Materials and Processes for CO_2 Capture, Conversion, and Sequestration

Edited by
Lan Li
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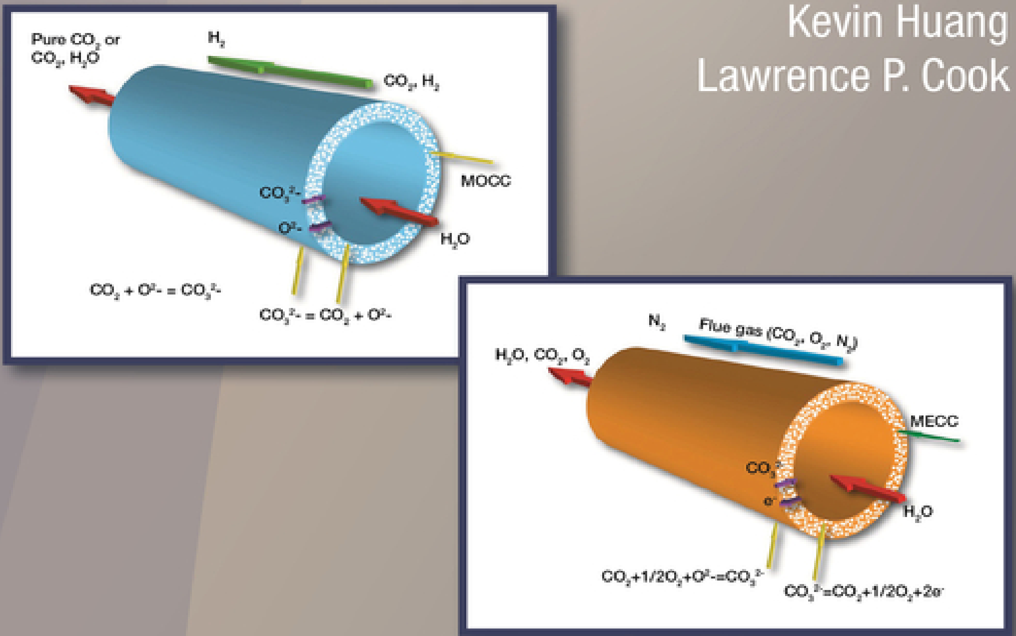

The American Ceramic Society

WILEY

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PREFACE

Our present dependence on fossil fuels increases, so do emissions of greenhouse gases, notably CO_2. To avoid the obvious consequences of climate change, the concentration of such greenhouse gases in the atmosphere must be mitigated. However, as populations grow and economies develop, future demands almost ensure that energy will be one of the defining issues of this century. This unique set of challenges also means that science and engineering have a unique opportunity—and a burgeoning challenge—to apply their understanding to provide sustainable energy solutions. Integrated carbon capture, and subsequent sequestration, is generally advanced as the most promising option to tackle greenhouse gases in the short to medium term, and efficient conversion of CO_2 into sustainable, synthetic hydrocarbon or carbonaceous fuels is regarded as a mid- to long-term strategy.

Since 2014, a symposium entitled "Materials and Processes for CO_2 Capture, Conversion, and Sequestration (CCS)" has been held at the annual MS&T (Materials Science and Technology) Meeting and Exposition. The symposium has brought together experts from the different areas of CCS research to address the scientific and engineering issues involved in the CCS processes. Topics included (1) selective CO_2 capture based on the principles of physical and chemical absorption/adsorption using liquid solvents, solid sorbents, and membranes; (2) new materials and structure/property relationships; (3) electrochemical capture of CO_2; (4) chemical conversion of CO_2 into hydrocarbons; (5) electrochemical conversion of CO_2 into hydrocarbons; (6) CO_2 sequestration; (7) computational modeling and modeling-experiment connection.

Partly based on the symposium content, we invited the symposium speakers and other experts in the field to contribute nine chapters. The resulting book encompasses up-to-date research topics of CCS and complements existing CCS technical publications with the newest research work as well as with reviews that present new evaluation and analyses of published work. The book also addresses the key challenges involved in CCS materials design, processing, and modeling. The topics include state-of-the-art synthesis, characterization, and measurement techniques applied to CCS materials, such as metal organic framework materials, electrochemical and physical sorptions, different membranes, sorbents, and solvents. This book can serve as a source material for researchers and managers working in the field.

The success of the symposium and the publication of the book could not have been possible without the effort and support of John Wiley & Sons and other organizers of the program. Special thanks are due to the symposium speakers, authors, and John Wiley & Sons book coordinators for their contributions.

