Toward carbon dioxide capture using nanoporous materials*

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Abstract: The development of more efficient processes for CO_2 capture from the flue streams of power plants is considered a key to the reduction of greenhouse gas emissions implicated in global warming. Indeed, several U.S. and international climate change initiatives have identified the urgent need for improved materials and methods for CO_2 capture. Conventional CO_2 capture processes employed in power plants world-wide are typically postcombustion "wet scrubbing" methods involving the absorption of CO_2 by amine-containing solvents such as methanolamine (MEA). These present several disadvantages, including the considerable heat required in regeneration of the solvent and the necessary use of inhibitors for corrosion control, which lead to reduced efficiencies and increased costs for electricity production. This perspective article seeks to highlight the most recent advances in new materials for CO_2 capture from power plant flue streams, with particular emphasis on the rapidly expanding field of metal–organic frameworks. Ultimately, the development of new classes of efficient, cost-effective, and industrially viable capture materials for application in carbon capture and storage (CCS) systems offers an immense opportunity to reduce atmospheric emissions of greenhouse gases on a national and international scale.

Keywords: adsorbent materials; carbon dioxide capture; gas separations; metal–organic frameworks; porous coordination polymers.

INTRODUCTION

The prodigious use of fossil fuels to power human society over the past 200 years has led to drastic changes in the composition of the Earth's atmosphere. Modern climate science projects that the accumulation of greenhouse gases in the atmosphere will contribute to an increase in surface air temperatures of 5.2 °C between the years 1861 and 2100 [1]. Since 1750, the concentration of the most ubiquitous greenhouse gas, CO_2, in the atmosphere has risen dramatically from 280 to 385 ppm today [2,3]. Efforts to delay and prevent the further rise in temperatures that could lead to irreversible destruction of the Earth's biosphere have focused on reducing the rate of CO_2 emissions to the atmosphere.

CARBON DIOXIDE CAPTURE

Coal-fired power plants provide 41 % of the world's electricity and currently contribute 42 % of anthropogenic CO_2 emissions [4]. Since coal is the world's cheapest and most widely used electricity source,

finding economically viable means of limiting CO_2 emissions from coal-fired plants is a key tactic in reducing the global atmospheric concentrations of greenhouse gases.

Toward this goal, numerous national and international governments and industries have established collaborative initiatives such as the Intergovernmental Panel on Climate Change [5] (IPCC), the United Nations Framework Convention on Climate Change [6], the Carbon Sequestration Leadership Forum [7], and the Global Climate Change Initiative [8]. The capture and sequestration of CO_2—the most predominant greenhouse gas—is a central strategy in these initiatives, as it offers the opportunity to meet increasing demands for fossil fuel energy in the short to medium term, whilst reducing the associated greenhouse gas emissions in line with global targets. Carbon capture and storage (CCS) will complement other crucial strategies such as improving energy efficiency, switching to less carbon-intensive fuels such as natural gas, and phasing in the use of renewable energy resources such as solar, wind, and biomass.

The IPCC estimates that CO_2 emissions to the atmosphere could be reduced by 80–90 % for a modern conventional power plant equipped with CCS technology [5]. Since the flue streams from coal-fired power plants, for example, contain dilute concentrations of CO_2 (typically 10–15 %) at low pressures (1 atm), it is estimated that CO_2 capture and compression will increase the energy requirements of a plant by 25–40 % [5]. The transportation (via pre-existing pipelines for instance) and storage of CO_2 will necessitate further investment and capital costs.

The long-term storage of CO_2 is a relatively untried concept, and is envisaged in deep geological formations such as saline aquifers or depleted oil/gas fields, by injection into oceans, or by sequestration in the form of mineral carbonates. To date, no large-scale power plant operates with a full CCS system, although three major pilot projects are currently underway in Sleipner (Norway), Weyburn (Canada), and In Salah (Algeria). In response to the imposition of carbon taxes, the Norwegian oil company Statoil has been stripping one million tons of CO_2 per year from its natural gas production and reinjecting it into offshore saline formations beneath the North Sea since 1996 [5]. In the United States, the FutureGen initiative is currently under construction in Mattoon, Illinois, and is envisaged as the 275-MW prototype for the world's first zero-emissions fossil fuel plant that integrates CCS technology with hydrogen production [9].

