

# Carbon Dioxide Capture Adsorbents: Chemistry and Methods

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Excess carbon dioxide (CO<sub>2</sub>) emissions and their inevitable consequences continue to stimulate hard debate and awareness in both academic and public spaces, despite the widespread lack of understanding on what really is needed to capture and store the unwanted CO<sub>2</sub>. Of the entire carbon capture and storage (CCS) operation, capture is the most costly process, consisting of nearly 70% of the price tag. In this tutorial

review, CO<sub>2</sub> capture science and technology based on adsorbents are described and evaluated in the context of chemistry and methods, after briefly introducing the current status of CO<sub>2</sub> emissions. An effective sorbent design is suggested, whereby six checkpoints are expected to be met: cost, capacity, selectivity, stability, recyclability, and fast kinetics.

## 1. Introduction

Regardless of its primary cause, global warming is real. Greenhouse gases are intimately related to this temperature surge, as either the reason or the result of this climate change. The fact that atmospheric carbon dioxide (CO<sub>2</sub>) levels are steadily increasing means that we need urgent action, mainly to prevent further acidification of oceans. A lower pH of the oceans will mean a reduction of large marine biota, and a complete change of the distribution of species, and their habitats, for example, reefs. The effects of this global impact are too large to ignore, too complicated to predict, and may be too late to finally reckon with. Scientific and political capital, therefore, should immediately be used to prevent and reduce CO<sub>2</sub> levels.

To mitigate CO<sub>2</sub> effectively and economically, research has been directed to improving current CO<sub>2</sub> capture and storage technologies. Capture sorbents (a *sorbent* is a material that can perform both adsorption and desorption) are the key to all efforts,<sup>[1]</sup> however, to date there is no introductory review that educates a newcomer to the field of CO<sub>2</sub> sorbent development. This brief tutorial is designed to bring any scholar at graduate school or later in their career to a beginner's level in CO<sub>2</sub> capture sorbent development and testing. We have identified chemistry and methods as the two major sides of the technical knowledge required. But first, let us summarize the basics of CO<sub>2</sub>, the status of emissions, and the main challenges.

### 1.1. Current status of CO<sub>2</sub> presence and distribution

CO<sub>2</sub> is the dominant greenhouse gas (GHG), accounting for at least 60% of all GHGs, and is an essential component of the global carbon cycle.<sup>[1a,2]</sup> There remains 16 gigatons (Gt) per year of excess CO<sub>2</sub> in the atmosphere after all the sinks reabsorb emitted volume (Table 1). A pre-industrial level of

280 ppm would indicate 952 Gt CO<sub>2</sub> increase has occurred over the past century.

Most major CO<sub>2</sub> emissions from combustion processes contain under 15% CO<sub>2</sub> in their feed, are warmer than room temperature (>25 °C), and at ambient pressures (Table 1). Non-CO<sub>2</sub> fractions are highly variable, although atmospheric gases are dominant. Water, particularly, is a very important fraction as it is present in every CO<sub>2</sub> source and competes with CO<sub>2</sub> at solid sorbent surfaces during attempted capture. It is, therefore, safe to say that most capture chemistry should be directed towards wet streams.

Carbon dioxide, once captured, is expected to be stored away, as the industrial demand for CO<sub>2</sub> as a feedstock is far smaller than the production (250 Mt market vs. 52 Gt year<sup>-1</sup> emissions).<sup>[1a,4]</sup> The locations for such high amounts of gas storage are not many; either the ocean floor or empty wells and caves underground. Even then we cannot continue storing CO<sub>2</sub> indefinitely as the storage space will run out. The simplest explanation for this is that fossil fuels take in twice as much oxygen as carbon in turning it into CO<sub>2</sub>, increasing their masses and volume considerably (more than three times in coal). It is, therefore, clear that carbon capture and storage (CCS) solutions that require underground storage for permanent sequestration of CO<sub>2</sub> will not be sustainable, mainly because of the scale of emissions.

As the CO<sub>2</sub> emissions are directly related to industrialization (and stronger economies)—unlike any other scientific challenges we have had in the past—it is hard to keep it apolitical. Hence, it is important for any researcher to understand the non-scientific parts of this problem that s/he is trying to create solutions for. Scientists need to create feasible paths for CO<sub>2</sub> avoidance; either by capturing and storing it or by preventing its excessive formation. The policymakers need to implement these viable methods put out by scientists into the public agenda. The situation is far from ideal, as one can easily observe.

One particular metric that is often avoided in CO<sub>2</sub> emissions policymaking is the CO<sub>2</sub> emissions per person. In the most basic sense of human equality, one must compare the nations (Figure 1) based on their per person emissions. It is not surprising that the most industrialized (and rich) countries are the most prolific emitters and they should be the ones initiating the CO<sub>2</sub> revolution.

In developed countries, particular attention must be given to fossil fuel burning power plants. For example, one 500 MW plant based on coal releases 11 000 tons of CO<sub>2</sub> per day.<sup>[1a]</sup> And there are 1440 coal-based power plants (647 in the USA alone)

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with a total electricity output of 1.22 TWs.<sup>[5]</sup> Considering that a 3600 Gt CO<sub>2</sub> increase in the atmosphere would heat the earth by 2 °C,<sup>[1a]</sup> also known as the point of no return,<sup>[3]</sup> we need to start all solutions immediately. Thus, it is evident that CO<sub>2</sub> capture is a global challenge and that it requires a new approach; one that includes not just interdisciplinary research but interdisciplinary people trained in various disciplines, simultaneously.

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## 1.2. Ideal scenarios for CO<sub>2</sub> capture

An ideal solution to CO<sub>2</sub> capture and storage would be to use the basic ocean water to scrub CO<sub>2</sub> out of power plant fumes (if one assumes no negative impact on the biota), because the oceans are already the largest CO<sub>2</sub> sinks. This, however, needs an efficient catalyst similar to carbonic anhydrase of the human respiration cycle, as the exchange between gaseous CO<sub>2</sub> and its soluble species (CO<sub>2(aq)</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) is very slow.

A solid-state, on-land alternative scenario is to make a sorbent material that reversibly captures CO<sub>2</sub> during the night and releases when the sun is up, effectively creating a greenhouse around the vegetation (Figure 2). This idea relies on a well-known practice to fertilize crops with chemically generated CO<sub>2</sub> gas in commercial greenhouses. As the concentration of the CO<sub>2</sub> in the air is very low, this scenario seems to be more fitting to small operations. Not surprisingly, direct air capture (DAC) is the toughest of all forms of capture and further research efforts are needed as it will create the baseline for the highest price of techniques to mitigate CO<sub>2</sub> emissions.

For an effective CCS process, it is well established that CO<sub>2</sub> capture is the most costly part of the process and therefore needs the most research and development (Figure 3). Aqueous amine solutions, the industrial standards in CO<sub>2</sub> capture, are the reason for the elevated costs as the solution has high heat capacity and the material losses are significant. Solid sorbents are expected to save considerable costs because of their low regeneration energy requirements and durability over many cycles.<sup>[6]</sup>

A particular advantage of a solid sorbent is its easy recovery and regeneration; the main cost drivers in CO<sub>2</sub> capture technologies. Speed of recovery is intimately related to the ease of regeneration and both are directly proportional to the binding energy, especially at low partial pressures of CO<sub>2</sub>. Expectedly, strong binding of CO<sub>2</sub> results in energy intensive regeneration of the sorbent media.

Liquid, aqueous amines provide strong binding to CO<sub>2</sub>, although considerably lower than the carbonates of alkali/earth alkali metals. They have been the industrial standard, monoethanolamine (MEA) being the chemical icon, and they are the costly absorbents that we need to improve.<sup>[7]</sup> Considering all the shortcomings of the potential replacements, porous solids emerge as the only viable replacements to liquid amine sorbents. The major advantages of porous solid sorbents are (1) easy handling, (2) fast diffusion, and (3) tunable sorbent chemistry. The debate on whether using a fixed batch of sorbents or a continuous gas flow through a membrane is still continuing. We will leave the superiority discussion to focused reviews such as that by Aaron et al.<sup>[8]</sup> In short, current membranes provide less selectivity of CO<sub>2</sub> than sorbents and therefore can be very useful for applications that do not need to produce high purity CO<sub>2</sub>. The development of solid sorbents, however, can fix the gap between membrane and sorbent technologies as they can be placed in the mixed matrix membranes or be made into highly porous membranes, such as those of polymers of intrinsic microporosity (PIM).<sup>[9]</sup> A com-

**Table 1.** Carbon dioxide emitting sources across the earth. Data adapted mainly from Refs. [1a,3], and the references therein. Values do not represent all the emissions nor the most current, but rather a range that is frequently observed and reflect the nature of the source. For industrial or vehicular exhaust compositions, we assumed complete compliance with the emissions regulations.

