Emerging Materials for Lowering Atmospheric Carbon

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ABSTRACT

CO_2 emissions from anthropogenic sources and the rate at which they increase could have deep global ramifications such as irreversible climate change and increased natural disasters. Because greater than 50% of anthropogenic CO_2 emissions come from small, distributed sectors such as homes, offices, and transportation sources, most renewable energy systems and on-site carbon capture technologies for reducing future CO_2 emissions cannot be effectively utilized. This problem might be mediated by considering novel materials and technologies for directly capturing/removing CO_2 from air. However, compared to materials for capturing CO_2 at on-site emission sources, materials for capturing CO_2 directly from air must be more selective to CO_2, and should operate and be stable at near ambient conditions. In this review article, we briefly summarize the recent devlopments in materials for capturing carbon dioxide directly from air. We discuss the challenges in this field and offer a perspective for developing the current state-of-art and also highlight the potential of a few recent discoveries in materials science that show potential for advanced application of air capture technology.

Keywords

Direct Air Capture, Negative Emissions, Independent of Emitting Source, Experimental-Theory Approach, Optimized Properties

Contents

1.   Introduction

Carbon dioxide (CO_2) emission from anthropogenic sources such as fossil fuels exceeded 9.8 ± 0.5 Gt tons (carbon) in 2014, at an average rate of 109.9 ± 0.3 Mt C/year as shown in **Figure 1** (Boden et al. 2015). Natural carbon sinks, such as oceans and land, captures atmospheric CO_2 at a much slower rate of 57.6 ± 0.94 Mt C/year, and therefore cannot offset anthropogenic CO_2 emissions. This leads to an increase in the concentration of CO_2 in the atmosphere at an average rate of 52.3 ± 0.91 Mt C/year as shown in **Figure 2** (C. Le Quéré et al. 2015).
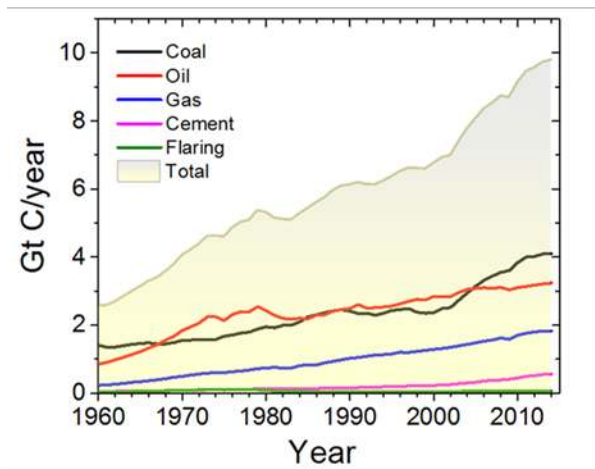
Figure 1. Trends of increasing CO_2 emission from various anthropogenic sources as a function of time measured from 1960.

Data Source: Boden, T. A., Marland, G., Andres, R. J. 2010. Global, regional, and National Fossil-Fuel CO_2 Emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National laboratory, U.S Department of Energy, Oak Ridge, Tenn., U.S.A. doi 10.3334/CDIAC/00001_V2010
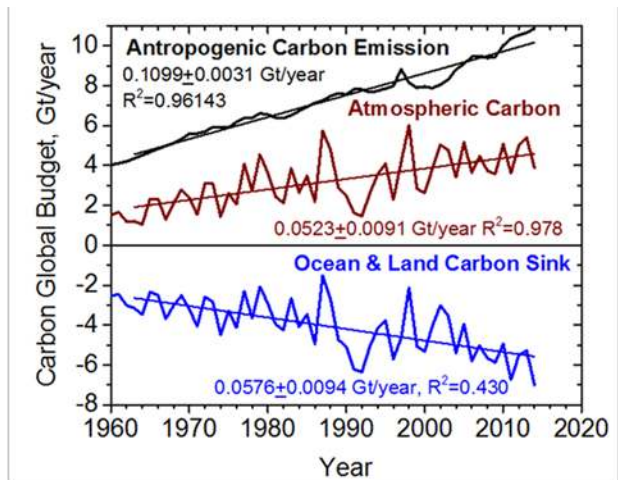
Figure 2. Global carbon budget as a function of time for emissions from anthropogenic sources and their uptake by natural carbon sinks.