Current status of carbon dioxide capture

Power plant flue gas streams consist primarily of N_2, H_2O, and CO_2 in a 13:2:2 ratio by weight [10]. Prior to the compression and liquefication of the captured CO_2 for transportation to storage sites, CCS requires the separation of CO_2 from all other flue gas components. Conventional technologies for large-scale CO_2 capture are already commercially available and are focused on postcombustion separation of CO_2 from flue gases by the use of amine absorbers ("scrubbers") and cryogenic coolers. These existing methods of capture, however, are energy-intensive and are therefore *not* cost-effective for carbon emissions reduction [5].

Industrially important alkanolamines include the primary, secondary, and tertiary alkanolamines methanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA), respectively, and the sterically hindered amine 2-amino-2-methyl-1-propanol (AMP), as shown in Fig. 1.

Current industrial separation processes involve the use of alkanolamine solutions (or "scrubbers") [11]. In the simplest case, the flue gas (typically at 50 °C) is passed through an absorber column containing a 25–30 wt % aqueous monoethanolamine (MEA) solution at high pressures (60–70 atm) [12]. CO_2 is strongly absorbed by the amine to form a carbamate species, while N_2 passes through the column and is released into the atmosphere. Following the absorption process, the solution passes into a desorber column that is heated to 110–140 °C in order to release the CO_2 in high purity [12].
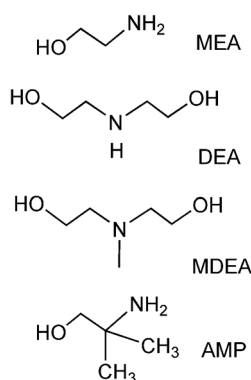
Fig. 1 Examples of primary (MEA), secondary (DEA), tertiary (MDEA), and sterically hindered (AMP) alkanolamines currently used for CO_2 absorption.

The reaction of CO_2 with the amine occurs via a zwitterion mechanism to form carbamates (see Fig. 2) [13]. The high heat of formation associated with carbamate formation leads to a considerable energy penalty for regeneration of the solvent. The CO_2 loading capacity lies in the range 0.5–1 mol of CO_2 per mol of amine for primary and secondary amines. The reaction of CO_2 with tertiary amines such as MDEA occurs with a loading capacity of 1 mol of CO_2 per mol of amine, albeit with a relatively lower reactivity toward CO_2 compared with the primary amines. The carbamation reaction cannot proceed for tertiary amines, leading instead to a base-catalyzed hydration of CO_2 to form bicarbonate (Fig. 2) [13]. In practice, the addition of small amounts of primary and secondary amines enhance the CO_2 absorption rates for the tertiary amines. Sterically hindered amines such as AMP have recently received considerable attention due to the lower stability of their carbamates, which gives rise to CO_2 absorption capacities of 1 mol of CO_2 per mol of amine and lower solvent regeneration costs compared with conventional primary and secondary amines [13].
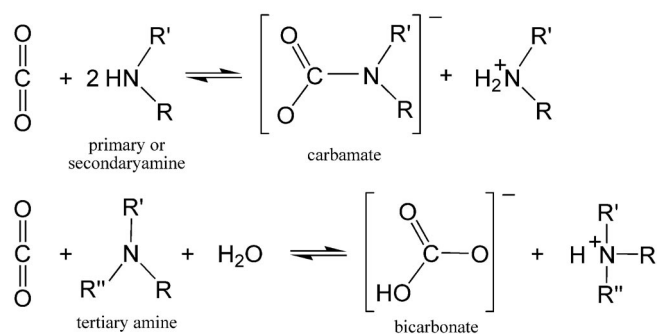
Fig. 2 General reaction schemes for the chemical absorption of CO_2 by amine-containing solvents.