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CARBON CAPTURE IN METAL–ORGANIC FRAMEWORKS

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1.1 INTRODUCTION

1.1.1 The Importance of Carbon Dioxide Capture

Carbon dioxide, an important chemical gas found in the atmosphere, is critical for the continuation of life on earth. This molecule is required for photosynthesis that fuels plants, which serve as the main source of food for all humans and animals and further produce oxygen that is essential for human respiration [1]. Studies have shown that a small accumulation of CO_2 in the atmosphere is necessary to warm earth to a level where glaciation is inhibited, producing an environment where plant and animal life can thrive [2]. However, there is recent evidence that human activity related to energy production is generating an abundance of CO_2 in the atmosphere that can no longer be balanced by earth's natural cycles, an act that is expected to confront mankind with serious environmental problems in the future. Since CO_2 is the most abundantly produced greenhouse gas (Figure 1.1) [3], it is directly

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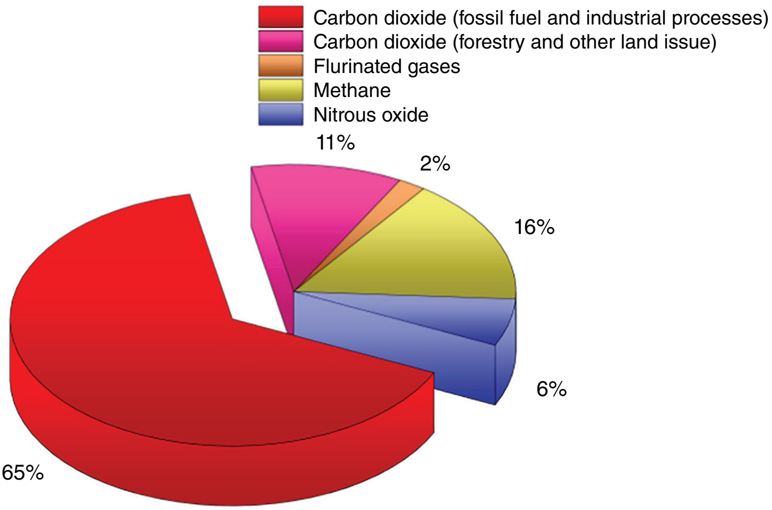


Figure 1.1 The contribution of different constituent in the greenhouse gas emission. *Source:* Victor et al. 2014 [3].

implemented in global warming. It is predicted that if the negligent release of CO_2 persists, it could have detrimental effects on our environment that include melting ice caps, rising sea levels, strong changes in weather patterns, ocean acidification, ozone layer depletion, poor air quality, and desertification; all of these things could lead to the potential demise of the human, plant, and animal life, making CO_2 mitigation an urgent need [4, 5].

Eighty percent of the world's energy is currently supplied by the combustion of carbon-based fossil fuels [6], an anthropogenic activity that has led to steady increase in atmospheric CO_2 levels. Since the beginning of the industrial revolution in the 1750s, atmospheric CO_2 concentration has increased from 280 ppm [7] to above 400 ppm in March 2015 [8, 9]. While the best remediation method is to transition from traditional carbon-based fuels to clean energy sources, like wind and solar, energy transitions are historically slow [9]. As such, it is projected that the use of fossil fuels will continue for years to come, requiring the development of materials that can remediate the effects of CO_2 through direct carbon capture and sequestration (CCS) and/or conversion of this greenhouse gas into value-added chemicals and fuels. While CO_2 capture directly from air is considered to be an unfeasible task, carbon capture from large point sources, such as coal- or gas-fired power plants, could be realized. Currently, 42% of the world's CO_2 emissions come from production of electricity and heat [10] and it is anticipated that approximately 80–90% of these emissions could be eliminated with the implementation of adequate CCS technology [11]. CCS is a multi-step process that includes the capture of CO_2 and its transport to sites where it is subsequently stored. While the processes of storage and transport are well-developed technologies, the actual implementation of capture process on a global scale is still constrained by the development of an adequate gas separation technology. Thus, the discovery of new materials with high separation ability is a pertinent obstacle that must be overcome.

1.1.2 Conventional Industrial Process of Carbon Capture and Limitations: Liquid Amines

The most mature capture technology, which has been around since the 1930s, includes aqueous alkanolamine-based scrubbers [12]. These chemical absorbents feature an amine functionality that undergoes a nucleophilic attack on the carbon of the CO_2 molecule (Figure 1.2) to form either a carbamate (in the case of primary or secondary amines) or a bicarbonate species (in the case of tertiary amines) [13]. While amine scrubbers are highly selective in the capture of CO_2 relative to other components in a gas stream, operate well at low partial pressures, and can be readily included into existing infrastructure at power plants, they have several limitations that inhibit their implementation on scales large enough for post-combustion carbon capture [14]. The materials are quite corrosive to sources of containment requiring their dilution with water to concentrations ranging from 20 to 40 wt% of the amine [15]. The high heat capacities of the aqueous amine solutions combined with high

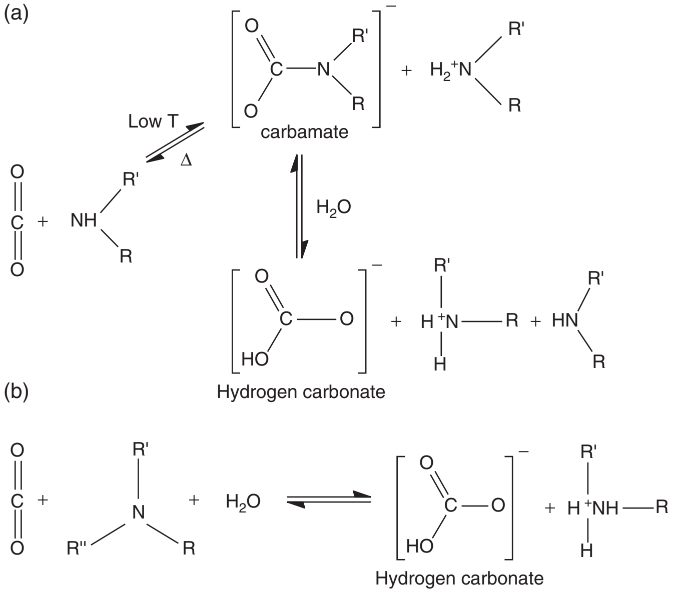


Figure 1.2 Reaction scheme for carbon dioxide with a (a) primary, secondary, or (b) tertiary amine.