Data Source: C. Le Quéré *et al. Earth Sys. Sci. Data* **2015**, 7, 349-396. http://www.earth-syst-sci-data.net/7/349/2015/essd-7-349-2015.pdf

If the steady rise in CO_2 emission continues, and technologies capable of removing CO_2 from the atmosphere faster than nature are not implemented, irreversible climate change could occur causing negative consequences which could include loss of habitat, food shortages, and increasing occurrences of natural disasters. To decrease CO_2 emissions by 30-85%, a target was set by the Intergovernmental Panel on Climate Change (IPCC) that coal-based emissions (a major contributor to anthropogenic emission, **Figure 1**) must be completely eliminated by 2050 and the emissions from other fossil fuel sources have to be substantially reduced (Kharecha and Hansen, 2008). However, state-of-art alternative energy sources such as biomass fuels, geothermal energy, solar energy, and wind energy cannot currently provide the energy needed to satisfy global demand (Lackner, 2005; Lund, 2007).

Moreover, renewable energy systems and carbon capture technologies to reduce future CO_2 emissions cannot curb the current climate risks caused by the CO_2 that is already in the atmosphere. Therefore, the strategic adoption and implementation of a hybrid approach based on a renewable and energy efficient infrastructure, combined with carbon capture technologies from on-site emissions as well as from air, is required to combat the climate challenge (Lackner, 2005; Lund, 2007; Lackner, 2012; Jones, 2011; Goeppert et al., 2012). More than 50% of anthropogenic CO_2 emissions come from distributed sources such as home and office heating and cooling, and the transportation sector (International Energy Agency (IEA) Statistics, 2014). To substantially reduce CO_2 emissions from anthropogenic sources, implementation of carbon capture and sequestration (CCS) technologies at on-site large fossil fuel-based power plants, as well as in numerous small distributed sources such as cars, trucks, airplanes, homes, and offices would be necessary. However, in most cases installing individual carbon capture units is not practical or cost-effective for distributed sources. For example, capturing CO_2 from on-board ground-based vehicles is technically feasible but after the CO_2 is captured, it would have to be transported to a sequestration site, requiring extensive and costly infrastructure. Capturing CO_2 on-board from airplanes is more complicated due to the added weight from the captured CO_2. Similar to ground-based vehicles, installing CCS units in homes and offices would also involve cost challenges associated with infrastructure (Goeppert et al. 2012). Given the high percentage of CO_2 emissions from small and distributed sources (**Figure 3**) coupled with the challenges and high costs associated with CCS, it is clear that other solutions should be explored.
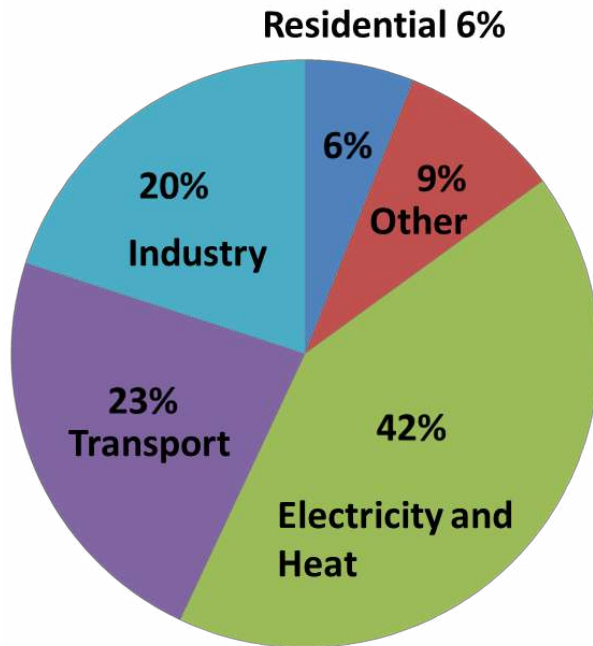
Figure 3. A pie chart breakdown of the global CO_2 emissions by sector. *Other: commercial/public services, forestry/agriculture, fishing, energy industries other than electricity and heat generation, and any emissions not mentioned elsewhere.

Data Source: International Energy Agency (IEA) Statistics (2014), CO_2 Emissions from Fuel Combustion 2014. Highlights, OECD/IEA, Paris sector (International Energy Agency (IEA) Statistics, 2014).