Despite improvements in conventional postcombustion chemical absorption methods in recent years, "wet-scrubbing" methods suffer a number of drawbacks. These include considerable heat requirements for solvent regeneration, the necessary use of inhibitors for corrosion control and sensitivity of the solvents to chemical degradation from other by-products in the flue gas streams, such as SO_x and NO_x, which lead to reduced efficiencies and increased costs for electricity production.

Alternative capture technologies

Two major alternatives to postcombustion CO_2 capture processes have been proposed and are currently in the test stages of development [14]. Precombustion processes involve a preliminary fuel conversion step using a gasification process and subsequent shift-reaction to form a mixture of CO_2 and hydrogen prior to combustion. The high pressure of the product gas stream facilitates the removal of CO_2 [15]. In oxyfuel (or denitrogenation) processes, fuel is combusted in oxygen instead of air by the exclusion of nitrogen, thereby producing a concentrated stream of CO_2 without the need for separation. While the emerging technologies associated with precombustion and oxyfuel processes cannot be readily incorporated (via retrofitting) into existing power plants, as can postcombustion CO_2 capture processes, the projections of the IPCC indicate that the extensive capital investments will be compensated by the relatively higher efficiencies of CO_2 separation and capture [5].

TOWARD NEW METHODS AND MATERIALS

A diverse range of promising methods and materials for CO_2 capture applications that could be employed in any one of the above-mentioned (postcombustion, precombustion, or oxyfuel) processes have been proposed as alternatives to conventional chemical absorption. These include the use of physical absorbents, membranes, cryogenic distillation, hydrate formation, chemical-looping combustion using metal oxides and adsorption on solids using pressure and/or temperature swing adsorption (PSA/TSA) processes [16]. The key requirements for these new materials are that they must exhibit: air and water stability, corrosion resistance, high thermal stability, high selectivity and adsorption capacity for CO_2, as well as adequate robustness and mechanical strength to withstand repeated exposure to high-pressure gas streams. A number of recent review articles, including our own [17], have elaborated the status of a number of new classes of materials for CO_2 capture. In particular, the field of metal–organic framework materials is progressing at an enormous pace and in this regard, we present here a review of the most recent studies in this burgeoning field.

Membranes

Membrane separation technologies are projected to attain a high efficiency for CO_2 capture owing to their selective extraction of CO_2 from mixed gas streams and their low energy requirements—since the cross-membrane transport is driven by a partial pressure difference of CO_2 across the membrane [18]. Supported liquid membranes facilitate CO_2 separations from flue gas streams via reversible chemical reactions with "carriers" such as carbonates, amines, and molten salt hydrates dissolved in the membrane liquid. Hydrogen transport membranes permit simultaneous hydrogen separation and CO_2 capture and are based on porous inorganic materials including zeolites, palladium alloy tubes, and ceramics (especially inorganic perovskite oxides) [18]. Membrane technologies, however, suffer from a lack of stability under the reforming environment (which contains steam and hydrogen sulfide) present in processing plants and currently remain in the research phase of development.

Physical absorbents

Physical absorbents such as Rectisol® (cold methanol, –40 °C) and Selexol™ (a mix of dimethylethers of polyethylene glycol) selectively bind CO_2 at high pressures (up to 130 atm). The advantage in this case is the lower heat consumption in the solvent regeneration step, as the stripping is driven by a pressure release (flash distillation) [16]. The physical adsorption of CO_2 onto solid materials including packed adsorbent beds containing a catalyst and selective adsorbent such as alumina, activated carbon, and zeolite molecular sieves has been demonstrated on the laboratory scale. In the latter approach, the

impregnation of polyethylenimine into MCM-41 mesoporous molecular sieves led to a 24-fold increase in the CO_2 absorption capacity of the solid support using a PSA approach [19].

Amine-modified materials

Numerous amine-modified silica materials have also been reported, including amine-tethered silica materials and porous silicas impregnated with amines [20]. The surface modification facilitates the adsorption of CO_2 via the carbamate species shown in Fig. 2, and permits the stripping of CO_2 at relatively lower temperatures (35 °C) than those required for the regeneration of amine solvents (typically >100 °C) [21,22]. However, these materials suffer from low CO_2 capacities and a lack of stability over repeated cycles, particularly for impregnated adsorbents containing physisorbed amines.