adsorption enthalpies of CO_2, approaching −100 kJ mol^{-1}, creates a large parasitic energy cost for the subsequent release of CO_2. While the strength of CO_2 binding can be tuned to some degree with amine substitution (1° > 2° > 3°, i.e., monoethanolamine, diethanolamine, or triethanolamine) [13], the regeneration process typically requires temperatures that range from 120°C to 150°C [16–18]. The instability of the materials at these temperatures leads to a slow decomposition and hence a decrease in the materials' performance with subsequent absorption cycles. Given all of these problems, this technology, which has already been employed in hundreds of plants worldwide for CO_2 removal from natural gas, hydrogen, and other gases, requires that approximately 30% of the energy produced from a power plant be put back into the carbon-capture process [12]. It is projected that solid adsorbent materials with lower heat capacities might cut the energy consumption assumed from the current carbon-capture technology considerably [19]. For this to be realized, much further work is required to design porous solid adsorbents that show (i) high stability in the presence of various components in the gas stream, particularly water, (ii) high selectivity and adsorption capacity, (iii) low cost, (iv) reversibility, and (v) scale ability [20]. To date, there are several classes of porous adsorbents studied for applications related to carbon capture including zeolites, activated carbons, and covalent organic frameworks; however, all of these materials suffer quite significantly from a minimal adsorption capacity and/or low selectivity [19, 21–25].

1.1.3 Metal–Organic Frameworks and Their Synthesis

One materials solution to the aforementioned carbon-capture problem is a relatively new class of porous adsorbents known as metal–organic frameworks (MOFs), which are constructed by metal ions or metal-ion clusters linked together by organic ligands (Figure 1.3) [26, 27]. Since the discovery in the late 1990s that these materials can exhibit permanent porosity [28], they have rapidly moved to the forefront of materials research. Looking at publications related to carbon dioxide adsorption in MOFs, one can see a significant increase in the number since 2005, with over 500 publications in 2015 alone [29]. This is in part due to their unprecedented internal surface areas, up to 7000 m^2 g^{-1} [30], which allows the adsorption of significant amount of guest species. Further, the molecular nature of the predefined organic linkers offers a modular approach to their design (Figure 1.3). Through judicious selection of the building blocks, MOF structures can be chemically tuned for a variety of environmentally relevant applications such as gas storage and separation, sensing, and catalysis [31–39]. MOFs have become particularly attractive due to recent reports of materials with high capacities and selectivities for the adsorption of various guest molecules [40, 41]. Currently, MOFs hold several world records related to small molecule adsorption that include (i) surface area [30], (ii and iii) room-temperature hydrogen [42] and methane storage [43], and (iv) carbon dioxide storage capacity [44]. The facile chemical tunability of MOFs is their primary advantage relative to other more traditional porous adsorbents such as activated carbons and zeolites.

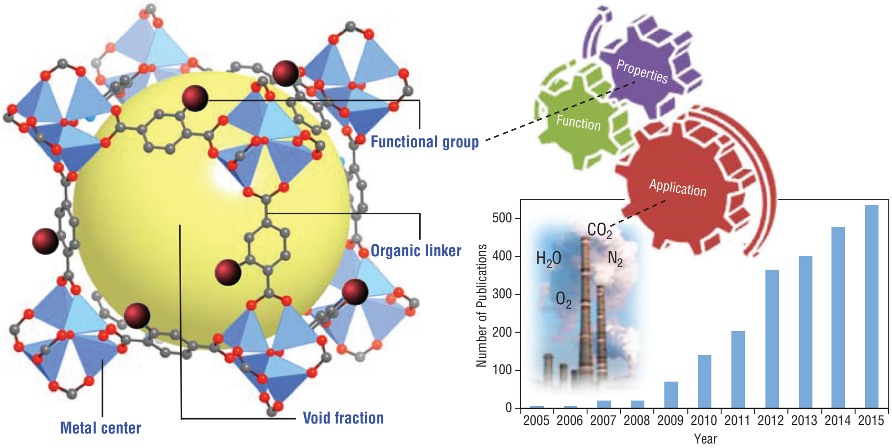


Figure 1.3 (Left) Ball-and-stick model of an MOF, MOF-5 or Zn_4O(1,4-benezendicarboxylate)$_3$ [27], showing the modular nature of the frameworks, which can be used to tune MOF properties for the selective binding of gas molecules, making the materials of particular interest in applications related to carbon capture. *Source:* Li et al. 1999 [27]. Reproduced with permission of Nature Publishing Group. (*Right*) The number of publications related to "CO_2 adsorption" and "metal–organic frameworks" increased significantly from 2005 to 2015. *Source:* Gallagher et al. 2016 [29]. Reproduced with permission of Royal Society of Chemistry.