Location	CO <sub>2</sub> content	Chemistry	Physics
Air	400 ppm 16 Gtyr <sup>-1</sup> excess 3172 Gt total	0.04% CO <sub>2</sub> 78% N <sub>2</sub> 20% O <sub>2</sub> 1% Ar 1% H <sub>2</sub> O	1 bar −60–60 °C (troposphere)
Power plant fumes	32 Gtyr <sup>-1</sup>	12–15% CO <sub>2</sub> 70–75% N <sub>2</sub> 4–6% H <sub>2</sub> O 4% O <sub>2</sub>	1 bar 40–75 °C 0.3–1 kg kWh <sup>-1</sup>
Vehicles	6 Gtyr <sup>-1</sup>	12–14% CO <sub>2</sub> 65–75% N <sub>2</sub> 6–12% H <sub>2</sub> O 10% O <sub>2</sub> (diesel)	1–4 bar > 70 °C 0.4 kg (mile × unit) <sup>-1</sup>
Cement factories	2 Gtyr <sup>-1</sup>	14–33% CO <sub>2</sub> 50–70% N <sub>2</sub> 5–10% H <sub>2</sub> O 2–5% O <sub>2</sub>	1 bar 40–75 °C
Steel industry	1 Gtyr <sup>-1</sup>	15% CO <sub>2</sub> 60–70% N <sub>2</sub> 5–10% H <sub>2</sub> O 2–5% O <sub>2</sub>	1 bar 40–75 °C
Refineries	0.85 Gtyr <sup>-1</sup>	3–13% CO <sub>2</sub> 70–75% N <sub>2</sub> 5–10% H <sub>2</sub> O 3–7% O <sub>2</sub>	1 bar > 40 °C
Petrochemical industry	0.38 Gtyr <sup>-1</sup>	8–20% CO <sub>2</sub> 70–75% N <sub>2</sub> 1–5% H <sub>2</sub> O	1 bar > 40 °C
Natural gas mining	0.05 Gtyr <sup>-1</sup>	5–70% CO <sub>2</sub> 50–95% CH <sub>x</sub> 1–20% H <sub>2</sub> S 1–5% H <sub>2</sub> O	1 bar 10–60 °C
Volcanos	0.2 Gtyr <sup>-1</sup>	2–50% CO <sub>2</sub> 1–12% SO <sub>2</sub> 35–95% H <sub>2</sub> O	> 1 bar > 500 °C
Human respiration	2.6 Gtyr <sup>-1</sup>	4–5% CO <sub>2</sub> 78% N <sub>2</sub> 5% H <sub>2</sub> O 13–16% O <sub>2</sub>	1 bar 30–35 °C 1 kg (day × person) <sup>-1</sup>

bined sorbent–membrane system has the potential to address all the requirements of high flux CO<sub>2</sub> contained in wet streams.

### 1.3. Leading solid CO<sub>2</sub> sorbents

Despite many efforts to develop one, an industry-ready sorbent that can replace amine solutions does not exist. In Table 2, we have selected several promising sorbents for comparison with MEA solutions. The reported values are from the corresponding research papers and not from an industrial pilot scale, therefore, they are prone to significant error.

### 1.4. Current challenges in CO<sub>2</sub> capture

The following is a summary of the leading challenges in CO<sub>2</sub> capture:

**1) Scale:** CO<sub>2</sub> emissions are huge and the equally vast amounts of sorbent synthesis represents a formidable challenge. Any costly ingredient or reagent in sorbent making (e.g., any metals) is undesired. Because of the scale, reusing CO<sub>2</sub> is also not sustainable.

**2) Sorbent:** The main challenge in sorbent design is to attain high CO<sub>2</sub> capacity and selectivity repetitively when water vapor is present. Pellet making and attrition index are not usually considered, although they are very important. Cost limitations prevent even most common metals from being used. Atom economy in synthesis is absolutely necessary. In addition, the yield of the sorbent synthesis and reactant/sorbent ratio are significant parameters when scaling up.

**(3) Storage:** Putting away such high amounts of CO<sub>2</sub> in physical and chemical means is untested.

**Table 2.** List of leading CO<sub>2</sub> capture sorbents.

Supporting porous material	Amine type	CO <sub>2</sub> adsorption [mmol g <sup>-1</sup> ]		Sorption temperature [°C] (adsorption–desorption)	Sorption partial pressure of CO <sub>2</sub> [bar] (adsorption–desorption)
		Dry CO <sub>2</sub>	Wet CO <sub>2</sub>		
MCM-41 <sup>[11]</sup>	Polyethylenimine	2.02	2.98	75–75	0.15–0
SBA-15 <sup>[12]</sup>	(3-Trimethoxysilylpropyl) diethylenetriamine	2.4	2.72	60–> 300	0.15–0
Mesoporous silica capsules <sup>[13]</sup>	Tetraethylenepentamine	–	7.93	75–100	0.1–0
Mesoporous silica foam <sup>[14]</sup>	Tethered amines	–	11.8	25–100	0.08–0
Mg-MOF-74 <sup>[15]</sup>	<i>N,N'</i> -Dimethyl ethylene diamine (mmen)	3.1	2.7	40–120	0.15–0
PPN-6-CH <sub>2</sub> DETA <sup>[16]</sup>	Linear amines	3.04	–	22–80	0.15–vacuum
COP-19 <sup>[17]</sup>	Polyethylenimine	1.57	2.27	40–80	0.15–vacuum
Hollow fibres (continuous) <sup>[18]</sup>	Amine impregnated silica	–	0.58	35–120	0.1–0
Aqueous amines <sup>[19]</sup>	Monoethanolamine (MEA)	–	0.83	80/120–120	0.15–0

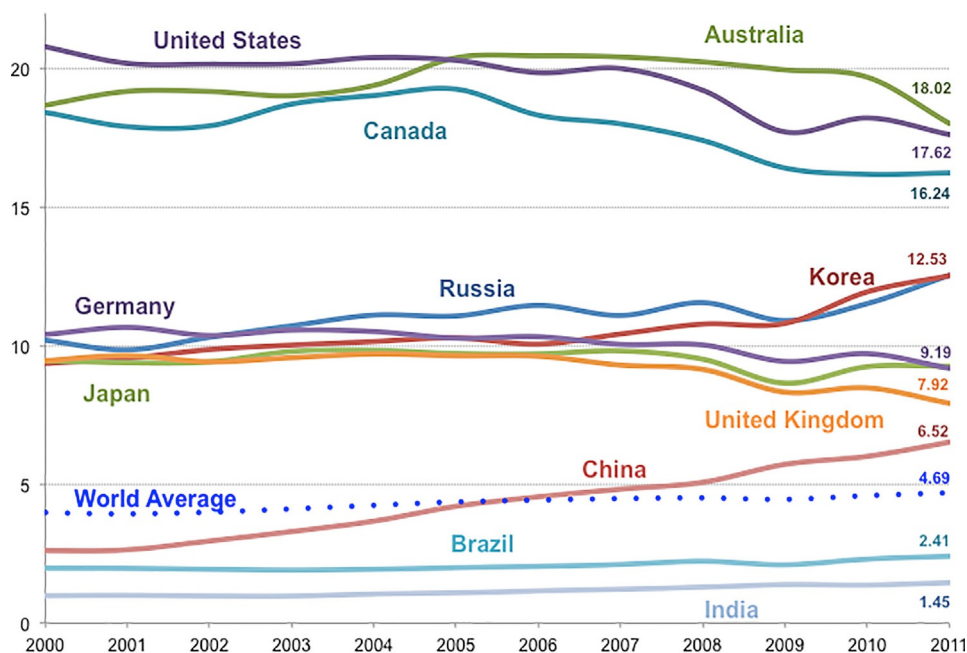


Figure 1. Per capita emissions by highly populated major CO<sub>2</sub> emitters (metric tons per person per year, adapted from US Energy Information Administration).

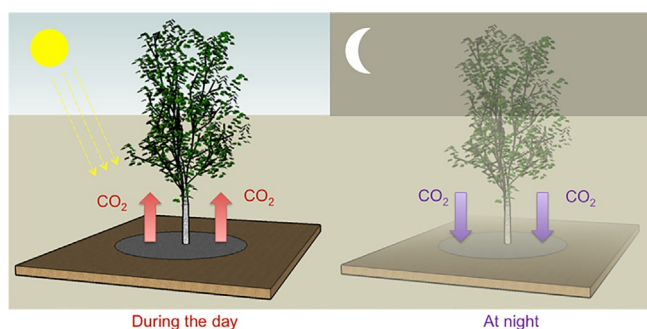


Figure 2. An ideal sorbent takes in CO<sub>2</sub> during the night and releases it during the day, promoting vegetation growth.

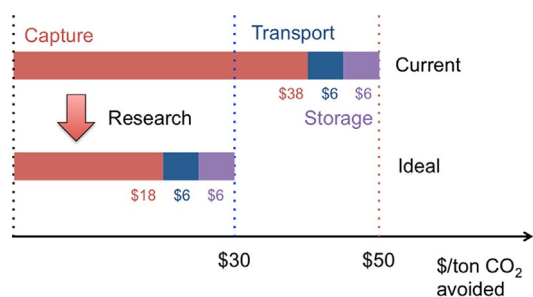


Figure 3. The minimum cost requirements of carbon capture and storage (CCS) with current and ideal scenarios. Transport and storage are mature technologies with minimal potential to improve (adapted from Ref. [10]).