An alternative solution to CCS, is "air capture," the capture of CO_2 directly from the air, which has recently gained significant attention. It addresses the capture challenge without the need for developing extensive CO_2-sequestration infrastructure (Jones, 2011; Goeppert et al., 2012). In this approach, the atmosphere serves as the transport medium for CO_2 from the site of emission to the site of capture (Jones, 2011; Goeppert et al. 2012; Specht, 1995; Pasel, 2000; Specht, 1999). This separates the CO_2 collection process from the CO_2 emitting source, unlike a conventional CCS facility. This provides an economic advantage because they can be constructed near the best geological sequestration sites, eliminating the cost attached with building extensive infrastructure for transporting CO_2 between emission and sequestration sites. Air capture has additional advantages over conventional CCS which is at best, a "carbon neutral

process." It aims to remove CO_2 from fossil fuel-based power plant emissions, prohibiting further increase in atmospheric CO_2 concentration. In contrast, air capture can be viewed as a "carbon negative process" by lowering the CO_2 atmospheric concentration from past emissions. Furthermore, when implemented with other CO_2 utilization and/or recycling technologies (**Figure 4**), (Damiani, 2011; Keith, 2006) it may lower the cost for overall CO_2 capture and regeneration. Additionally, compared to industrial flue gas, the lower concentration of acid-gas contaminants such as NO_x and SO_x in the atmosphere makes air capture an even more attractive strategy to consider (Keith, 2006).
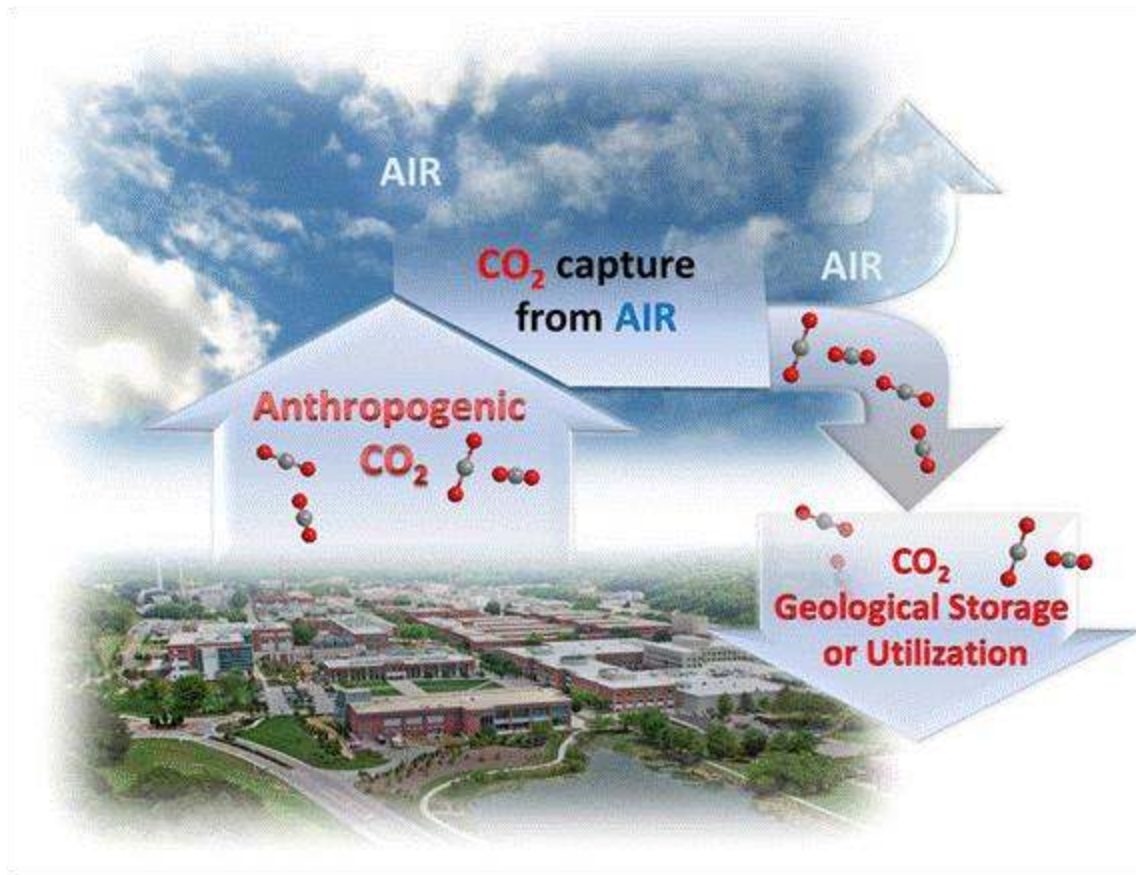
Figure 4. Schematic representation demonstrating the advantage that technologies for capturing CO_2 directly from air are independent from the site of CO_2 emissions and can be built close to CO_2 geological sequestration or utilization sites for lowering the overall cost of CO_2 capture.

Footnote: Early approaches for direct air capture (DAC) were energy intensive and were therefore criticized in an early APS report (Direct Air Capture of CO_2 with Chemicals, 2016). Obviously, any DAC approach that is not substantially carbon negative is not a viable means for DAC for climate change mitigation purposes.