Further, their highly crystalline nature combined with a non-homogenous van der Waals potential energy landscape on the internal MOF surface dictates that incoming guest molecules bind in well-defined positions and orientations; this allows diffraction techniques to be used to readily unveil their site-specific binding properties. Understanding the structure function relationship allows one to tune the properties of existing materials or rationally design new materials with specified function.

MOFs are typically synthesized using a combination of metal salts and ligands via standard hydrothermal or solvothermal methods; reactions are usually carried out inside of sealed vessels or using Schlenk line techniques with reaction times that range from hours to days. The aforementioned methodologies are typically limited to small-scale reactions, from milligram to gram size yields, making them only suitable for standard laboratory-based characterization. To reduce the energy requirements associated with these traditional procedures, recent efforts have been made to search for reaction conditions necessary to produce MOFs at room temperature; however, many of these methods involve non-aqueous solvents such as DEF, DMF, and ETOH [45]. Given this, more recent efforts have been made to develop MOF syntheses in water, an effort that makes industrial production of these materials more feasible [46, 47]. Other research has abandoned the more traditional forms of laboratory-based techniques and moved toward more innovative methods to assist in materials scale-up; some examples of non-traditional techniques include microwave [48], mechanochemical methods [49, 50] (such as solvent-free neat grinding or extrusion), continuous flow reactions [51, 52], and spray drying [53]. Of these techniques, the highest space time yields (STY, kg per m^3 per day), a process parameter that is used to determine industrial profitability, are reported for the mechanochemical extrusion methods developed by James et al.; these methods have remarkable STY values that range between 1 and 3 orders of magnitude greater than those for other methods, a result of the absence or near absence of solvent and high reaction rates. Further, it should be noted that the reported surface areas and pore volumes for the as-prepared materials are similar to those produced on small scales [50, 51]. The latter is an important note because many reports show that surface areas and CO_2 adsorption properties suffer quite significantly in the scale-up procedure [54].

While industrial scale synthesis of MOFs is currently limited to a handful of iconic frameworks, it is expected to become a developing trend as companies like BASF have shown proof of concept for the production of MOFs on large scales [55–57] using green synthetic methods (in aqueous media). These materials, targeted for applications related to on-board storage in natural gas and hydrogen powered vehicles, are currently available under the trade name Basolite® and include a few eminent frameworks such as HKUST-1 (Basolite C300 or [Cu_3(1, 3,5-benzenetricarboxylate)$_2$]), MIL-53 (Basolite A100 or [Al(OH)(1,4-benzenedicarboxylate)]), ZIF-8 (Basolite Z1200 or [Zn(2-methylimidazole)$_2$]), and Fe-BTC (Basolite F300 or [Fe(1,3,5-benzenetricarboxylate)]), and MOF-177 (Basolite 7377 or Zn_4O(1,3,5-benzenetribenzoate)$_2$]) [58–60]. The most critical parameters that must be considered for the industrial scale-up of MOFs have been recently identified as the following: (i) the cost of raw material per kg of obtained MOF, (ii) the amount of MOF produced per m^3 of reaction mixture per day, (iii) conditions required for reaction agitation during synthesis, (iv) length of time required and amount of solvent required for sample filtration, and (v) washing conditions necessary for drying (activating) prepared solids [61].

1.1.4 CCS Technologies and MOF Requirements

Growing energy demands related to continued population growth and the industrialization of developing countries, like China, imposes the need for the continued combustion of fossil fuels, including coal, natural gas, and oil [62, 63]. Considering that carbon capture from air is not a feasible task, capture at large point sources is certainly one of the best-case scenarios to significantly reduce global CO_2 emissions despite the tremendous effort that is required. It is projected that global reserves of coal, which has the highest carbon content and is responsible for 43% of CO_2 emissions from fuel combustion [64], will last over 110 years at the current production rate [65]. For comparison, oil reserves are projected to exist for the next 40–55 years [65–67].

Currently, there are three existing chemical processes used for the combustion of fossil fuels at large point sources such as coal and gas-fired power plants. These three processes, which include (i) post-combustion capture, (ii) pre-combustion capture, and (iii) oxy-fuel combustion capture, result in the need for a collection of separation materials capable of operating at different temperatures and pressures and offer selective adsorption for several different gas mixtures (Table 1.1). The three processes are briefly described below.