### 1.5. Six checkpoints for an ideal CO<sub>2</sub> capture sorbent

An ideal CO<sub>2</sub> sorbent has to bind to CO<sub>2</sub> favorably, leading to a high enough capacity (first checkpoint), for example, 2 mmol or more of net CO<sub>2</sub> per gram of sorbent (Table 3). The key

Table 3. Benchmark checkpoints for an effective CO <sub>2</sub> sorbent. All conditions have to be met to get the best working sorbent.	
Checkpoint	Desired
Capacity	> 2 mmol CO <sub>2</sub> per g of sorbent
Recyclability	> 1000 cycles
Selectivity	> 100 (CO <sub>2</sub> /other gases)
Stability	> 150 °C, boiling water, H <sub>2</sub> S, SO <sub>x</sub> , NO <sub>x</sub> , HCl, NaOH, mechanical strength with low attrition index (AI)
Cost	< \$50 kg <sup>-1</sup> (sorbent cost < \$10 kg <sup>-1</sup> )
Kinetics	> 1 mmol(g × min) <sup>-1</sup>

metric here is the isosteric heat of adsorption ( $Q_{st}$ ), the heat released when CO<sub>2</sub> molecules are chemically attached. An optimal  $Q_{st}$  is between 35 and 50 kJ mol<sup>-1</sup> of CO<sub>2</sub>, above which recyclability (to take CO<sub>2</sub> back and regenerate the sorbent; second checkpoint, Table 3) is energy intensive, leading to high parasitic energy, the extra heat you need in a CO<sub>2</sub> capture/release cycle. Below 35 kJ mol<sup>-1</sup>, weak binding usually results in low capacity. The  $Q_{st}$  for the industrial standard, monoethanolamine (MEA) solution, is above 75 kJ mol<sup>-1</sup>, depending on the concentration, explaining why we are in need of an alternative sorbent. The working capacity (capacity difference between adsorption and desorption) for MEA-based solutions is up to 1.5 mmol (60 mg) of CO<sub>2</sub> per gram of sorbent solution. Ideally, new sorbents need to win over this capacity. Recent studies on ionic liquid-based CO<sub>2</sub> sorbents have demonstrated exceptional CO<sub>2</sub> capture capacity,<sup>[20]</sup> despite the uncertainty in their implementation on the industrial scale and also in spite of their being liquid-based scrubbing techniques.

Activated carbons are often used for gas treatments, as they are inexpensive, highly porous, and robust.<sup>[21]</sup> However, they lack specificity towards CO<sub>2</sub>, leading to a low CO<sub>2</sub> selectivity

(third checkpoint, Table 3) over the rest of the gas mixture (e.g., N<sub>2</sub>). To produce a near-pure CO<sub>2</sub> feed (> 99%) from capture operations, one needs at least 100 times more selectivity for CO<sub>2</sub>. It was previously shown<sup>[22]</sup> that selectivity makes more difference above 3 mmol g<sup>-1</sup> capture capacities. Ideally, one needs 1000 times or more selectivity to make a significant impact.

Flue gas mixtures are the most likely CO<sub>2</sub> sources and they account for at least 50% of all CO<sub>2</sub> emissions. In that mixture, water is present in saturation at 5–7% [e.g., 100% relative humidity (RH) is 70 mbar or 7% at 40 °C] and the temperature of the feed is never found to be below 40 °C. Any sorbent to be considered has to have stability (fourth checkpoint, Table 3) in water, then steam (or boiling water), and in high-temperature (> 150 °C) gas mixtures. The high thermal stability of a sorbent is necessary, especially for amine-grafted sorbents. The irreversible formations of carbamate, bicarbonate, or urea upon CO<sub>2</sub> sorption lower the sorption capacity, and deactivated sorbents can only be regenerated by heating at high temperatures under an inert gas flow.<sup>[23]</sup> Not to mention, trace amounts of acidic gases (NO<sub>2</sub>, SO<sub>2</sub>), oxygen (O<sub>2</sub>), and even mercury (Hg) are present in flue gases. Then, there are mechanical stability requirements, because hurling tons of sorbents in cyclones will not be easy with sorbent materials that can be dismantled on mechanical impact. Nanoscale powders are also not suitable; having pellets of at least micrometer sizes are non-negotiable.

The biggest obstacle is the cost (fifth checkpoint, Table 3) of the CO<sub>2</sub> sorbent, as it directly affects the economics of CCS. The cost–benefit relationship for similar sorbents will lead to industrial decisions to use a lower cost sorbent if the cost per CO<sub>2</sub> capacity is much lower. As amine solvent-based CCS costs \$50 ton<sup>-1</sup> of CO<sub>2</sub> avoided, only a sorbent cost of \$10 per kg (considering 10000 cycles with 90% capacity retention) would make it more affordable. Most advanced sorbents cost in the range of millions of dollars per kg, far exceeding these limits. The only other method of cutting costs is to find suitable markets for the captured CO<sub>2</sub>. The current CO<sub>2</sub> market is too small (250 million tons per year vs. over 40 Gt of emissions from point sources) to make any impact; however, it can drive early projects such as the Saskatchewan plant. Converting CO<sub>2</sub> back into fuel (e.g., artificial photosynthesis) is also seriously considered, although that brings a philosophical question of why we should use carbon as the energy carrier as opposed to hydrogen or batteries.

The speed of CO<sub>2</sub> uptake, in other words, the kinetics (sixth checkpoint, Table 3), also limits the potential use for many advanced ultra-microporous sorbents.<sup>[24]</sup> Any uptake beyond five minutes of contact time will not be feasible. Ideally, 80% uptake should take place within two minutes. This will also eliminate many exciting new CO<sub>2</sub>-philic solids because small, uniform pores often slow down the diffusion of CO<sub>2</sub>. Just like in our lungs, the most effective O<sub>2</sub> absorption plus CO<sub>2</sub> desorption machines, we need channels of various sizes to create diffusive paths. An ideal porous solid, therefore, should provide a lung-like network of pores.

## 2. Chemistry

Molecular interactions between CO<sub>2</sub> and sorbents define the principles of the CO<sub>2</sub> capture operations. Solid-phase sorbents offer much less energy intensive operations for CO<sub>2</sub> capture and porosity is crucial for effective diffusion through the powders and pellets. To develop an effective, solid, porous sorbent, we need to identify what would be the best network structure and chemical functionality that would carry out the process. Below we discuss the sorbent design and chemistry for CO<sub>2</sub> capture.

### 2.1. Sorbent design principles

As mentioned earlier, designing a sorbent for CO<sub>2</sub> capture for industrially acceptable parameters requires six qualities in the sorbent materials: (1) high CO<sub>2</sub> uptake ( $\geq 40$  °C and 0.15 bar) and desorption at  $\leq 110$  °C, (2) high CO<sub>2</sub> selectivity, (3) cyclability over at least 1000 cycles, (4) fast kinetics, (5) stability in water vapor and acidic gases, and (6) the sorbent should be constructed from the cheap raw materials.

Industrial practices in fossil fuel based power plants provide two options for CO<sub>2</sub> scrubbing: (1) post-combustion, and (2) pre-combustion.<sup>[26]</sup> A third one, oxy-fuel combustion, does not require CO<sub>2</sub> capture from a mixture and therefore should not be considered as challenging CO<sub>2</sub> chemistry. At high pressures of CO<sub>2</sub> (e.g., pre-combustion), a selective physisorptive sorbent (predominantly with mesoporous/macroporous) or solvent is enough (Figure 4) as the CO<sub>2</sub> is abundant and there is no need for stronger binding to collect. In lower CO<sub>2</sub> presence, however, one must tune a sorbent for chemical binding to get 90% or more of the CO<sub>2</sub> from the mixtures or tune the microporosity to fit only CO<sub>2</sub> molecules perfectly in the pores of the sorbents. The diffusion of gas molecules is a major hurdle for highly microporous sorbents whereas, on the other hand, strong binding of CO<sub>2</sub> molecules in chemisorption requires high thermal input for sorbent regeneration.

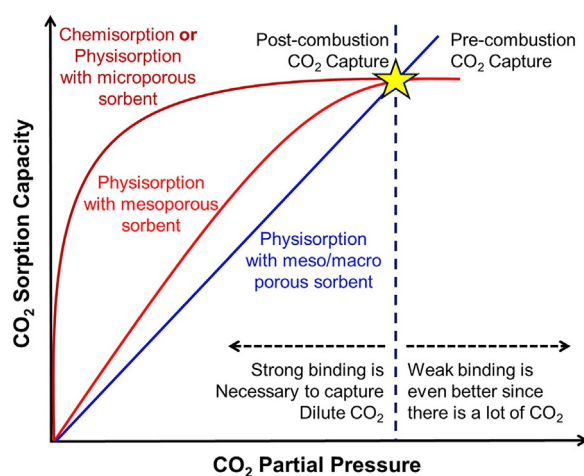


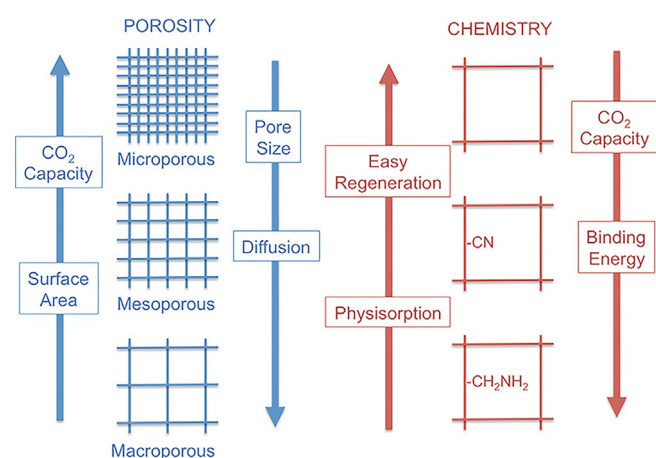
Figure 4. Selection of the right type of sorbent for CO<sub>2</sub> capture (adapted from Ref. [25]).