To overcome these limitations, a *covalently* tethered hyperbranched aminosilica material was recently synthesized via aziridine polymerization at the surface of mesoporous silica [20]. The material was shown to exhibit reversible CO_2 binding (with a capacity of 2 mmol CO_2/g adsorbent) and multi-cycle stability under simulated flue gas conditions using a TSA approach.

Physical adsorbents

Zeolites

Several experimental [23] and computational [24] screening studies have been undertaken to assess zeolite-based adsorbents for CO_2 removal from flue gas (mixture of CO_2 and N_2). The most promising adsorbents showed a near linear CO_2 isotherm and a low SiO_2/Al_2O_3 ratio with cations in the zeolite structure which exhibit strong electrostatic interactions with CO_2 [23]. While these potential adsorbents were shown to be adequate for PSA applications, their regeneration required a significant energy input.

Zeolitic imidazolate frameworks

Zeolitic imidazolate frameworks (ZIFs) in which (i) transition-metal ions such as Zn^{II} and Co^{II} replace the tetrahedral atoms such as Si and Al, and (ii) imidazolates and benzimidazolates replace the bridging oxides in the afore-mentioned zeolites, have been shown to exhibit exceptional selective capture and storage of CO_2 [25–27]. By virtue of their high stabilities, high porosities, and uniform but tunable pore sizes, these frameworks are promising candidates for gas separation of CO_2 from mixtures. More recently, the mechanism for CO_2 sorption in a number of ZIF materials has been elucidated with the aid of density functional theory (DFT) calculations. For example, calculation results indicated the presence of Lewis acid–base interactions between CO_2 molecules and the nitro groups in ZIFs containing the 2-nitroimidazole linker. The presence of electron-withdrawing groups on the benzimidazole linkers in ZIFs increases the interaction between the oxygen atoms of CO_2 and the hydrogen atoms of the phenyl rings [28]. A recent combined experimental and computational study of five Zn^{II}-based ZIFs containing 4,5–functionalized imidazole units provided insights into the dependence of adsorption on the polarization and symmetry of the functionalization on the linker [29]. For the frameworks containing symmetric functionalization, the electrostatic field within a cavity was found to be significantly smaller than that for nonsymmetric functionalization owing to the increased symmetry of the surface charge density in the former case. An increase of up to two in the adsorption of CO_2 at 1 bar was thus observed for nonsymmetric functionalized ZIFs.

High-throughput synthetic methods have recently provided new examples of ZIFs with high thermal stability (up to 390 °C) and chemical stability in refluxing aqueous and organic media [25]. The frameworks exhibit high selectivity for CO_2/CO separations and reversibly adsorb CO_2 at 0 °C with a capacity of 82.6 (162 g) of CO_2 per liter of ZIF-69, for example.

Metal–organic frameworks

ZIFs may be classified as one subset of a vast array of highly porous three-dimensional solids known as metal–organic frameworks which incorporate metal ions (e.g., Zn^{II}, Mg^{II}, etc.) linked by organic bridging units [30]. By the judicious choice of the molecular building blocks (i.e., the metal cations and organic bridging ligands), the functionality and morphology of frameworks can be controlled [31]. A rapidly growing structural database for such materials has thus been established, and a plethora of applications have been investigated including those in catalysis, gas storage, and gas separations [32].