(i) Post-combustion capture at a coal-fired power plant (Figure 1.4a) involves the separation of CO_2 from flue gas (1 bar) that consists primarily of CO_2 (13–15% by volume), N_2 (73–77%), H_2O (5–7%), O_2 (3–4%), and other minor contaminates like SO_x and $NO_{x.}$ Flue gas is generated after the combustion of fuel in air [78]. The high N_2 content in air lends to flue gas mixtures with low partial pressures of CO_2; as such, the selectivity for CO_2/N_2 is one of the most critical factors considered in the selection of a separation material. As in the case of the liquid amine-based scrubbers, finding a balance between CO_2 selectivity and binding affinity in MOFs

TABLE 1.1 Typical composition of gas for three carbon capture technologies

Molecules and conditions	Post-combustion[a] [23, 62, 68–73] by volume		Pre-combustion[a] [23, 74, 75] by volume		Oxyfuel[a] [76, 77] by volume
	Natural gas	Coal	Nautral gas	Coal	Air purification[b]
CO_2	3–9%	13–15%	15–25%	26–34%	400 ppm
N_2	70–76%	73–77%	Trace	0.3–2.2%	78%
H_2O	7–18%	5–7%	—	18–38%	—
H_2	—	—	70–80%	35–45%	0.5 ppm
CH_4	—	—	3–6%	—	—
O_2	2–15%	3–4%	—	—	21%
H_2S	—	—	Trace	0.1–0.2%	—
SO_2	—	800 ppm	—	—	—
SO_3	—	10 ppm	—	—	—
HCl	—	100 ppm	—	—	—
Hg	—	1 ppb	—	—	—
CO	200–300 ppm	20–50 ppm	1–3%	0.5–0.6%	—
NO_x	10–300 ppm	500 ppm	—	—	0.3 ppm
Ne	—	—	—	—	18 ppm
Kr	—	—	—	—	1 ppm
Xe	—	—	—	—	0.087 ppm
Ar	—	—	—	0.04%	0.9%
Temperature	40–75°C	40–75°C	40°C	40°C	25°C
Pressure	1 bar	1 bar	5–40 bar	5–40 bar	1 atm

[a] The values are from some references reporting typical values for these streams. Although the values for other power plants may slightly differ from each other, they will be in the same range.

[b] This value is for the dry air.

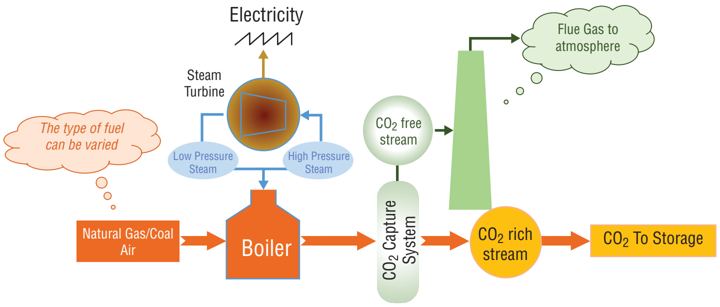
is necessary. Very high CO_2 binding energies on the sorbents affords high regeneration energies significantly reducing power plant efficiency [79].

(ii) Pre-combustion capture (Figure 1.4b) involves the separation of CO_2 from H_2 prior to the combustion process and hence zero carbon emission afterward. In this process, coal undergoes gasification to produce a syngas that typically consists of CO, CO_2, H_2, and H_2O. Afterward, the syngas is reacted with steam in a process called the water-gas shift reaction to form CO_2 (26–34%), H_2 (35–45%) with small amounts CO, H_2S, and N_2. It should be noted that there is also a significant amount of water present in the flue gas stream after the water-gas shift reaction. However, much of the water could be removed using existing technologies. From this point, the separation is carried out to remove CO_2 producing a nearly pure H_2 fuel that is then combusted to form water. This separation is significantly easier, relative to post-combustion capture, due to the higher partial pressures and concentrations of CO_2, approximately 5–40 bar and up to 34% CO_2, respectively, making the consideration for the separation medium a bit more versatile to include solid adsorbents, liquid absorbents, and membranes [80, 81].

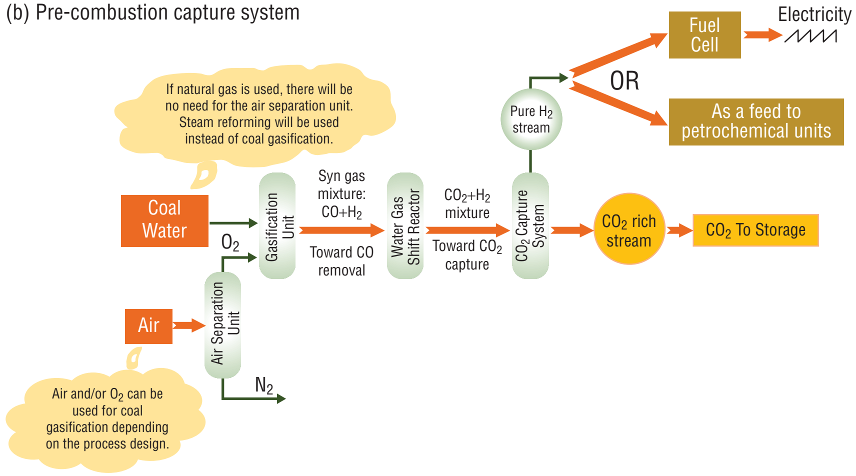
(iii) As the final alternative, rather than using air for the combustion of fossil fuels, oxy-fuel combustion (Figure 1.4c) involves a separation of O_2 from air before the combustion process. Post-separation this technology involves a nearly pure feed of O_2 (purity usually >95%) that is then used in the combustion step, eliminating the need for the separation of CO_2 and N_2 later. The problems with this separation is that it is currently limited to energetically unfavorable distillation as most adsorbents designed to date, such as lithium-containing zeolites, only show limited selectivity of N_2 over O_2 giving rise to gas mixtures with inadequate purity levels [82]. After combustion, the final gas mixture has CO_2 (72–85%) with some amount of water (6–7%) that can easily be condensed giving rise to CO_2 capture rates higher than 95%, a feat not yet achieved by pre-combustion and post-combustion capture separations. Compared with aforementioned processes utilizing N_2-rich air for combustion, the formation of NO_x is largely inhibited due to the initial removal of N_2; this will allow for a significantly smaller NO_x removal than in typical power plants.