In this developments article, we highlight current materials for direct CO_2 capture from air and discuss recent developments and challenges. We also offer a perspective on the design and development of new and improved air-capture materials by integration of theoretical modeling and experimental methods.

2. Overview of CO$_2$ sorbent materials

2.1 Inorganic Sorbents

Inorganic salts such as lithium hydroxide (LiOH) have high CO$_2$ sorption capacities and have been used to capture CO$_2$ directly from air in spacecraft and submarines (Norfleet, 2003; Matty, 2008). Other similar highly basic inorganic candidates include: calcium hydroxide (Ca(OH)$_2$), potassium hydroxide (KOH), sodium hydroxide (NaOH), and aqueous solutions of these alkaline sorbents (Lackner et al., 1999; Keith et al., 2010). Recently, "Carbon Engineering," a start-up company based in Calgary, Canada, has designed a new technology using strong basic hydroxide solutions that capture 100 kt CO$_2$/yr directly from air (Holmes et al. 2013). The main advatages of inorganic sorbents is that they are simple, inexpensive, and have minimal environmental risks due to their low vapor pressure (Carbon Engineering, 2015). Carbon Engineering has attracted the attention of private investors such as Bill Gates and Murray Edwards who are providing funding to further improve this technology (Global Warming, 2015). However, CO$_2$ sorbents derived from these metal hydroxides are hindered by the high energy input required to regenerate them for cyclic use. For example, the recovery of a NaOH solution uses a "caustic recovery" process to regentate the NaOH from a solution of Na$_2$CO$_3$ (Jones, 2011; Goeppert et al. 2012; Carbon Engineering, 2015; Mahmoudkhani and Keith, 2009). In this process, the Na$_2$CO$_3$ solution is reacted with a solution of Ca(OH)$_2$ and forms a CaCO$_3$ precipitate, regenerating the NaOH solution. CaCO$_3$ is then dried and calcined at a very high temperature (> 700 °C) to liberate CO$_2$ and obtain calcium oxide (CaO). Ca(OH)$_2$ is regenerated later for the recycling process by the hydration of CaO (Jones, 2011; Goeppert et al. 2012). The high temperatures needed for regeneration of NaOH from Na$_2$CO$_3$ mean the process requires a large energy input and is generally quite expensive. Recently, non-conventional causticization methods such as

auto-causticization, direct causticization, or partial auto- or direct causticization have gained traction as methods to reduce the cost and energy requirement for regenerating the CO_2 capturing inorganic sorbents (Mahmoudkhani and Keith, 2009; Baciocchi et al. 2006; Canadell et al. 2007).

2.2 Zeolites

Zeolites are 3-dimensional crystalline aluminosilicate frameworks, which can contain highly basic alkali and alkaline earth elements such as sodium, potassium, and calcium. Zeolites are denoted by the empirical molecular formula: $M_{2/n}O. Al_2O_3.xSiO_2.yH_2O$, where M = Na, K or Ca; n = valence of the cation and x and y are integers (Hardie et al. 2005). The crystalline structure of zeolites is formed by the sharing of adjacent oxygen atoms in SiO_4 and AlO_4 tetrahedra (Breck, 1974) creating a network of uniformly sized molecular pores (Breck, 1974; Flanigen, 1991). The isomorphous substitution of aluminum for silicon in the crystalline lattice of zeolites results in a structure with a net negative charge and a high affinity for quadrupolar molecules such as CO_2. At ambient temperature and pressure, zeolites can be used for capturing CO_2 from air. However competitive adsorption from water, nitrogen, and oxygen, which typically follows the order $H_2O > CO_2 > N_2 > O_2$, must be considered (Breck, 1974). For example, Stuckert and Yang reported that a low silica type X zeolite with a high lithium content (Li-LSX) has excellent CO_2 adsorption capacity (1.34 mmol CO_2 adsorbed/ g adsorbent) from dry air under ambient conditions (Stuckert, 2011). However, in the presence of 80% relative humidity, the adsorption capacity is decreased by 96%. Therefore, more robust and moisture stable zeolite systems need to be designed for zeolites to have practical application in capturing CO_2 directly from air. Currently, there are a large number of potential structures in the zeolite database that could, in principle, be useful for capturing CO_2 (Deem et al. 2011). While it is impractical to synthesize

