VPSA (two stages)	13X zeolite	fixed	0.15	96.5	93.4	21	2.64	194
VPSA (two stages)	activated carbon	fixed	0.10	95.3	74.4	37	3.61	202
VTSA	13X zeolite	fixed	0.15	97.3	97.7	72	3.22	183
VTSA	13X zeolite	fixed	0.15	94.4	98.5	12		192

<sup>a</sup>Energy consumption, energy required for sorbent regeneration; productivity, CO<sub>2</sub> productivity; purity, CO<sub>2</sub> purity; and recovery, CO<sub>2</sub> recovery.

consumption are remarkably increased as the electric current and electrification time increased. Under optimal conditions, they obtained a CO<sub>2</sub> purity of 52% and a recovery of 76% with an energy consumption of 5.64 MJ kg<sup>−1</sup> of CO<sub>2</sub>.

It is worth noting that the theoretical energy penalty for a component (CO<sub>2</sub>) separation from a mixture can be evaluated on the basis of an energy balance for a closed adiabatic system.<sup>188</sup> The required energy increases as the initial concentration of the component to be separated decreases. It turns out equal to 0.223 and 0.158 MJ kg<sup>−1</sup> of CO<sub>2</sub> for CO<sub>2</sub> at 5 and 15 vol %, respectively.

**4.2. Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA).** Both PSA and VSA rely on the variation of the pressure to regenerate the sorbent. In particular, in PSA, CO<sub>2</sub> is captured at a high pressure, whereas it is desorbed and the spent sorbent is regenerated lowering the pressure at an atmospheric value.<sup>183</sup> Even though this technique is widely used in the industrial sector, PSA holds important drawbacks when applied in post-combustion capture applications. Indeed, it must be considered that the flue gases are emitted at atmospheric pressure with a relatively low CO<sub>2</sub> concentration (<20 vol %). Therefore, large volumes of gases, which are in a large fraction inert N<sub>2</sub>, would be compressed, which clearly destroys the economics of the process. Besides that, it should be taken into account that the sorbent selectivity for CO<sub>2</sub> drops with increasing pressure, thus making it more difficult to achieve high-purity CO<sub>2</sub> in the desorption gas.<sup>189,190</sup>

Aiming at overcoming these issues, VSA has been proposed as a viable solution. In VSA, the CO<sub>2</sub> adsorption is performed at atmospheric pressure, whereas the CO<sub>2</sub> desorption and sorbent regeneration are performed under vacuum.<sup>191</sup> However, even though the basic VSA process is operatively simple, it suffers from either a low CO<sub>2</sub> purity or low CO<sub>2</sub> recovery level;<sup>10</sup> indeed, as a result of the low CO<sub>2</sub> partial pressure in the feed, it can hardly meet high CO<sub>2</sub> purity with a high recovery level, required to meet the specification of CCS, in the simplest one-stage configuration.<sup>192</sup> Therefore, for VSA to be efficiently applied to post-combustion capture, i.e., for CO<sub>2</sub> to be captured with purity higher than 90% with a relatively high recovery level, it must envisage at least two stages.

Another solution reported to improve the performances of both PSA and VSA is to use a two-stage vacuum pressure swing adsorption (VPSA) process.<sup>193</sup> Typically, the first stage

can achieve a CO<sub>2</sub> recovery of about 95% with the CO<sub>2</sub> purity of 40–60%, whereas the second stage is used to further improve the CO<sub>2</sub> purity up to 95%.<sup>183</sup> In this framework, Wang et al.<sup>194</sup> simulated a two-stage VPSA process to capture CO<sub>2</sub> from flue (16.5% CO<sub>2</sub>) using 13X-APG and AC as sorbents in the first and second stages, respectively. A CO<sub>2</sub> purity of 95.6% and a CO<sub>2</sub> recovery of 90.2% have been obtained with an energy consumption of 2.44 MJ kg<sup>−1</sup> of CO<sub>2</sub>. Nikolaidis et al.<sup>195</sup> also studied a two-stage VPSA scheme using zeolite 13X and Mg-MOF-74 in the first and second stages, respectively, obtaining a 97.57% CO<sub>2</sub> purity and 90.16% CO<sub>2</sub> recovery with a total energy requirement of 0.7 MJ kg<sup>−1</sup> of CO<sub>2</sub>.