For the aforementioned carbon-capture cases, there are three potential processes for regeneration after adsorbent bed saturation including (i) temperature swing adsorption (TSA), pressure swing adsorption (PSA), and vacuum swing adsorption (VSA). TSA is a process where the temperature of the bed will be increased (likely using heat from the power plant) post saturation allowing desorption of the small molecules from the surface of the adsorbent. The resulting pressure increase drives the adsorbate out of the bed, and once no further desorption is observed at the target temperature, a purge gas can additionally be run through the bed to push out

(a) Post-combustion capture system



(b) Pre-combustion capture system



(c) Oxy-fuel combustion capture system

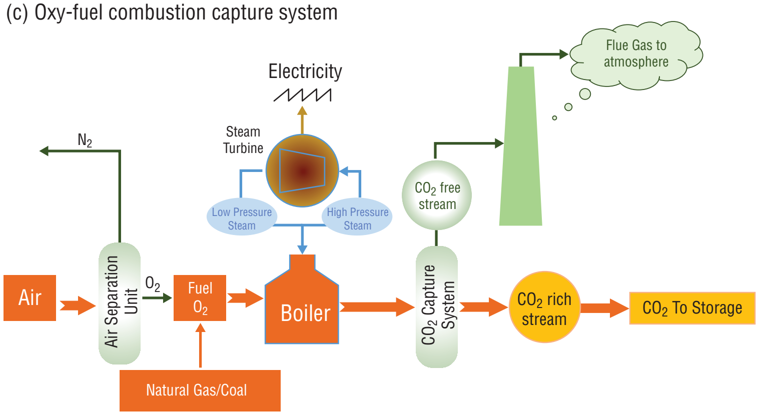


Figure 1.4 Schemes for the three different carbon capture technologies including (a) post-combustion capture, (b) pre-combustion capture, and (c) oxy-fuel combustion capture.

additional adsorbate. Subsequently, the bed can be cooled and additional adsorption cycles can be run. On the other hand, PSA and VSA processes entail lowering the pressure from which adsorption takes place to permit removal of the surface-bound guests. For PSA, the inlet valve, where high-pressure gas is allowed to flow into the bed, is simply closed allowing the pressure inside the bed to approach atmospheric pressure. Albeit similar, VSA entails lowering the bed pressure below atmospheric. The low partial pressure of CO_2 in post-combustion capture makes TSA the most plausible method for bed regeneration, as it would be energetically unfeasible to expand the bed or pull vacuum on such a large volume of gas. Considering pre-combustion capture involves high-pressure flue gas, it is much more feasible to employ PSA for the regeneration method.

Considering the parameters for these capture technologies and their subsequent regeneration methods are not easily modified, it is necessary to design adsorbents with all of these parameters in mind. As MOFs are the most chemically tunable adsorbent available, they offer unmatched opportunity to find the necessary balance between various parameters such as binding energies and densities of adsorption sites, capacities, and selectivities, which influence the ability to achieve high working capacities and low regeneration energies. The final decision related to which adsorbent should be applied to the carbon-capture process should be taken after a detailed evaluation of the technical performance and assessment of economic feasibility. Such an evaluation is imperative for implementation of carbon-capture processes on a global scale.

1.1.5 Molecule Specific

The elevated temperature at which carbon capture is carried out, combined with low boiling points (Table 1.2) of many of the small molecules in flue gas and air, makes cryogenic distillations, carried out on scales large enough for CCS, energetically unfeasible; hence, large energy savings could be realized with the use of solid adsorbents that function at much higher temperatures. When working to design adsorbent materials capable of separating gases, one must first consider the differences in the physical properties of the molecules of interest. The similarities in the kinetic diameters for most of the molecules in flue gas or air make separations dependent on size exclusion difficult; this makes thermodynamic-based separations that are dictated by the nature of the adsorptive interactions between the guest molecules and internal framework surface more feasible. For physisorptive-type interactions, the separation process relies on guest molecules having small disparities in their physical properties that include polarizability, quadrupole moment, and dipole moment. For most of the components in flue gas and air, the values for these aforementioned physical properties are listed in Table 1.2. While some important differences exist for instance between CO_2 and N_2, regarding the nature of their intermolecular interactions and their chemical reactivity, these differences are minimal and necessitate the careful design of carbon-capture materials that exhibit strong, molecule-specific chemical interactions on their internal surface.