every possible structure and investigate its ability to capture CO_2, Lin and coworkers employed a computational screening approach to identify potential zeolite and zeolitic imidazolate framework structures for CCS applications (**Figure 5**) (Lin et al. 2012). Integration of computational methods and synthesis to identify zeolite structures should lead to improved zeolite-based materials for CO_2 capture, though the ability to provide high CO_2 sorption capacities without competition from water will remain a significant challenge.
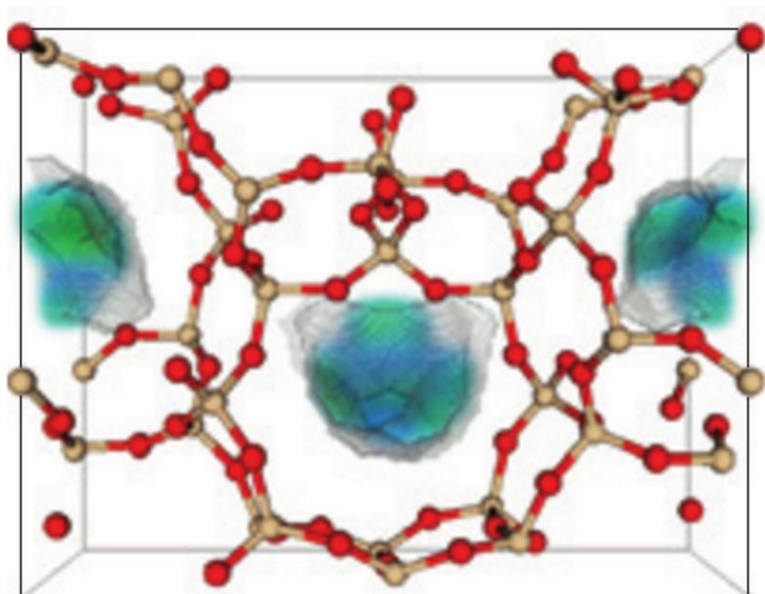
Figure 5. Computational method showing optimal zeolite structure for CO_2 capture. Color code: oxygen atoms (red atoms), silicon atoms (tan), colored surface (regions in the zeolite pores with high potential for capturing CO_2).

2.3 Metal-Organic Frameworks (MOFs)

Similar to zeolites, metal-organic frameworks (MOFs) consist of a porous 3-dimensional crystalline framework, however MOFs are formed by metal ions or a cluster of metal-ions connected by organic linkers (Chen et al., 2001; Cheetham and Rao, 2007; Rowsell et al., 2005;

Zhao et al., 2004; Eddaoudi et al. 2002; Li et al. 1999). In contrast to zeolites, the organic component of the hybrid structure of MOFs have potential for task-specific design through control of pore architecture and linker functionalization (Li et al., 1999). MOFs have recently gained attention due to their excellent CO_2 capture efficiency from CO_2 emitting sources such as precombustion and post-combustion flue gas, natural gas, and bio gas (Caskey et al., 2008; Sumida et al., 2012; Sayari et al., 2011; Nugent et al., 2013). However, to our knowldege, there are only a few reports detailing MOFs' potential to remove CO_2 from ultra-dilute sources through direct air capture (Jones, 2011; Goeppert et al. 2012; Xue et al., 2013; McDonald et al., 2012; Choi et al., 2012; Shekhah et al., 2014; Kumar et al., 2015) . For example, McDonald *et al.* reported two metal-organic frameworks labelled M_2(dobpdc), where M = Zn(**1**), Mg(**2**) and dobpdc = 4,4'-dioxido-3,3'-biphenyldicarboxylate, functionalized with N,N'-dimethylethylenediamine (mmen) results in a compound with excellent CO_2 adsorption capacity at low pressures (2.0 mmol/g at 0.39 mbar at 25 °C) that are comparable to the conditions for direct CO_2 capture from air (McDonald et al. 2012). Like zeolites, humidity significantly decreases the efficiency of MOFs which use open metal sites for binding to CO_2. However, Shekhah *et al.* has recently reported a synthetic approach to construct a two dimensional square grid metal-organic framework (**SIFSIX**-3-Cu) with a pyrazine/copper (II) connected by silicon hexafluoride anions (**Figure 6**) (Shekhah et al., 2014). The high CO_2 selectivity of this material is a result of tuning pore size and interaction energy for allowing favorable, yet reversible, physical adsorption-desorption of CO_2 from ultra dilute CO_2 concentration sources such as air. The **SIFSIX**-3-Cu structure was able to adsorb 1.24 mmol of CO_2 per gram of adsorbent at 0.4 mbar over four cycles at a relative humidity of 74%, demonstrating excellent selectivity of CO_2 vs H_2O, offering the possibility to capture CO_2 over water. However, follow-up reports