**4.3. Hybrid Regeneration Strategies.** Aiming at overcome the drawbacks of the regeneration modes based on the variation of either pressure or temperature, hybrid regeneration strategies have also been investigated. In this framework, the hybrid vacuum temperature swing adsorption (VTSA), combining VSA and TSA, has been proposed to circumvent, on the one hand, the need in TSA to use a relatively high temperature for desorption and overcome, on the other hand, the impossibility of realizing deep vacuums in large-scale VSA to obtain the required high CO<sub>2</sub> recovery.<sup>10</sup> As a consequence, in VTSA, the spent sorbent can be regenerated under milder operating conditions with respect to both VSA and TSA, thus reducing the energy consumption and capture cost.<sup>134</sup> In this framework, Jiang et al.<sup>183</sup> recently investigated a VTSA process using zeolite 13X as the adsorbent, obtaining a 97.27% CO<sub>2</sub> purity and 97.66% CO<sub>2</sub> recovery with an energy consumption of 3.22 MJ kg<sup>−1</sup> of CO<sub>2</sub>. Webley et al.<sup>133</sup> also proposed a non-conventional hybrid microwave-assisted VTSA using 13X zeolite. A brief exposure to microwave radiation was found to improve the rates of CO<sub>2</sub> and water desorption at the investigated vacuum levels, thus suggesting that overall energy penalty may be reduced as a result of the positive effect yielded by the microwave application. Likewise, Plaza et al.<sup>134</sup> designed a low-temperature (30–80 °C) multi-bed VTSA process using microporous carbon obtained from olive stones to capture 85% of CO<sub>2</sub> emitted by an advanced supercritical coal-fired power plant (820 MW<sub>e</sub>) with a purity of 95%. They obtained a specific heat duty of 2.41 MJ<sub>th</sub> kg<sup>−1</sup> of CO<sub>2</sub> (lower than that of the benchmark technology), which could be satisfied using low-grade heat, and a specific electricity consumption of 1.15 MJ<sub>e</sub> kg<sup>−1</sup> CO<sub>2</sub> (higher than that of the benchmark

technology mainly as a result of the use of vacuum to regenerate the adsorbent).

Steam-aided VSA (SA-VSA) has also been proposed as a possible hybrid regeneration mode. In this framework, Fujiki et al.<sup>196</sup> investigated low-temperature SA-VSA using an amine-based sorbent. They demonstrated that an effect similar to the direct heating can be obtained by diluting with steam under vacuum. A high CO<sub>2</sub> purity (>98%) and recovery level (>93%) were obtained against a recovery of 45% with only VSA.

A hybrid process combining ESA with VSA (VESA) was studied by Zhao et al.<sup>197</sup> using a monolith reactor. Even though the total energy consumption of the investigated VESA process (3.25 MJ kg<sup>-1</sup> of CO<sub>2</sub>) was found to be lower than that of ESA alone (3.04 MJ kg<sup>-1</sup> of CO<sub>2</sub>), it was still higher than that of VSA alone (2.45 MJ kg<sup>-1</sup> of CO<sub>2</sub>).

**4.4. Summary of Regeneration Strategies.** In summary, the sorbent can be regenerated by acting on either the temperature or the (total or partial) pressure. Both of these two approaches hold different advantages and disadvantages when applied to post-combustion capture applications. Table 10 provides the comparison of the performances of different regeneration strategies (in terms of energy consumption, CO<sub>2</sub> productivity, purity, and recovery), also highlighting the type of reactor configuration and adsorbent material. It is evident that quite good process performances can be achieved, with energy consumption falling in the range of 2–3.5 MJ kg<sup>-1</sup>, which is in well below conventional MEA absorption processes (>4 MJ kg<sup>-1</sup>).

With reference to TSA, in which CO<sub>2</sub> adsorption takes place mostly at a lower temperature and the sorbent is regenerated by heating, the main advantages are that this system is operated at low values of pressure (<4 bar), thus implying easy maintenance procedures, and that it is only little impacted by the presence of impurities (e.g., NO<sub>x</sub>, SO<sub>x</sub>, and water vapor) in the flue gas (i.e., there are not very strict requirements on the composition of the feed). Therefore, TSA is one of the lowest risk and shortest term implementation alternatives.<sup>198</sup> However, considering that temperatures as high as 150–200 °C should be used for the sorbent regeneration, whereas adsorption is performed at lower temperatures (about 50 °C), the repeated heating and cooling may negatively affect the overall process efficiency. In this framework, several works have been focused on reducing the energy consumption by optimization of the capture process, through energy integration and development of novel cutting-edge sorbents characterized by a high adsorption capacity and low regeneration temperature.<sup>4</sup> In this framework, it is important to underline that TSA can be relatively easily integrated into existing power plants, where large amounts of low-grade energy may be used for sorbent regeneration. With regard to the other important issues linked with TSA in its standard configuration, namely, the dilution caused by the use of a large volume of an inert purging gas (such as air or N<sub>2</sub>), it can be avoided using either steam/CO<sub>2</sub> as purging gas or adopting an indirect heating mode.<sup>181</sup>