TABLE 1.2 Chemical properties of small molecules involved in carbon capture

Molecules	Normal boiling point (K)	Kinetic diameter[a] [62]	Quadrapole moment[a] [62]	Dipole moment[b]	Polarizability[c] [40]
CO_2	216.55	3.3	43.0	0	29.1
N_2	77.35	3.64	15.2	0	17.4
H_2O	373.15	2.64	—	18.5	14.5
H_2	20.27	2.89	6.62	0	8.04
CH_4	111.66	3.76	0	0	25.9
O_2	90.17	3.46	3.9	0	15.8
H_2S	212.84	3.62	—	9.78	37.8
SO_2	263.13	4.11	—	16.3	37.2
HCl	188.15	3.34	38.0	11.1	26.3
CO	81.66	3.69	25.0	1.1	19.5
NO	121.38	3.49	—	1.59	17.0
NO_2	302.22	—	—	3.16	30.2
Ne	27.07	2.82	0	0	3.96
Kr	119.74	3.66	0	0	24.8
Xe	165.01	4.05	0	0	40.4
Ar	87.27	3.54	0	0	16.4

[a] The numbers are expressed with the following unit: 10^{-27} esu^{-1} cm^{-1}.
[b] The numbers are expressed with the following unit: 10^{-19} esu^{-1} cm^{-1}.
[c] The numbers are expressed with the following unit: 10^{-25} cm^3.

1.2 UNDERSTANDING THE ADSORPTION PROPERTIES OF MOFs

There are a variety of techniques used to assess MOFs for CO_2 capture applications. These include single-component adsorption isotherms, breakthrough analysis, multicomponent adsorption and a host of *in situ* techniques. Several studies have shown that pairing many characterization methods, particularly adsorption, with *in situ* characterization can provide molecular-level insight into the adsorption process giving direct evidence of the structural components that give rise to enhanced or diminished properties [83]. There is hope that in-depth experimental efforts like these can provide the insight necessary for the eventual deliberate design of new MOF for energetically favorable carbon-capture technologies.

1.2.1 Single-Component Isotherms

Nitrogen adsorption isotherms, collected at 77 K and up to 1 bar, are typically used to first assess the pore volume, pore size distribution and surface area of as-prepared MOF materials. Subsequently, adsorption isotherms can also be used to further assess a materials performance related to carbon-capture processes. For this, the isotherms are collected using carbon dioxide (or other small molecules) as probes. These experiments are typically carried out using commercially available equipment at temperatures ranging from 25°C to 40°C and from low pressures up to 50 bar. It should be noted that these measurements provide insight into a materials (i) adsorption capacity, (ii) selectivity, and (iii) enthalpy of adsorption [84]. These three metrics will be briefly discussed below.

1.2.1.1 Adsorption Capacity Adsorption capacity is expressed gravimetrically or volumetrically as the amount of adsorbed CO_2 per unit volume or mass of adsorbent, respectively. While reports of gravimetric capacity are more predominate throughout the literature, it is equally important to look at the volumetric properties of materials as it dictates the required volume of the adsorbent bed and both parameters also influence the efficiency with which the materials can be regenerated. It was recently shown that MOF-177, a high surface area adsorbent (BET surface area >4500 m^2 per gram of adsorbent), exhibits a volumetric capacity at room temperature and 35 bar of 320 cm^3 (STP) per cm^3, a value that is over nine times larger than the quantity of CO_2 that can be stored in the same empty container without the MOF [85]. More often than not, high surface areas lend to high capacities in the high-pressure regime, while low-pressure adsorption measurements <1 bar are more strongly impacted by the strength and density of the binding sites (Figure 1.5). It should be noted that high-pressure CO_2 adsorption isotherms are important for pre-combustion capture while low-pressure, typically not higher than 1 bar, are more relevant for post-combustion capture.

1.2.1.2 Small Molecule Selectivity Selectivity can be kinetic in nature, based on size exclusion of molecules of varying size, or thermodynamic in nature, based on significant differences in interaction energies on the internal MOF surface. It can be seen from Table 1.2 that the kinetic diameters of the small molecules of interest for carbon capture, CO_2/N_2, CO_2/H_2, and O_2/N_2, are all less than 4 Å. Considering these issues and that MOF pore sizes are more often than not above 4 Å, kinetic-based selectivities become problematic. Instead, the gas separations are based on thermodynamics. Therefore, chemists must take other physical and chemical characteristics into consideration when designing separation materials.

The selectivity factor (S), is simply calculated using the following equation (1.1), where q represents the amount adsorbed of each gas and p represents the partial pressure of each gas. While this factor is a good way to compare different materials, it is not real selectivity because it is calculated from single-component isotherms where the gas molecules are not actually competing for adsorption sites.