demonstrate that water still poses a problem, even for MOFs of this class, under air capture conditions (Kumar et al., 2015).
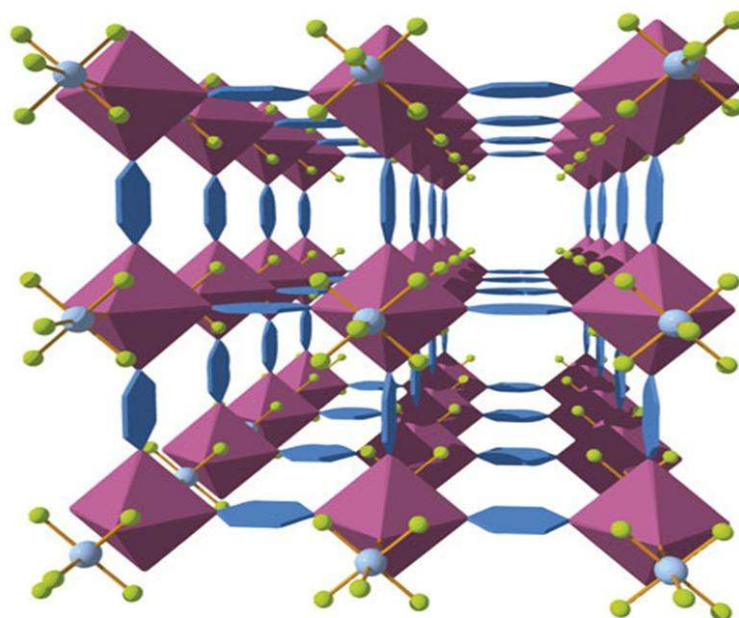
SIFSIX-3-Cu

Figure 6. Pore size tuning of the channel structures of **SIFSIX**-3-Cu. Color code: pyrazine(blue polygon), Cu (purple polyhedra). Si (light blue spheres), F (light green spheres).

Judicious design of MOFs with controlled pore size and functionalizaion, coupled with inorganic-organic substitution strategies, has the potential to create new materials capable of removing CO_2 via direct air capture. This is one area where compuational modeling and simulation can aid in the guided design and stability analysis (mechanical, thermal and chemical) of new CO_2 selective MOFs (Walton and Sholl, 2015; Burtch and Walton, 2015; Nie et al. 2015).

2.4 Microporous Organic Polymers (MOPs)

Similar to zeolites and MOFs, microporous organic polymers (MOPs) are porous materials with an average pore size less than 2 nm. However they are composed of light, non-metallic elements such as carbon, hydrogen, oxygen, nitrogen and boron (Jiang and Cooper, 2010). MOPs have ultra-high surface areas, with (to our knowledge) the highest surface area reported for a MOP being 6460 m^2g^{-1}, made of a polyphenylene structure, PPN-4 (Yuan et al. 2011). A recent review by Dawson *et al.* highlights various types and functionalized MOPs for selective CO_2 sorption over a range of different temperatures and pressures (Dawson et al., 2013). Ultra-high surface area MOPs such as PPN-4 are excellent CO_2 scavengers at elevated pressures (total CO_2 uptake: 48.20 mmol/g at 295K and 50 bar) (Yuan et al., 2011; Dawson et al., 2013). Introduction of functional groups into the MOP framework have recently been identified as an efficient and potential strategy to greatly enhance the CO_2 uptake of MOPs at atmospheric pressure. This has been mainly attributed to the polarizability and large quadrupole moment of CO_2, which can be exploited by introducing CO_2-philic functional groups. This create strong interactions between CO_2 and the material's surface. Ideal adsorption solution theory (IAST), developed by Myers and Prausnitz (Myers and Prausnitz, 1965), is frequently used to evaluate the ability of a porous material to selectively adsorb CO_2 with respect to a mixture of gases (Krishna et al. 2002; Krishna and van Baten, 2011). This method recently reported a mixed component isotherm for an amine grafted porous polymer network, PPN-6-CH$_2$DETA that can achieve a very high CO_2 selectivity and a loading capacity of 1.04 mmol/g by capturing CO_2 directly from air (**Figure 7**) (Lu et al., 2013). Moreover, a hypothetical regeneration process can be carried out at 98 °C and the purity of CO_2 after separation can approach 99.99 % (Lu et al., 2013).
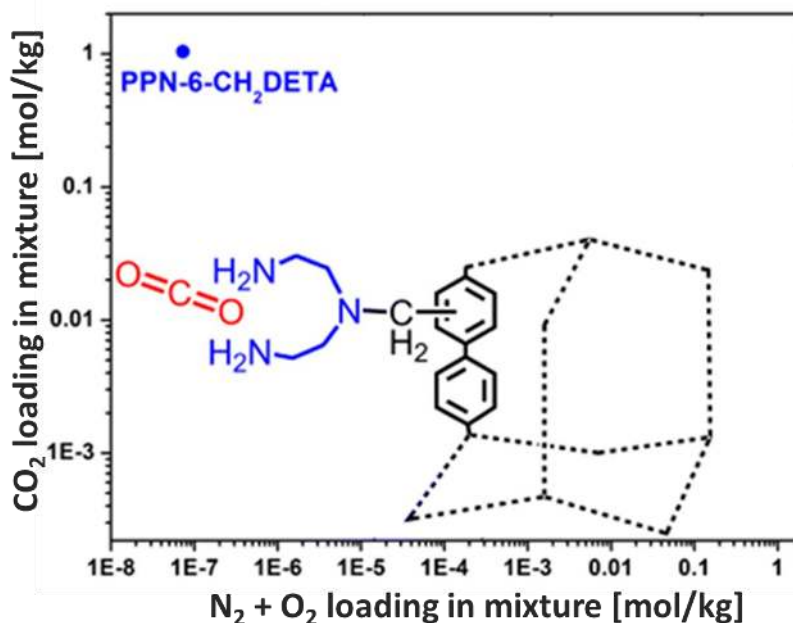
Figure 7. Amine-grafted PPN-6-CH$_2$DETA showing high CO$_2$ selectivity (3.6 X 10^{10}) and loading capacity (1.04 mol/Kg) for capturing CO$_2$ directly from air (400 ppm CO$_2$, 78.96% N$_2$, and 21% O$_2$) as investigated using IAST.