With reference to PSA/VSA, in which CO<sub>2</sub> is recovered by decreasing the pressure with respect to the capture step, they can both be performed at a low temperature, thus avoiding the energy penalty associated with the repeated heating/cooling.<sup>10</sup> However, both pressurization, needed in the adsorption step in the case of PSA, and vacuum, needed in the regeneration step in the case of VSA, are very energy-consuming. In particular,

vacuum levels below 100 mbar (absolute pressure) are not advisable in industrial processes.

Therefore, a promising solution is represented by the combination of TSA and VSA, thus combining the advantages of the two different approaches. In particular, VTSA can reduce the temperature required by a standard TSA (i.e., using a proper low-grade waste heat, the energy consumption can be remarkably limited) and improve the CO<sub>2</sub> purity and recovery of a standard VSA.<sup>10</sup>

## 5. CHALLENGES AND PERSPECTIVES

In light of the discussion presented in the previous section, it appears quite clearly that, among all of the available technological options, adsorption-based CO<sub>2</sub> capture processes hold great potential for future application. However, it is also clear that remarkable enhancement of the state of the art is needed in different directions, meaning that a multi-disciplinary approach must be used.

First of all, the selection of the sorbent is a crucial step for retrofitting the current power generation infrastructure with CO<sub>2</sub> capture processes. In this framework, it can be argued that the key scientific challenges mainly concern the development of new materials with enhanced CO<sub>2</sub> capture properties by means of environmentally benign and easily scalable synthesis routes; in particular, their chemico-physical features should be controlled at the molecular level thanks to a clearer understanding of the structure/function relationships. In this context, aiming at addressing the issues related to the economics and environmental aspects of adsorbent manufacturing, great attention should be focused on environmentally friendly raw materials, such as agricultural and food residues. It must also be highlighted that the possibility to have an enormous number of possible adsorbent materials (e.g., in the case of MOFs, which counts thousands of compounds already synthesized, and much more can be possibly synthesized in the future) might also be one of the reasons for the slow deployment of the CO<sub>2</sub> adsorption technology because the task of synthesizing and testing all of them can be somehow overwhelming. Therefore, strictly related to this point, the development of new characterization and computational approaches seems to be necessary. Indeed, performed in parallel with experimental investigations, they will play a crucial role for the further refinement of the promising structures and might also be a very powerful tool to perform quick large-scale screening of new materials and predict their performances. As a matter of fact, the real applicability of a sorbent on an industrial scale is determined by the ease and cost of its large-scale synthesis. It can also be argued that this adsorbent screening challenge is also made more complex by the great number of performance criteria that must be considered during the design process (Figure 2). Also regarding the area of material testing and screening, a focus of the research community on solving the poisoning issue of most of the available sorbents seems to be now of utmost importance. Indeed, while there is a very good understanding and wide knowledge on the performance of different families of sorbents under equilibrium conditions in a simple CO<sub>2</sub>/N<sub>2</sub> atmosphere, there is a lack of information on how the most promising sorbents behave under dynamic conditions in more realistic multi-component mixtures. Even though a detailed examination of this goes beyond the scope of this review, serious attention from researchers in the field is demanded on this.

**Table 11. Demonstration Status of Different Adsorption-Based CO<sub>2</sub> Capture Concepts**

reactor	regeneration mode	scale	adsorbent	sector	reference
fixed bed	VSA (two stages)	pilot	zeolite 13X (stage one) and activated carbon (stage two)	coal	201
fixed bed	VSA (four stages) with LPP <sup>a</sup>	pilot	zeolite 13X	coal	203
fixed bed + membrane	VSA–membrane	laboratory	zeolite 13X	coal	204
fluidized bed	TSA	pilot	K-based material	coal	205
fluidized bed (RTI) <sup>b</sup>	TSA	pilot	PEI-impregnated silica <sup>c</sup>	cement	206
multi-stage fluidized bed	TSA	pilot	aminated ion-exchange resin	coal	207 and 208
multi-stage fluidized bed	TSA	bench	amine-functionalized material	gas	146
multi-stage fluidized bed	VTSA	laboratory	PEI-impregnated silica	coal	170
sound-assisted fluidized bed	TSA	laboratory	activated carbon	coal/gas	20, 22, 140, and 151
moving bed (KCC) <sup>d</sup>	TSA	pilot	amine-impregnated material	coal	166
moving bed (SRI) <sup>e</sup>	TSA	pilot	carbon sorbent	coal	165

<sup>a</sup>LPP = light product pressurization. <sup>b</sup>RTI = Research Triangle Institute International. <sup>c</sup>PEI = polyethylenimine. <sup>d</sup>KCC = Kawasaki CO<sub>2</sub> capture system. <sup>e</sup>SRI = SRI International.