$$S = \frac{q_1/q_2}{p_1/p_2} \tag{1.1}$$

Another method commonly used for predicting selectivities from single-component isotherms is using the ideal adsorbed solution theory (IAST) developed by Meyers and Prausnitz [86]. For this method, single-component isotherms are used to predict the adsorption equilibria for gas mixtures. The adsorption isotherms are collected for two gases at the relevant temperature and they are mathematically fit to extract the mole fraction of each species in the adsorbed phase. While the method is not extensively reviewed here, it is becoming more visible throughout MOF literature due to the difficulty in acquiring multicomponent adsorption isotherms [87]. The validity of IAST estimations for the systems of CO_2/CH_4, CO_2/H_2, CH_4/H_2, and CO_2/N_2 mixtures in a variety of MOFs (MgMOF-74, MOF-177, and BTP-COF) and zeolites (FAU, LTA, MFI, and CHA) has been established in literature [88–91]. While it is true that IAST theory can be utilized in many cases to give a relatively accurate estimation of the selectivity of different compounds relative to each other, there are some cases where the accuracy of estimated selectivities is questionable. A recent study of Cessford et al. investigated the applicability of IAST to a variety of MOFs with varying structural features and also to a variety of small molecules with differing sizes, shapes, and polarities. The results, which were directly compared with GCMC (grand canonical Monte Carlo) simulations, showed that IAST has difficulty in predicting accurate selectivities when the adsorbates have large differences in size and shape or the MOF framework exhibits heterogeneities such as large variations in cavities or pore sizes [92].

1.2.1.3 Isosteric Heat of Adsorption

Isosteric heat of adsorption ($-Q_{st}$) is an important parameter that gives an indication of the affinity of an MOF toward a specific small molecule. Often defined as the average enthalpy of adsorption at constant coverage, it can give further insight into the energy required for the molecule's subsequent release, a crucial point to be considered for lowering the overall energy consumption in carbon-capture processes. Although a high isosteric heat implies stronger binding of the guest molecule to the surface, large values also indicate a larger amount of energy for the subsequent release of the guest molecule upon regeneration of the adsorbent. And so, chemists are constantly striving to find a balance where a small molecule binds strong (and selectively) enough to give large amounts of high purity gas after the separation, but weak enough so that the materials can be easily regenerated.

To calculate the isosteric heat, first single-component adsorption isotherms are collected for at least two temperatures (or more) usually within 10 to 15 K of one another. These isotherms are then fit using a high order polynomial or other more physically meaningful mathematical models such as the single or dual site Langmuir model to formulate an expression representative of the adsorption isotherm [93, 94]. Then the (ln P) is plotted as a function of $1/T$.

$$\left(\ln P\right)_N = -\left(Q_{st}/R\right)\left(1/T\right) + C \tag{1.2}$$

From the Claussius Clapeyron [95] equation (1.2) (where P = pressure, R = universal gas constant, T = temperature, and C = a constant), the isosteric heat of adsorption can be determined.

Another mathematical model for determining the isosteric heat is using a virial-type equation (1.3) shown below, which is first used to again model the adsorption isotherm. Afterward, the isosteric heat can be extracted using equation (1.4) [95].

$$\ln P = \ln(n) + (1/T)\sum_{i=0}^{m} a_i n^i + \sum_{j=0}^{k} b_j n^j \tag{1.3}$$

$$Q_{\mathrm{st}} = -R\sum_{i=0}^{m} a_i n^i \tag{1.4}$$

The biggest advantage of this mathematical model lies in the fact that the isosteric heat can be obtained by the direct derivation of the equation (1.3). However, it should be noted that the dual site Langmuir model is particularly good for accurately fitting data that have a combination of both strong and weak adsorption sites. Without a proper fit to the adsorption isotherm, which meaningfully models the physics of the adsorption of interest, inaccurate determination of isosteric heats will likely be the result. This is apparent throughout the literature where the same MOF can have markedly different reported values for isosteric heats. A few examples include HKUST-1 whose isosteric heats range from 15 to 35 kJ mol^{-1} [96, 97] and Mg_2(dobdc) whose isosteric heats range from 39 to 47 kJ mol^{-1} [98, 99]. This inconsistency in reported results could be related to improper activations, varied sample quality, or issues regarding the method chosen to determine the low-coverage isosteric heat. In these cases, theory capable of accurately determining enthalpies of adsorption can be quite useful for experimentalists to gauge the quality of their results [83].

1.2.2 Multicomponent Adsorption

A more realistic, yet somewhat experimentally intractable method to assess the performance of a material for carbon-capture applications is through multicomponent adsorption isotherms. While single-component isotherms are readily accessible using commercially available equipment, multicomponent adsorption measurements are time-consuming, require customized equipment, and pose challenges regarding data analysis. Binary adsorption measurements in MOFs were first carried out in 2009 by Férey et al. [100] who measured the co-adsorption in a mixture of CO_2/CH_4 in a flexible framework known as MIL-53(Cr) [101] (also known as Cr(OH)(1,4-BDC) where 1,4-BDC = 1,4-benzenedicarboxylate, MIL = Material des Instituts Lavoisier). Since this time, other studies have been limited to a few other systems [102] exposed to binary mixtures and none of these reports assess CO_2/N_2 mixtures. However, in 2015, Mason et al. reported multicomponent adsorption carried out in ternary mixtures of $CO_2/N_2/H_2O$ at temperatures of 298 and 313 K in 15 iconic frameworks that include MOFs, zeolites, activated carbons, and mesoporous silica [87]. The amount of CO_2 adsorbed in these materials in the $CO_2/N_2/H_2O$ mixtures at 40°C can be seen in Figure 1.5. This gas mixture was meant to assess materials performance in a mixture of the main components found in post-combustion flue gas. It can be seen that the amount of CO_2 adsorbed in the single (pure)-component