Nanoporous frameworks are promising materials for gas storage and separations due to their extremely high surface areas, and the uniformity and tunability of their internal pores. These characteristics also underscore many successful advances toward the application of MOFs as hydrogen storage materials in mobile applications [33–35]. As an alternative to conventional hydrothermal and solvothermal methods for framework synthesis, microwave methodologies have recently been shown to enable fast large-scale synthesis of materials [36]. Such considerations are clearly important where industrial application is sought. The purification and activation of frameworks is a further concern, given that as-synthesized materials often contain solvent-filled pores. Supercritical CO_2 processing has recently been shown to effect the mild and efficient activation of such solvent-filled pores to yield frameworks with high internal surface areas [37]. High-throughput synthetic methods have proven particularly useful for screening reaction conditions (reactant concentrations, temperature, etc.) and aiding the identification of new frameworks. For example, the recently disclosed framework $Fe_3[(Fe_4Cl)_3(BTT)_8(MeOH)_4]_2$ {BTT = 1,3,5-benzenetristetrazolate} was identified using high-throughput methods and has been shown to exhibit coordinatively unsaturated Fe sites upon removal of the solvent. Correspondingly high CO_2 uptake over H_2 was observed due to strong, preferential sorption at the coordinatively unsaturated metal sites [38].

High surface area frameworks

Among the frameworks with the highest capacity for CO_2 adsorption is $Zn_4O(BTB)_2$ {MOF-177, BTB^{3-} = 1,3,5-benzene-tribenzoate}, which if added to a container pressurized to 35 bar could store nine times more CO_2 than the same container without the adsorbent material [39]. With the goal of maximizing the uptake of gases including CO_2, a series of frameworks exhibiting ultrahigh porosities and pore diameters up to 48 Å have been reported [40]. In comparison with $Zn_4O(BTB)_2$ which exhibits a CO_2 uptake of 1470 mg g^{-1} at a saturation pressure of ~30 bar and 298 K, the uptake of 2870 mg g^{-1} in $Zn_4O(BTE)(BPDC)$ {MOF-210, BTE = 4,4',4"-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoate and BPDC = biphenyl-4,4'-dicarboxylate} at a saturation pressure of ~50 bar is the highest reported to date in a framework material. It is crucial to note that despite the high adsorption capacity of these carboxylate-based frameworks for CO_2, they do not necessarily exhibit high selectivities for CO_2 adsorption over other components of a gas mixture. In particular, for low-pressure postcombustion applications which predominantly require CO_2 separation from a mixture of N_2 and H_2O, functionalized frameworks have often proven more effective.

Functionalized frameworks

While the volumetric CO_2 capacities of the materials have been found to scale predominantly with surface areas, computational calculations to elucidate the adsorption mode of CO_2 [41–45] have revealed an increased affinity of arylamine [46], alkylamine [47], and hydroxyl [42] groups in the frameworks toward CO_2 adsorption. The influence of these functional groups on CO_2 sorption is often observed in the low-pressure region (0–1 bar) relevant to CO_2 separation from flue gas. Thus, while frameworks with high void volumes may be advantageous for high-pressure applications (e.g., for precombustion CO_2 capture), functionalized frameworks are often superior for CO_2 capture at low pressures. This enhancement arises from both the selective interactions between CO_2 and the functionalized molecule, as well as the constriction in the pore space of the functionalized framework compared with the parent nonfunctionalized material.

The $M_2(RCO_2)_4$ paddlewheel motif represents a common structural component of carboxylate-based frameworks and is easily amenable to postsynthetic functionalization via exchange of solvent molecules on the axial metal coordination sites. Most recently, the functionalization of a framework based on Zn_2 paddlewheel units linked by 3,3"-dicarboxy-1,1':4',1"-terphenyl with DABCO {1,4-diaza-bicyclo[2,2,2]octane} led to preferential CO_2 sorption over N_2 and H_2 [48]. The enhancement was attributed to the presence of an exposed nitrogen atom on the DABCO ligand which interacts relatively strongly with the quadrupolar CO_2 molecule.

The influence of the pore volume on the capacity of a framework for CO_2 sorption at low pressures (0–1 bar) was evaluated in the anionic framework $Zn_8(ad)_4(BPDC)_6 \cdot 0.2DMA$ {ad = adeninate, DMA = dimethylammonium cation} [49]. The systematic replacement of DMA with successively larger tetramethylammonium (TMA), tetraethylammonium (TEA), and tetrabutylammonium (TBA) cations led to a successive decrease in the pore volume, however, the CO_2 capacity did not scale accordingly. Rather, the TMA and TEA functionalized frameworks exhibited the highest CO_2 capacities, indicating that smaller pores may be ideal for CO_2 capture in the low-pressure regime.