Ideally, a CO<sub>2</sub> sorbent for post-combustion CO<sub>2</sub> capture is either ultra-microporous (pore aperture similar to the steric size of CO<sub>2</sub> molecules, following physisorptive, sieving-based weakly binding mechanisms) or mesoporous with strong enough basic amines tethered on its walls (chemisorptive, strongly binding mechanisms). When CO<sub>2</sub> is at low pressure (0.15 bar, maximum), these two sorbent types can lead us to high uptake with strong but reversible CO<sub>2</sub> affinity.

Microporous materials with very narrow pore size distribution centered at 0.3–0.4 nm can be effectively used for efficient CO<sub>2</sub> uptake,<sup>[27]</sup> although increases in the sorption temperature will be detrimental on CO<sub>2</sub> capacity (owing to the thermal contribution to desorption) if the networks do not have any CO<sub>2</sub>-philic, chemisorptive sites. Furthermore, only very few structures with desired stability proved to have nearly identical pores in the range 0.3–0.4 nm and selectivity for CO<sub>2</sub> over water is hard to come by.

When inside a pore, the binding affinity of CO<sub>2</sub> molecules can be improved through incorporation of CO<sub>2</sub>-philic functionalities.<sup>[28]</sup> This, however, might result in limited diffusion in micropores as adding tethered chemical groups will block the pathways for gas transport. This is why larger pores are ideal for chemical, CO<sub>2</sub>-philic modifications. Polyamines can be loaded covalently and still leave room for efficient diffusions. Macropores (larger than 50 nm) are a little too large for permanent grafting as they have both low surface area and large openings that lead to reactive group leaching. The major benefit of having amines on the mesoporous materials is to preserve CO<sub>2</sub> uptake capacity at high temperatures through enhanced chemisorption. Additionally, polyamines tend to expand at warmer temperatures, leading to higher CO<sub>2</sub> capture than at ambient temperatures.

In short, the porosity and chemistry of a sorbent have to be tuned simultaneously to bring about the best of both (Figure 5). It is clear that strong enough basic amines in large enough pores are optimum for chemical and reversible binding of CO<sub>2</sub> molecules.



**Figure 5.** Porosity and chemistry (PC rule) have to be considered together in optimizing a sorbent choice.

## 2.2. Porosity tuning through chemical routes

According to the international nomenclature,<sup>[29]</sup> pore diameters define the materials classification into three categories: (1) microporous are materials with pores less than 2 nm, (2) mesoporous materials are those with pores between 2 and 50 nm, and (3) macroporous materials contain pores larger than 50 nm. A new definition of “nanoporous” emerged recently, considering the common perception that most porous materials with exciting new properties have pores less than 100 nm.

Gaseous molecules have a high affinity for micropores, especially the ultra-micropores (pores less than 7 Å in diameter). Except the few ordered microporous crystals (which are stable enough for CO<sub>2</sub> operations), most conventional sorbents with high micropore density suffer from limited diffusion, as commonly observed when the same materials are tested for surface area and pore size analysis. So, the ideal design should focus on providing enough space for CO<sub>2</sub> to get in and out, but at the same time allow molecular contact to happen more frequently by narrowing the openings just enough. This difficult task of constructing a perfect framework remains a significant challenge for chemists.

In a pore with sub 7 Å dimensions, a CO<sub>2</sub> molecule (a dynamic molecular size of 3.3 Å)<sup>[30]</sup> can interact with both side-walls of the pore. This gives a perfect fit, as is exploited previously in the metal–organic framework SIFSIX-2-Cu-I, with pore openings large enough for CO<sub>2</sub> (5.15 Å) but not for other gases.<sup>[22]</sup> This is called molecular sieving, and historically, zeolites are known to show perfect sieving properties. Their use in CO<sub>2</sub> capture is severely limited because of their stronger affinity towards water. The quest to build perfect structures that capture CO<sub>2</sub> without sacrifices in diffusion is still open, despite the recent efforts in conventional silicates, for example, copper silicate.<sup>[31]</sup> The challenge, however, is greater than ever as introducing hyperfine pore sizes and geometries bring significant synthetic challenges, both on the lab scale, and more importantly, at industrial quantities.

The presence of voids (accessible or inaccessible) in materials is generally referred to as porosity.<sup>[32]</sup> The remote porosity in solid-state materials is not useful for gas adsorption and separation, therefore it is necessary to choose the synthetic methodology that can generate accessible porosity. There have been several techniques employed for devising porous materials: controlled synthesis routes, templation, block copolymer self-assembly, and the use of sacrificial porogens.<sup>[33]</sup> Among them, porosity is commonly introduced by two methods: (1) during the synthesis of the porous material, and (2) by using sacrificial templates or porogens that are thermally activated.<sup>[33b, 34]</sup> In most sorbents, once the pores are established it is very difficult to change them back. Most attempts usually end up collapsing the framework, an undesired outcome. This is why porosity should be planned into the sorbent design early on. Synthetic conditions should be varied to furnish the best CO<sub>2</sub>-philic pore networks. Post-modification synthetic methods are also employed to tune the porosity, although the grafted functionalities almost always shrink the pores. Carbonization should not be considered as a post-modification proce-

procedure as it is a synthetic procedure that runs on thermal decomposition.

Measuring the pore size distribution accurately is highly important as it gives crucial information on how the sorbent captures CO<sub>2</sub>. In smaller pore diameters, one would expect physisorptive mechanisms such as molecular sieving and pore condensation take place. In the following sections, we will assess both the phenomena and the methods in more detail.

### 2.3. Isosteric heat of adsorption ( $Q_{st}$ ): Tuning the chemical binding strength of CO<sub>2</sub>

CO<sub>2</sub> adsorption, in chemical terms, is a typical surface event for which favorable energetics are required for a product, in this case adsorbed CO<sub>2</sub>, to form (Figure 6). In weakly binding physisorptive solids, the energies are far below a reasonable chemical bond, even sometimes less strong than hydrogen bonds (Table 4). It is commonly accepted that the  $Q_{st}$  chemisorption–physisorption boundary varies between 40 and 50 kJ mol<sup>-1</sup>. A 50 kJ mol<sup>-1</sup> set value, however, would be safe to be considered as the upper maximum borderline for a chemisorptive event as opposed to a physisorptive one.<sup>[27c,30,35]</sup> We have to note that this is rather a guideline, not a definitive breaking point. It is, however, useful to describe the behavior of the adsorbent solids with respect to the observed energy change.

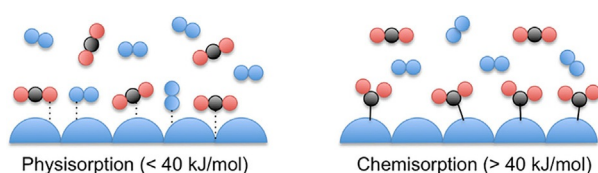


Figure 6. Energetics of CO<sub>2</sub> interactions on a heterogeneous sorbent surface.

sorptive solids, the energies are far below a reasonable chemical bond, even sometimes less strong than hydrogen bonds (Table 4). It is commonly accepted that the  $Q_{st}$  chemisorption–physisorption boundary varies between 40 and 50 kJ mol<sup>-1</sup>. A 50 kJ mol<sup>-1</sup> set value, however, would be safe to be considered as the upper maximum borderline for a chemisorptive event as opposed to a physisorptive one.<sup>[27c,30,35]</sup> We have to note that this is rather a guideline, not a definitive breaking point. It is, however, useful to describe the behavior of the adsorbent solids with respect to the observed energy change.

Table 4. The $Q_{st}$ of related processes for CO <sub>2</sub> binding.	
Type	$Q_{st}$ [kJ mol <sup>-1</sup> ]
Thermal energy at room temperature	2.5
Latent heat of vaporization of CO <sub>2</sub>	3.8
Hydrogen bond	5–30
Physisorption–chemisorption boundary	50
<b>Ideal CO<sub>2</sub>-philic binding energy</b>	<b>35–50</b>
Heat of vaporization for H <sub>2</sub> O at 100 °C	40.66
Monoethanolamine regeneration energy <sup>[a]</sup>	75
Ammonium bicarbonate formation in water	95
C–C covalent bond	350
C=O covalent bond in CO <sub>2</sub>	805

[a] Monoethanolamine in 30% aqueous solution.