However, it is important to underline that merely choosing the most promising adsorbent (i.e., the adsorbent providing the best combination of required properties) cannot be made *a priori* because several other aspects will affect the overall process performance and economics. With this clear understanding and aiming at minimizing the operating and capital costs and accelerating the commercial deployment of the adsorption technology, the potential of each sorbent can be fully exploited only using the most suitable combination of gas–solid reactor configuration and regeneration mode. Indeed, it is evident that the capture performance, in terms of CO<sub>2</sub> recovery, purity, and productivity, in addition to the energy demand and overall footprint, is critically affected by the fundamental behavior of the gas–solid contacting system and regeneration strategy.

On the basis of the sorbent material, reactor configuration, and regeneration mode, different adsorption-based CO<sub>2</sub> capture concepts have been demonstrated in the last years at different scales, even though proper techno-economic and life cycle assessment (LCA) studies, providing a clear estimation of the cost of retrofitting existing plants and CO<sub>2</sub> avoidance and practical energy penalties caused by this capture approach, are still lacking. A summary is provided in Table 11. As is clearly inferable, only few concepts have been demonstrated at the pilot scale, thus indicating that there is still a long way to go before the adsorption-based CO<sub>2</sub> capture processes can be applied in real plants. Moreover, it is also evident that the target of the available demonstration studies is predominantly the CO<sub>2</sub> capture from coal power plants, thus highlighting a strong need to extend them to other CO<sub>2</sub>-intensive sectors, such as cement, biofuel, and metal industries. It is also important to point out that the techno-economic analysis and LCA of the adsorption-based CO<sub>2</sub> capture process is far from being well-defined and systematic, as confirmed by the rather scattered values of all of the performance parameters (Table 10) inferable from the limited number of works available on this specific topic. Therefore, to date, it is still not possible to draw a clear and firm conclusion on how the global performance of the adsorption-based capture technology is linked to the sorbent material, reactor configuration, and regeneration mode.

In light of the above considerations, great research effort, mass of different expertise, and deep scientific collaboration are demanded to standardize the assumptions for the techno-

economic assessment of the different reactor configurations combined with the different regeneration modes and adsorbent families, to provide a clear and solid comparison. Experimental studies and validation at both laboratory and pilot scale should be focused on assessing the feasibility of the integration between the most promising reactor configurations (such as the multi-stage fluidized bed and the structured fixed bed reactors) and the regeneration mode, also confirming the possibility to achieve high separation performances in a sufficiently short cycle time. In this framework, the best combination might be identified also taking into account the CO<sub>2</sub> partial pressure in the feed, namely, the CO<sub>2</sub> source, to provide real breakthrough insight for the different industrial sectors.

## 6. CONCLUSION

This review analyzes the most recent progresses of the adsorption-based post-combustion CO<sub>2</sub> capture, thus providing the state-of-the-art research activity and application focused on this topic.

It is important to point out that, even though adsorption-based separation technology is mature in a number of large-scale industrial applications, its use in real post-combustion CO<sub>2</sub> capture processes still poses several challenges related to the sorbent materials, the gas–solid contact system, and the regeneration mode. Therefore, in the first section of this review, the CO<sub>2</sub> adsorption performances of different classes of solid sorbents are presented and discussed on the basis of the most important evaluation parameters (equilibrium adsorption capacity, multi-cyclic stability, etc.). The second section reviews different types of gas–solid contacting systems (fixed beds and fluidized beds), highlighting their strengths and limitations. Finally, in the third section, a review of the different regeneration modes (temperature, pressure, or hybrid swings) is provided, with particular attention on the possible strategies available to limit the energy demand.