Computational studies using DFT and grand canonical Monte Carlo (GCMC) simulations have corroborated several experimental findings and should serve as a guide to experimentalists to aid the design of functionalized frameworks with the greatest likelihood of exhibiting enhanced CO_2 uptakes. Recent simulations on Al(OH)(BDC) {BDC = 1,4-benzenedicarboxylate} wherein the ligands were functionalized with OH–, COOH–, NH_2–, and CH_3– has led to the prediction that polar groups such as OH– and COOH– enhance CO_2 sorption at low pressures relative to bulky nonpolar groups such as CH_3–, which have a penalizing influence [50].

DFT and MC calculations have predicted that the lithiation of anionic frameworks will increase CO_2 sorption and selectivity over H_2 and CH_4 uptake at low pressures due to strong electrostatic interactions between Li^+ cations and polar CO_2 molecules [51,52]. The presence of water in the framework structures appears to shield the cationic charge, thereby reducing CO_2 sorption and selectivity. Similar predictions have been made for the incorporation of Na^+ ions into anionic frameworks [53], while the incorporation of NO_3^- ions into cationic frameworks has been suggested as a strategy to enhance the selectivity of CO_2/H_2 separation relevant to precombustion capture processes [54].

To date, studies on the viability of MOFs as CO_2 capture materials under realistic flue stream conditions has received limited attention. While the high robustness and stability of ZIFs (in the presence of air and water and toward thermal degradation) has been established [25], the majority of metal–organic frameworks (MOFs) exhibit comparatively lower stabilities. Ultimately, the integration of MOFs into practical CO_2 capture processes requires an assessment of their performance as membranes for gas separation, or in large adsorbent beds where PSA/TSA approaches may be employed. In many cases, the sensitivity of the materials toward chemical degradation in the presence of air and water, however, poses a major impediment to their practical application.

Recent computational work has sought to predict the influence of water present in the flue stream on CO_2 sorption in frameworks. Investigations on two of the most extensively studied MOFs, namely, Ni_2(dobdc) {dobdc = 2,5-dihydroxyterephthalate} and Cu_3BTC_2 {BTC = 1,3,5-benzenetricarboxylate}, which exhibit coordinatively unsaturated Ni^{II} and Cu^{II} sites, respectively, revealed slightly increased CO_2 capacities with low H_2O loadings due to enhanced interactions between the polar molecules. The uptakes decreased at high H_2O content [55].

CONCLUDING REMARKS AND PROSPECTS

Clearly, the development of more efficient, cost-effective, and industrially viable CO_2 capture materials is essential for the deployment of large-scale CCS schemes. Postcombustion capture from power plant flue streams provides one strategy toward reducing CO_2 emissions to the atmosphere; however, there is an urgent need for new methods and materials that perform this separation. In contrast to the

low-pressure, predominantly CO_2/N_2 separation required for postcombustion capture, materials for pre-combustion (high-pressure, predominantly CO_2/H_2) capture and natural gas sweetening (predominantly CO_2/CH_4) have distinct requirements. Careful consideration must therefore be afforded to the specific technology and stage in a particular process at which capture occurs in order to tailor the properties of a given material.

While numerous new methods and materials have been developed over the past two decades, it is clear that the ultimate integration of these into industrially useful platforms requires significant cooperation between scientists, engineers, venture capitalists, policy makers, and governments. To date, no fully integrated, commercial-scale CCS projects are in operation; however, many of the component technologies are relatively mature. Progress has been made on testing new materials at the pilot plant stage, however, there is now an urgent need to facilitate large-scale deployment of the most promising technologies. From this perspective, it is apparent why the problem of CO_2 capture is regarded as one of the grand challenges for the 21st century. The time is ripe for us as a chemistry community to play a role in solving the CO_2 capture problem.

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