The  $Q_{st}$  for CO<sub>2</sub> gives an immediate measure of how strongly CO<sub>2</sub> is bound to the adsorbent. In many sorbents, a variety of binding sites exist and therefore it is not uncommon to find steps when  $Q_{st}$  is plotted against CO<sub>2</sub> capacity.<sup>[15b,36]</sup> Most sorbents, however, give an exponential profile because of the hop-

ping mechanisms between binding sites within the pores of the sorbents. Ideally, a sorbent should have a fixed  $Q_{st}$  up until the highest working capacity so that the regeneration procedures can be set on a definitive sequence of steps. A strong bond between CO<sub>2</sub> and the sorbent will make it very difficult (in engineering terms, energy intensive) for cycled operations. A weaker interaction will penalize the working capacity for low partial pressure CO<sub>2</sub> feeds.

Energy changes and requirements define the feasibility of a CO<sub>2</sub> capture process because of the need to lower the energy penalty.<sup>[38]</sup> CO<sub>2</sub> binding, just as any other adsorptive event, has a favorable enthalpy change and thus is an exothermic process. This  $Q_{st}$  in principle, is also the minimum energy that needs to be provided to desorb the adsorbed CO<sub>2</sub> for recovery of the sorbent. In large amounts of porous solids, heat generated by the CO<sub>2</sub> adsorption becomes a significant issue as the heat conductivity of mainly empty volumes cannot be high. This is why heat exchanger liquids are suggested to be circulated amidst the sorbent packing through pipes.<sup>[18]</sup>

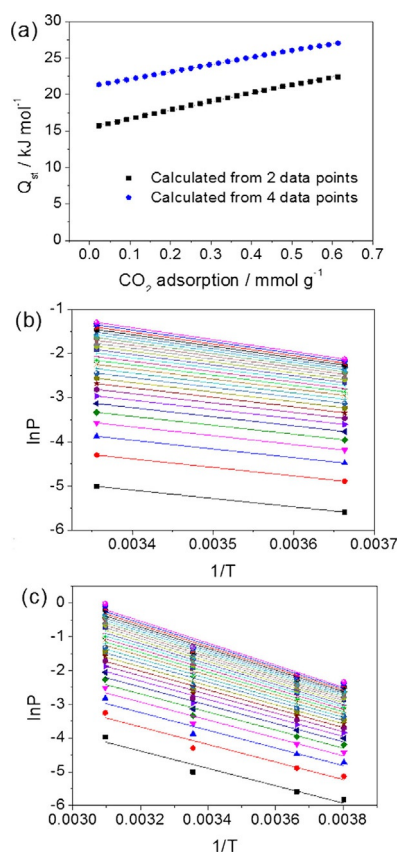
$Q_{st}$  is commonly calculated from the CO<sub>2</sub> uptake values (e.g., volumetric/gravimetric gas adsorption) at different temperatures. The well-known Clausius–Clapeyron equation is used, assuming that the  $Q_{st}$  is unchanged over the range of temperatures included in the calculation. Common volumetric/gravimetric gas sorption equipment provides a quick calculation from two temperature data points and it has been reported that there could be some deviation from the actual values (Figure 7). Although equipment manufacturers recently introduced a three-point calculation, researchers are advised to manually plot three or more temperature points to extract a more reliable  $Q_{st}$ . Although  $Q_{st}$  determined from the two temperature data points provides trend for heat evolved during CO<sub>2</sub> interaction with the surface of sorbents, it is always recommended to plot  $Q_{st}$  by using three or more than three data points for accurate results and this will be helpful for setting-up engineering parameters for large-scale experimental designs.

In an important contribution, Smit and co-workers laid out the parasitic energy, the total energy for the CCS operation that includes capture, recovery, and compression of the captured CO<sub>2</sub>.<sup>[38a]</sup> Out of 60 materials they tested, the best improvement was a 30% lower parasitic energy. And the data did not even consider wet flue gas.

### 2.4. Mechanisms of CO<sub>2</sub> capture

CO<sub>2</sub> adsorption can take place by physisorption, chemisorption, or as almost always happens, a mixture of both. Beyond the monolayer coverage of a surface adsorption event, the pore size and volume dictates the progression of the uptake capacity. Chemisorption takes place in the first layer, resulting in a perfect type I (Langmuir) isotherm.<sup>[39]</sup> Subsequent deposition into multilayers is truly physisorptive and gradually loses the binding strength.



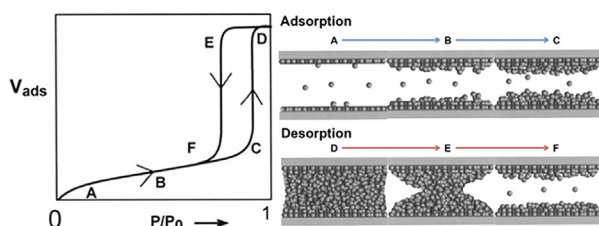


**Figure 7.** Deviation in the  $Q_{st}$  values for two or more sorption temperatures. (a) Comparison of the  $Q_{st}$  calculation for azo-COP-1 from two temperatures (273 and 298 K) versus four temperatures (263, 273, 298, and 323 K). Corresponding adsorption data fitted with the Clausius–Clapeyron equation ( $\Delta H = R[\partial \ln P / \partial (1/T)]_0$ ) for (b) the two temperatures and (c) the four temperatures. Note the significant difference in the  $Q_{st}$ .<sup>[37]</sup>

### 2.4.1. Physisorption

On any solid surface,  $\text{CO}_2$  interacts first through predominantly intermolecular forces, such as van der Waals. If there is no chemical interaction that would favor a chemical bond, the interaction will follow simple condensation principles where layer-by-layer deposition is likely to take place.

Adsorption of  $\text{CO}_2$  on the pore walls is a favorable event and leads to  $\text{CO}_2$  capture. This leads to a steep increase in uptake capacity until the pore is filled, for example, in a micropore. In a mesopore (Figure 8), two such steep curves are observed, first in the logical micropore filling behavior but then the second, at which the remaining opening is a micropore



**Figure 8.** Layer-by-layer deposition in a mesopore (adapted from Ref. [40]).

itself. Filling that second pore is called pore condensation, a phenomenon that contributes to gas uptake significantly. In between, an equilibrium plateau of adsorption–desorption is observed.  $\text{CO}_2$  uptake in mesopores is important to understand as in any sized pore one or more of these events will take place.

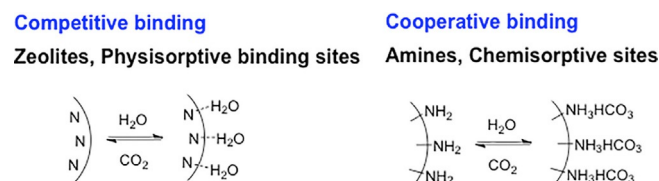
### 2.4.2. Chemisorption

Carbon dioxide is a non-polar, highly stable, linear molecule with an electropositive carbon atom and two electronegative oxygen atoms. Main pathways for activating  $\text{CO}_2$ —either for capture or conversion—rely on a nucleophilic interaction with the electrophilic carbon atom.<sup>[41]</sup> The oxygen atoms of  $\text{CO}_2$  can also be activated by electrophilic substrates such as protons or Lewis acids; however, this route ends up facilitating the same nucleophilic track on the electropositive carbon atom.

The fundamental chemistry of a chemisorptive sorbent, therefore, should rely on the nucleophilic nature of the functional groups. Basicity helps improve the nucleophilicity but does not directly mean more capture. The reversibility of the capture relies on the strength of binding, defined by the  $Q_{st}$ . The stronger the binding, the more energy is required to regenerate the sorbent.

#### 2.4.2.1. Effect of water and formation of carbamate/bicarbonate

The presence of water in a  $\text{CO}_2$ -containing gas stream is almost always inevitable (Table 1). At low pressures and in physisorptive solids,  $\text{H}_2\text{O}$  competes with  $\text{CO}_2$  for the binding sites, leading to loss of uptake capacity, for example, in zeolites (Figure 9). In slightly chemisorptive media, such as amine-impregnated porous solids, water aids the carbamate formation by acting as a solvent and catalyst for deprotonation.

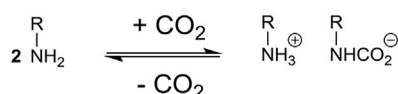


**Figure 9.** Chemisorptive sorbents promote cooperative binding rather than the competition that is often found in physisorptive solids.