(1) With reference to the sorbent materials, both physisorbents and chemisorbents, several chief criteria must be satisfied to successfully address the economic and performance requirements of a capture process. In this framework, carbon- and zeolite-based sorbents are very cheap and can provide fast adsorption kinetics in combination with low regeneration energy. However, their adsorption capacity is affected by the presence of moisture and other



contaminants present in the feed; likewise, increasing temperatures have a strong detrimental impact on their adsorption performances. Also, in the framework of physisorbents, MOFs are considered to be a very promising solution for post-combustion CO<sub>2</sub> capture because they can provide relatively high adsorption capacity. However, great research effort is still needed to make them suitable under flue gas conditions from both economic and technical points of view. In contrast to physisorbents, chemisorbents, such as amine-functionalized materials, have great potential because they are capable of combining the advantages of solid sorbents (large specific surface area) and solvents (high numbers of adsorption sites). Therefore, with relatively low production costs, they are characterized by quite high CO<sub>2</sub> adsorption capacity. The open challenges for their utilization are related to the possibility to enhance the uniformity of distribution of the liquid amines onto the porous substrate, thus minimizing the diffusion limitations while maximizing capture and release performance, and improve the long-term thermal/oxidative stability.

(2) With reference to the gas–solid reactor configuration, both fixed and fluidized bed reactors in their conventional configuration are not able to fully express their potential for post-combustion CO<sub>2</sub> capture applications. Indeed, fixed beds, on the one hand, can rely on the configuration simplicity and the plug-flow nature, which is beneficial for adsorption thermodynamics; however, they suffer from high pressure drops and mass/heat transfer limitations. Fluidized beds, on the other hand, can rely on very good mixing and high heat/mass transfer coefficients, which is advantageous for achieving good thermal and reaction rates but detrimental for adsorption thermodynamics (i.e., fast CO<sub>2</sub> breakthrough and, in turn, poor CO<sub>2</sub> working capacity). Aiming at overcoming the limitations of both fixed and fluidized bed reactors, the research effort is focusing on the study and development of innovative configurations, such as structured packing, in the case of fixed beds, and counter-current multi-staging, in the case of fluidized beds. Even though these smartly designed systems hold great promise, being able to provide quite good performances with respect to their standard counterparts, they are both characterized by increased construction and operating complexity, thus posing relevant scale-up challenges. Similar to the multi-stage fluidized bed concept, the moving bed configuration is capable of further improving the sorbent working capacity. However, challenges still remain regarding the heat transfer efficiency and the low employable gas velocities.

(3) With reference to the regeneration mode, both pressure and temperature swings can provide different advantages and disadvantages when applied to post-combustion capture applications. TSA, on the one hand, being performed at atmospheric pressure, can rely on easy maintenance procedures and operations and is just a little influenced by the presence of impurities. However, it suffers from the a higher energy penalty associated with the repeated heating and cooling. On the other hand, PSA/VSA can be performed at a low temperature, thus circumventing the energy-intensive heating/cooling steps; however, both pressurization, in the case of PSA, and vacuum, in the case of VSA, are very energy-consuming. Therefore, hybrid regeneration modes, i.e., combining temperature and pressure swings, are receiving increasing research interest, being able to exploit the advantages of the two different approaches. For example, VTSA has been proven to limit the temperature required by a

standard TSA, using a proper low-grade waste heat, and improve the CO<sub>2</sub> purity and recovery of a standard VSA.

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### Notes

The authors declare no competing financial interest.

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## NOMENCLATURE

AC = activated carbon  
AEAPS = *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane  
AP = aminopropyl  
APTES = (3-aminopropyl)triethoxysilane  
APG = aminopropyl gel  
BEA =  $\beta$  zeolite  
CNT = carbon nanotube  
CCS = carbon capture and storage

DBU = diazabicyclo[5.4.0]undec-7-ene  
 DEA = diethanolamine  
 DETA = diethylenetriamine  
 EDA = ethylenediamine  
 FAU = faujasite  
 ITQ = Instituto de Tecnología Química  
 LTA = Linde type A zeolite  
 MCM-41 = Mobil composition of matter number 41  
 MEA = monoethanolamine  
 MOF = metal–organic framework  
 MWCNT = multi-walled carbon nanotube  
 PAA = polyallylamine  
 $P_{\text{CO}_2}$  = CO<sub>2</sub> partial pressure  
 PEI = polyethylenimine  
 PE-MCM-41 = pore-expanded MCM-41  
 PMMA = polymethyl methacrylate  
 PPI = polypropylenimine  
 PSA = pressure swing adsorption  
 SBA-15 = Santa Barbara amorphous number 15  
 SBA-16 = Santa Barbara amorphous number 16  
 T = temperature  
 TEPA = tetraethylenepentamine  
 TRI = (3-aminopropyl)trimethoxysilane  
 TSA = temperature swing adsorption  
 VSA = vacuum swing adsorption  
 VTSA = vacuum temperature swing adsorption  
 $y_{\text{feed,CO}_2}$  = CO<sub>2</sub> molar ratio in the feed stream

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