To date, relatively little effort has been devoted to computational analysis of improved MOP structures for cabon capture. Therefore, combining the strengths of molecular simulation methods with synthetic techniques offers exciting opportunities for scientists to design and create new MOP-based materials for efficiently capturing/separating CO$_2$ directly from air.

2.5 Activated Carbon

2.5.1 Microporous Carbon

Activated carbon has high surface areas (typically >1000 m^2/g), low chemical activity, and the ability to adsorb molecules from gas and liquid phases due to its highly developed porosity ranging from micropores (<2 nm) to mesopores (2-50 nm) and macropores (>50 nm) (Rodriguez-Reinoso, 2006; Sun et al. 2015). In activated carbon, more than 90% of the adsorption occurs in the micropores; however meso- and macropores aid the overall performance of the material, because they provide facile pathways to the molecules absorbed into the micropores (Rodriguez-Reinoso, 2006; Sun et al. 2015). Recent reports have shown that narrow microporosity (<0.7 nm) is the key factor for adsorbing CO_2 at low pressures (~ 1 bar) and suggest that adsorption occurs via a "pore-filling" mechanism (Martin et al., 2011; Sun et al. 2013). Carbon based adsorbents for CO_2 capture are attractive due to their low cost, fast kinetics, ultra-high stability, ease of regeneration, hydrophobicity, and adsorption capacities at elevated (partial) pressures that are appropriate for CO_2 capture and separation from power plant sources (Sun et al., 2015; Choi et al. 2009; Shafeeyan et al., 2011). However, the ability to capture CO_2 directly from the atmosphere require more selective and higher CO_2 binding affinities. Recent studies have reported several effective strategies to enhance the low pressure CO_2 binding affinities of these materials. For example, using polymers as precursors has been identified as a useful technique to generate task-oriented carbon-based sorbents with targeted properties such as purity, porosity, and surface chemistry (Sun et al., 2015). Furthermore, introducing electron-donating hetero-atoms such as nitrogen via reaction with ammonia, nitric acid and amines, (Przepiorski et al., 2004; Zhong et al., 2012; Nandi et al., 2012; Zhao et al., 2012) or sulfur into the carbon framework (Seema et al., 2014) has also been suggested to enhance the CO_2

adsorption capacities for these materials. Nitrogen containing functional groups, such as amide, imide, lactam, pyrrolic, and pyridinic groups increase the basic character of activated carbon, and enhance the interaction between CO_2 and the surface *via* dipole-dipole, hydrogen, and covalent bonding. High temperature treatment of activated carbon (with surface area <900m^2/g) with ammonia has been suggested as a potential method to increase CO_2 capture by about 25% (Shafeeyan et al., 2011; Przepiorski et al., 2004). However, a recent report also suggests that presence of up to ~3 wt% of N heteroatoms as functional groups in the structure of microporous carbons obtained from pyrrole/pyridone, pyridine, quaternary amines, and pyridine-N-oxide did not significantly improve the CO_2 adsorption, with pore size again being the most important factor controlling CO_2 sorption. The adsorption proceeded through volume-filling mechanism on micropores with diameter ~0.7−0.8 nm for N-functionalized material whereas on non-functionalized material, the CO_2 adsorption proceeded on micropores with diameter smaller than 0.8 nm (0−25 °C, ~ 0−1 bar of CO_2) (Sevilla et al., 2013). An independent report by Mokaya *et al.* showed that presence of nitrogen had no beneficial effects on CO_2 adsorption and minute differences are related to the change in pore size distribution (Adeniran and Mokaya, 2016). It is interesting to note that modified pyrrole molecules assembled with pluronic template *via* hydrogen bonding and carbonization at low temperatures demostrate high (124:1) specificity of CO_2 to N_2 adsorption for materials with N-content of 6-8 wt. %. The observed CO_2 adsorption specificity is a result of large fraction of ultra small (0.5 nm) pores with preserved nitrogen functionality (To et al., 2016). Recently, Ludwinowich *et al.* studied the effect of adding surface-active chemicals and measured the CO_2 adsorbing ability of microporous carbon obtained from polymer-based precursors (Ludwinowicz et al., 2015). This study showed that addition of chemical activators to microporous carbon materials improve CO_2 adsorption in the following