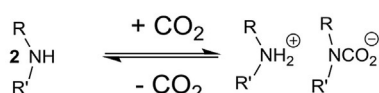
The best performing  $\text{CO}_2$  capture materials are based on anchored amines/polyamines on porous organic, inorganic, or organic–inorganic hybrids. As  $\text{CO}_2$  adsorption is governed by chemisorption in such sorbents, the  $\text{CO}_2$  uptake kinetics are very fast and selective over other gases. It has been well-established that the primary and secondary amino groups in polyamines form carbamates upon  $\text{CO}_2$  interaction, which subsequently transform into bicarbonate if water is present during adsorption (Figure 10).<sup>[42]</sup> Two amino functionalities are needed for each  $\text{CO}_2$  to be adsorbed in the dry  $\text{CO}_2$  capture, however,

**Dry condition  
(carbamate formation)**

**Primary amines**



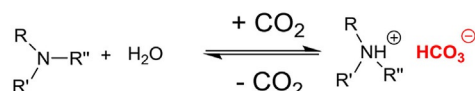
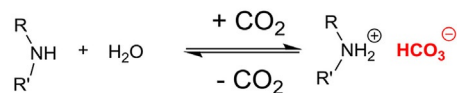
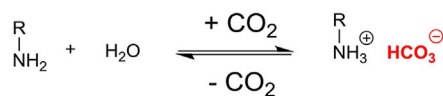
**Secondary amines**



**Tertiary amines**

No carbamate formation

**Humid condition  
(bicarbonate formation)**



**Figure 10.** Interaction of CO<sub>2</sub> with amines, which form carbonates in dry conditions and bicarbonates in the presence of water. Chemisorptive reaction mechanisms of CO<sub>2</sub> with primary, secondary, or tertiary amines in dry and humid conditions.

theoretically one amino functionality is required for a CO<sub>2</sub> molecule in a humid environment. Therefore, the CO<sub>2</sub> capture capacity of polyamines should be higher under humid conditions. Indeed, the CO<sub>2</sub> capture capacity increase in the presence of water vapor has been demonstrated in several reports where polyamines immobilized on porous substrates were subjected to dry and humid CO<sub>2</sub> streams.<sup>[17]</sup>

This mechanism clearly demonstrates that primary and secondary amines can undergo carbamate formation in dry conditions through chemisorption and carbamates formation is not possible in tertiary amine containing porous materials in dry CO<sub>2</sub> capture. Most of the nanoporous polymeric networks that have been synthesized for CO<sub>2</sub> capture applications are decorated with tertiary amines<sup>[43]</sup> (mainly because of the reactivity of the protic amines) and CO<sub>2</sub> capture capacity with these structures is almost always measured under dry conditions where formation of carbamates species is not possible unless there is water or hydroxyl functionality within the network (Figure 10). This is the reason why nitrogen (tertiary)-rich porous materials do not show stoichiometric CO<sub>2</sub> capture. This implies a need to develop porous tertiary amine networks with side hydroxyl functionalities or measurements of CO<sub>2</sub> capture capacity under humid streams.

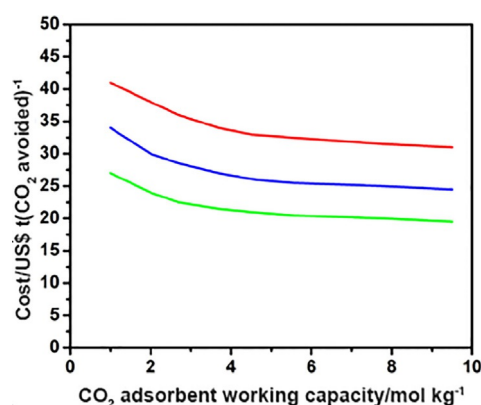
## 2.5. Discussions of the sorbent quality

When designing a CO<sub>2</sub> sorbent, there are a few questions we need to consider in more detail. These are: (1) what is more important, CO<sub>2</sub>/N<sub>2</sub> selectivity or CO<sub>2</sub> capture capacity? (2) how fast are the CO<sub>2</sub> sorption kinetics? (3) how expensive can the sorbent be? (4) would recycling matter? (5) how much energy is involved in sorbent production?

### 2.5.1. Selectivity or capacity, which one is more important?

Ideally, a CO<sub>2</sub> sorbent needs to be infinitely selective for CO<sub>2</sub> and have capacity tens of times of its weight.<sup>[44]</sup> This, however, means very strong binding and energy intensive regeneration. This is why we postulated earlier that Q<sub>st</sub> for CO<sub>2</sub> should be between 35 and 50 kJ mol<sup>-1</sup>. For such moderate binding strength, we cannot expect high capacity or selectivity. In fact, the industrial aqueous amine solution has a working capacity of around 1 mmol CO<sub>2</sub> per gram of solution<sup>[19]</sup> despite near perfect selectivity (Table 2).

An alternative sorbent needs to provide higher capacities than MEA. But the studies show that beyond 3 mmol of CO<sub>2</sub> per gram sorbent (Figure 11) the capture cost per ton of CO<sub>2</sub> avoided levels off at a fixed selectivity value.<sup>[22,45]</sup> Thus, selectivity becomes more important once we reach to a high enough



**Figure 11.** Effect of CO<sub>2</sub>/N<sub>2</sub> selectivity on the capture cost and working capacity. Selectivity becomes more important as capacity passes beyond 3 mmol of CO<sub>2</sub> per gram sorbent. Red CO<sub>2</sub>/N<sub>2</sub> selectivity = 50; blue CO<sub>2</sub>/N<sub>2</sub> selectivity = 100; green CO<sub>2</sub>/N<sub>2</sub> selectivity = 500 (adapted from Refs. [22,45]).

capacity value. Moreover, the high CO<sub>2</sub>/N<sub>2</sub> selectivity reduces the total cost of CO<sub>2</sub> capture and it demonstrates the importance of having high CO<sub>2</sub>/N<sub>2</sub> selectivity with moderate CO<sub>2</sub> capture capacity.

### 2.5.2. Kinetics of CO<sub>2</sub> binding

The combination of connected channels, micropores, and CO<sub>2</sub>-philic sites (e.g., amines) can facilitate CO<sub>2</sub> sorption. A solid-gas interface with unimpeded gas diffusion is preferred and can take place faster than in the liquid solutions. One challenge with molecular sieving is the diffusion limitations, for example, some ultra-microporous sorbents are known to fill all their pores in more than a day under constant pressure. Metal-organic frameworks have a significant advantage in not having pore walls, but only a few of them are stable enough to provide promising applications (e.g., SIFSIX-2-Cu-*l*).<sup>[22]</sup> For chemisorptive solids, the kinetics are always fast as there is a favorable chemical binding (an exothermic event). The presence of water also promotes chemical binding (Figure 10), making the capture process a spontaneous one.

Industrial feasibility dictates a fast adsorption and desorption, increasing the capture output of a facility. The time for each cycle should be no longer than five minutes and each cycle should feature 90% retention of the working capacity.<sup>[17]</sup>

### 2.5.3. Sorbent cost and atom economy

A new sorbent eventually hits the cost evaluation. Quite often the cost is the reason for exciting new materials to remain in the developmental stage. In a global problem like CO<sub>2</sub> capture with billion tons scale, we cannot ignore this task until we finish all the other requirements. It would be a waste of time.

Any metal-containing porous material has to include highly abundant metals, such as Na, Mg, or Ca. Others, even aluminum, are hard to consider as the sorbent demand would drain world reserves in a very short time. One common mistake is considering a metal abundant because of its planetary existence but not in its pure form. We must consider how pure (e.g., free of other metals or anhydrous) we need the metal source. This is similar to the computer chip industry where silicon in high purity is needed. From this perspective, it is evident that a fully organic (petroleum based) sorbent is highly desired.

Atom economy (e.g., E-factor),<sup>[46]</sup> where how much waste is generated per sorbent mass, is critical, as the scale of the sorbent production is huge. This means that the use of side reagents, such as solvents, bases, and catalysts, are not desirable.

A good start for a researcher is to compare chemical prices for sorbents.<sup>[47]</sup> In that, one would simply add up the cost of consumed chemicals in the reaction stoichiometry to arrive at the per mass cost for the sorbents. This way, a meaningful assessment is made and that would form the ceiling prices for the sorbent as industrial production will always cost less. Keeping the chemical supplier the same also eliminates the price variation.

### 2.5.4. Sorbent recycling

One of the major problems with amine solutions (e.g., MEA) is their lower recyclability. Solid-sorbent-based technologies feature advantages of reusability without deterioration of the adsorption properties, for example, zeolite-based sorbents for gas and solvent purification is an established technology and the success of this technology in industry is due to its exceptional recyclability for thousands of cycles. The total cost of CO<sub>2</sub> capture is also directly proportional to the recyclability of the sorbent. If the production cost of the sorbent is higher but it shows exceptional stability in water and acidic conditions, the repeated cycles of adsorption-desorption would reduce the total operation costs. Control over recyclability of the CO<sub>2</sub> sorbent is possible by designing porous networks with low to moderate Q<sub>st</sub>. Ideally, a solid CO<sub>2</sub> sorbent should run 1000 cycles with 90% capacity retention.<sup>[23,41b]</sup>

### 2.5.5. Sorbent thermal stability

The thermal stability of the CO<sub>2</sub> sorbent is important when it is subjected for pre-combustion or oxy-fuel combustion CO<sub>2</sub> capture because of the higher gas sorption/separation temperature compared with post-combustion CO<sub>2</sub> capture. Furthermore, CO<sub>2</sub> sorbents with high Q<sub>st</sub> (> 50 kJ mol<sup>-1</sup>) require high desorption temperatures (> 120 °C). Sorbents developed for post-combustion CO<sub>2</sub> capture should be thermally stable up to 150 °C in oxidative environments whereas thermal stability up to 350–400 °C in oxidative environments is necessary for sorbents developed for pre-combustion or oxy-fuel combustion CO<sub>2</sub> capture. Sorbents with higher thermal stability may degrade with prolonged heating (repeated cycles) even at 100–150 °C, therefore, thermal degradation of porous materials—especially those that contain organic building blocks—need to be verified. Unfortunately, studies have shown that the thermal stability for a single cycle does not necessarily reflect the true thermal stability of sorbent material developed for CO<sub>2</sub> capture from flue gas. Moreover, to the best of our knowledge, no publication has evaluated the thermal degradation of the most prominent CO<sub>2</sub> capture materials.

### 2.5.6. Sorbent chemical stability

Chemical stability in terms of structural integrity of porous materials in the acidic flue gas flow is necessary for a potential CO<sub>2</sub> capture technology. CO<sub>2</sub> sorbents should be designed while considering the fact that the flue gas also contains water vapor and acidic gases such as sulfur dioxide and hydrogen sulfide. As the efficient CO<sub>2</sub> adsorption phenomenon relies on the robustness of porosity and stability of the CO<sub>2</sub>-philic functionalities, it is always beneficial to have highly stable sorbent networks. A good benchmark test is boiling the sorbent candidates in water (open to air) for a week and then checking their CO<sub>2</sub> uptake capacities.<sup>[47,48]</sup> Furthermore, the presence of 4% O<sub>2</sub> (Table 1) in the flue gas stream at high temperature causes the oxidation of CO<sub>2</sub>-philic functionalities or organic frameworks and degrades them overtime. Thus, the sorbent oxida-

tive stability needs to be studied before employing these materials for CO<sub>2</sub> capture experiments.<sup>[30,35b,49]</sup>

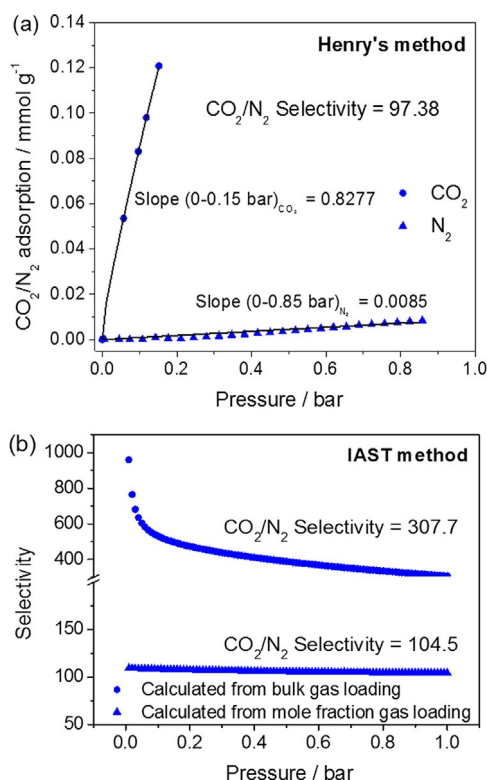
### 3. Methods

The chemical design and synthesis of a sorbent needs to follow a thorough examination of its properties and CO<sub>2</sub> capture performance. Methods vary greatly, as many tools for determining porosity, chemistry, and gas uptake capacity are widely available. In this section of our tutorial, we will briefly review those options with key aspects highlighted.

#### 3.1. Surface area and pore size analysis

Characterization of a porous solid requires surface area analysis by low molecular size inert gas probes that can penetrate all of the available pores. Although N<sub>2</sub> and Ar are the most common, extracting surface area from CO<sub>2</sub> may be necessary when a supposedly non-porous (based on N<sub>2</sub> probe) solid shows considerable CO<sub>2</sub> uptake capacities.<sup>[22,50]</sup> Large surface area is one of the parameters (but not the only) for high CO<sub>2</sub> capture as condensation of CO<sub>2</sub> molecules on the surface of the materials leads to high uptake capacities, and is considerably higher than the gas stored in the rest of the porous structure. Generally, the common perception is to not pursue CO<sub>2</sub> capture capacity measurements once sorbents are found to be non-porous (with N<sub>2</sub> probes) or have very low surface area even though it may contain functionality designed for enhancing CO<sub>2</sub> capture capacity.<sup>[51]</sup> In light of this, researchers working on CO<sub>2</sub> capture studies should rather first collect CO<sub>2</sub> isotherms, especially when sorbents are decorated with CO<sub>2</sub>-philic functionalities. This strategy will save considerable time. Once the desired CO<sub>2</sub> capacities are observed, the non-specific surface characterization based on classic Brunauer–Emmett–Teller (BET) theories should resume (see the book by Lowell, Shields, and colleagues for concise information about porous materials characterization).<sup>[40]</sup>

Having collected the CO<sub>2</sub> and N<sub>2</sub> isotherms, CO<sub>2</sub>/N<sub>2</sub> selectivity can be measured by either the direct ratio of CO<sub>2</sub>/N<sub>2</sub> adsorbed, the CO<sub>2</sub>/N<sub>2</sub> adsorbed quantity obtained from Henry's plot, or the CO<sub>2</sub>/N<sub>2</sub> mixture gas through the ideal adsorbed solution theory (IAST). These methods can result in very different selectivities. For example, CO<sub>2</sub>/N<sub>2</sub> selectivity of azo-COP-10 material based on the above methods (Figure 12)<sup>[48a]</sup> can yield significant differences: 14.34 and 97.38 for the simple CO<sub>2</sub>/N<sub>2</sub> ratio and Henry's plot, respectively. CO<sub>2</sub>/N<sub>2</sub> selectivity can also be calculated from experimental data without fitting gas adsorption isotherms. In that, the quantities of CO<sub>2</sub> and N<sub>2</sub> adsorbed at 0.15 and 0.85 bar are divided by the partial pressure ratio (0.15/0.85). CO<sub>2</sub>/N<sub>2</sub> selectivity observed by this method is 81.28 for azo-COP-10. The more accurate, IAST method is most widely used for CO<sub>2</sub>/N<sub>2</sub> selectivity.<sup>[52]</sup> IAST analysis is performed by fitting the adsorption data, and from that gas selectivity (*S*) is determined as follows:  $S = (q_{\text{CO}_2}/q_{\text{N}_2}) / (p_{\text{CO}_2}/p_{\text{N}_2})$ , where  $q_{\text{CO}_2}$  and  $q_{\text{N}_2}$  are the gas loadings for CO<sub>2</sub> and N<sub>2</sub>, respectively, and  $p_{\text{CO}_2}$  and  $p_{\text{N}_2}$  are the partial pressure of CO<sub>2</sub> and N<sub>2</sub> (0.15/0.85), respectively. At this point there are two approaches to calcu-



**Figure 12.** CO<sub>2</sub>/N<sub>2</sub> selectivity of azo-COP-10 at 323 K by (a) Henry's method and (b) IAST method from both bulk gas loading and mole fraction gas loading. Henry's method: CO<sub>2</sub>/N<sub>2</sub> selectivity obtained from the slope of CO<sub>2</sub> (0–0.15 bar) and N<sub>2</sub> (0–0.85 bar) adsorption. IAST method: CO<sub>2</sub>/N<sub>2</sub> selectivity (mixture of gases in the ratio of 15:85 CO<sub>2</sub>/N<sub>2</sub>) calculated from the data of individual gas.

late the gas loadings (*q*): by simulating (1) bulk gas loading and (2) mole fraction gas loading on adsorbents in binary gas mixtures. In bulk gas loading, each CO<sub>2</sub> and N<sub>2</sub> loading is directly taken from the isotherm fits, whereas the latter considers the adsorbed mole fraction of CO<sub>2</sub> and N<sub>2</sub> by assuming that the spreading pressures of the two gases become identical when the adsorption equilibrium is reached. The IAST selectivities of azo-COP-10 are 307.7 and 104.5 for the bulk gas loading approach and mole fraction loading approach, respectively. These methods provide different values of CO<sub>2</sub>/N<sub>2</sub> selectivity and the best suited method for CO<sub>2</sub>/N<sub>2</sub> selectivity is the IAST method as it provides information more related to the actual gas mixture of CO<sub>2</sub>/N<sub>2</sub> in flue gas,<sup>[16]</sup> although the exact CO<sub>2</sub>/N<sub>2</sub> selectivity can only be determined by breakthrough experiments by using real gas mixtures.

The amount of sorbents for CO<sub>2</sub> and N<sub>2</sub> adsorption by volumetric methods directly affects the reliability and accuracy of sorption measurements as the results are divided by the mass of the sorbent. In particular, volumetric N<sub>2</sub> adsorption at temperatures higher than ambient conditions require sufficient amounts of sorbents to show non-negative uptake values. It should be recommended to use more than half a gram of the sorbent or use reference pillars (usually provided with the equipment) for reducing the free volume in the measurement tube/cell to collect accurate results of N<sub>2</sub> adsorption in warm conditions.

It is important to note that adsorption theories rely heavily on the range in which the isotherm data was re-plotted to extract the constants in the equations. In volumetric gas adsorption analysis, Rouquerol plots help in identifying the best pressure range to keep a key value above zero.<sup>[50]</sup> Other techniques and equations to refine isotherms are available through the software provided by the equipment manufacturers.

When calculating pore size averages, the most accurate method is non-local density functional theory (NLDFT), provided that a suitable theoretical model for the porous solid in question exists. In most mesoporous structures (that have pores larger than 10 nm), the classical Barrett–Joyner–Halenda (BJH) theory, which is based on macroscopic thermodynamic assumptions, is also valid.

### 3.2. Equipment choice for CO<sub>2</sub> uptake

There are a handful of techniques available (Table 5) for measuring CO<sub>2</sub> uptake capacities of porous sorbents. Although volumetric equipment is the most commonly used, thermogravimetric analysis (TGA) offers a quick and affordable means of CO<sub>2</sub> uptake measurements. Temperature-programmed desorption (TPD) is traditionally used for catalytic experiments, however, it can provide good information about the textural properties of solids. The most expensive technique is based on magnetic suspension balance (MSB) where gravimetric CO<sub>2</sub> uptake is measured with a wide range of pressures and temperatures. Mass spectrometry (MS) that is coupled with a tubular reactor can give accurate readings on mixed gas breakthrough experiments, with or without humidity. Each of these techniques have advantages and disadvantages, and research-

ers are advised to use a mixture of these techniques to verify their claims.

At low CO<sub>2</sub> pressures, volumetric analysis offers fast and direct measurement of precise CO<sub>2</sub> uptake, without the need for excessive corrections. Post-combustion CO<sub>2</sub> capture through vacuum/pressure swing adsorption requires measurement within flue gas conditions and up to atmospheric pressure. The volumetric gas sorption analysis is therefore an easy and fast screening podium for newly developed materials for CO<sub>2</sub> capture at laboratory scale. As the volumetric method is often used for the determination of textural properties such as surface area, pore volumes, and pore size distribution, this technique is suitable for low-pressure gas adsorption testing. Furthermore, most of the sorbents for post-combustion CO<sub>2</sub> capture were studied and reported through volumetric methods, thus, it is more convenient to compare the results between newly developed and established materials. Volumetric gas sorption analysis has better precision in measurements in the range of vacuum to atmospheric pressure compared with gravimetric sorption analysis. Easy-to-operate instrumentation, user-friendly software, and multimodal methodologies related to surface phenomena are accessible through volumetric analysis. Volumetric gas sorption equipment can, therefore, prepare the newcomer for the more advanced techniques.

At high pressures (> 1 bar), gravimetric analysis is the most reliable, although careful calculations of buoyancy and density corrections are necessary. Gravimetric CO<sub>2</sub> capture analysis is therefore more suitable for pre-combustion capture as the pressure of gas mixtures can go up to 40 bar. CO<sub>2</sub> capture at high pressure can also be analyzed through volumetric analysis, however, the gravimetric technique is well established and reported for high pressures CO<sub>2</sub> capture studies.

### 3.3. Working capacity

Adsorbed CO<sub>2</sub> can be present in high quantities but this would not matter if the sorbent cannot be regenerated for a similar capacity in a subsequent cycle. The amount of replaceable capacity, known as working capacity, is therefore the quantity for which your sorbent should be known (Figure 13). The industrial standard, MEA, has a working capacity of up to 1 mmol CO<sub>2</sub> per gram of amine solution, if desorbed at 120 °C. Ideally, a new sorbent should be better than this value with lower desorption temperature. For desorption, a temperature of 100 °C or more is important as water is also adsorbed in both competitive and cooperative binding scenarios (see section 2.4.2). Knowing that flue gas mixtures are mainly warmer than room temperature, for example, 40 °C, the operation range for temperature should be between 40 °C and 100 °C.

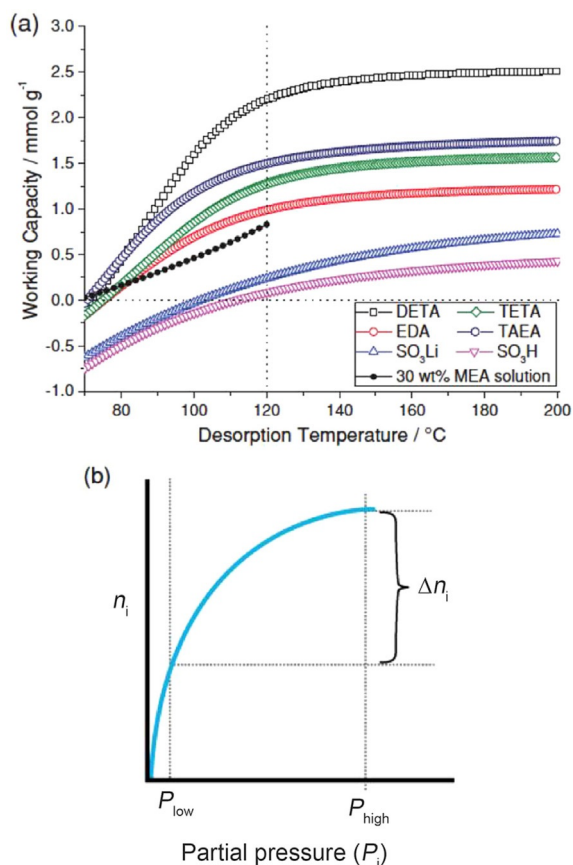
## 4. Outlook

CO<sub>2</sub>, the predominant greenhouse gas, is undeniably a great concern for the world and the industries that rely on carbon must be the first to implement preventive measures. The sources of CO<sub>2</sub> are widespread, but in surprisingly similar conditions and compositions. Most feeds contain less than 15% CO<sub>2</sub>

**Table 5.** Advantages and disadvantages of equipment for CO<sub>2</sub> capture measurements. The researchers are advised to use multiple techniques to verify their claims.

Technique <sup>[a]</sup>	Best for	Shortcomings
VSA/PSA	Daily usage for precision, volumetric uptake for dry, pure gases	Impractical to use with wet conditions, mixed gas feeds
TGA	Chemisorptive, high uptake sorbents. Mixed gas possible. Cheapest instrument to start CO <sub>2</sub> sorbent work	Need an MS or GC attachment for accurate mixed gas readings. Less sensitive, wet flue gas is possible but needs custom setup
TPD	Detection of adsorptive, catalytically active sites, simple breakthrough with mixed, humid gas possible	Detector choices limit the components of mixed gases
MSB	Gravimetric CO <sub>2</sub> readings for wide pressure and temperature, and small sample amounts	Buoyancy corrections are very important and can produce misleading results if not done correctly
MS	Ultimate technique for breakthrough measurements with mixed gas, humid or not	Gas input must have low concentrations

[a] VSA/PSA: vacuum swing adsorption/pressure swing adsorption, TGA: thermogravimetric analysis, TPD: temperature-programmed desorption, MSB: magnetic suspension balance, MS: mass spectrometry.



**Figure 13.** Working capacity is the true measure of gas uptake. (a) Example screening of sorbents for their working capacity at various desorption temperatures. Note that there are negative working capacities. (b) The definition of working capacity  $\Delta n_i$  is the difference in CO<sub>2</sub> adsorption capacity  $n_i$  at the adsorption pressure/temperature and the desorption pressure/temperature (adapted from Refs. [19, 28a]).

and are at ambient pressures and temperatures, hinting at a need for CO<sub>2</sub> capture at low partial pressures. Water is present in almost every CO<sub>2</sub> source, suggesting sorbent designs that take into account stability and CO<sub>2</sub> selectivity in its presence. Chemical binding of CO<sub>2</sub> can be assisted by water and in a cooperative binding, mildly basic nitrogen functionalities can give an optimum range of the  $Q_{st}$  (35–50 kJ mol<sup>-1</sup>) for effective regeneration.

Six pillars of sorbent design are suggested: (1) CO<sub>2</sub> working capacity of at least 2 mmol per gram sorbent, (2) CO<sub>2</sub> selectivity of more than 100, (3) sorbent stability in water, acidic gases, and temperature swings up to at least 150 °C, (4) sorbent recyclability for at least 1000 cycles, (5) cost below \$10 per kg of sorbent, (6) fast sorption kinetics with 5 minutes for each cycle. At each checkpoint, the sorbent must qualify these minimums. In addition to these, sorbents must be able to be made in kg quantities with the correct morphology that the application demands (e.g., pellets or fibers).

Challenges for CO<sub>2</sub> capture sorbent design mainly revolve around the scale of the problem. As we need millions of tons of the sorbent with a price cheaper than dirt, most highly tuned structures are ruled out without even being tested at

the pilot scale. This is why this task is much harder than anything before. Despite the difficulties, we believe that it is still possible and hope that CO<sub>2</sub> sorbent developers take away some of the design principles we have laid out here in this tutorial review.

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