order $ZnCl_2$ < H_2O < NH_3 < CO_2 < KOH. High volume pores with a diameter <1 nm can be achieved by pre-treating carbon with KOH and results in a CO_2 uptake of 0.304 g CO_2/g of carbon (6.9 mmol/g at 0 °C and 1 bar).

2.5.2 Carbon Nanomaterials

High volume pores with a diameter <1 nm can be achieved by pre-treating carbon with KOH and results in a CO_2 uptake of 0.304 g CO_2/g of carbon (6.9 mmol/g at 0 °C and 1 bar). Carbon nanomaterials including graphene, carbon nanotubes (rolled up sheet of graphene in the form of a tube) and nanohorns (horn-shaped rolled graphene sheets) also present a promising altrernative to activated carbon because their size is in the nanometer range (suggested to be optimal for CO_2 capture) (Chandrakumar et al., 2013).
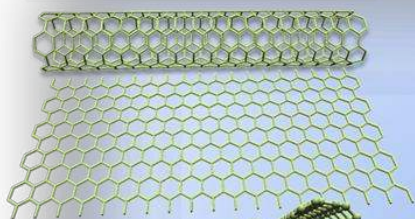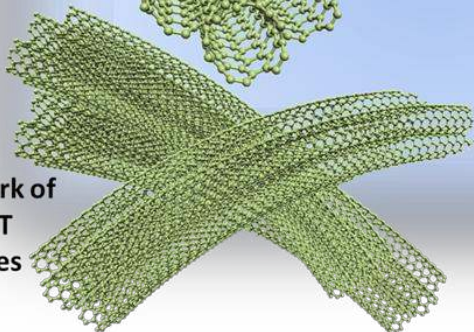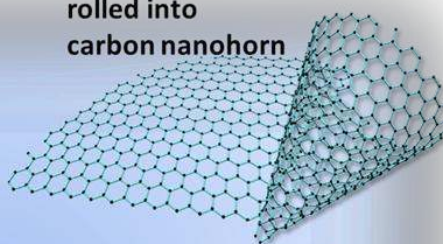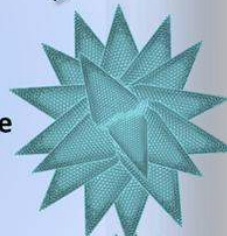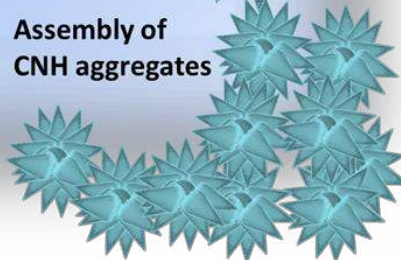
Figure 8. Multi-scale morphology of carbon nanotubes and carbon nanohorns for CO_2 capture. CNT morphologies: a bundle of SWNT intercolating network (~2nm diameter) of carbon nanotubes generated from intersection of micron long bundles are shown for (5,5) SWNT. CNH morphologies: an assembly of carbon nanohorn spherical aggregate formed by multilayer-carbon nanoaggregates. Also shown the graphene sheet cut-out for making 0.6 nm (5,5) SWNT and carbon nanohorn (240° disclination angle, 3 nm long)

Typical multi-scale structures of interconnected networks of single wall carbon nanotube(SWCNT) bundles and single wall carbon nanohorn (SWCNH) aggregates are shown in **Figure 8** along with a graphene sheet cut-out for making a single (5,5) SWNT and 240° disclination angle SWCNH (Puretzky et al., 2008)**.** Iijima's group recently reported on the thermodynamics of CO_2 adsorption on carbon nanohorns (Krungleviciute et al., 2012; Krungleviciute et al., 2013). It was found that unlike other adsorbates (N_2 & CH_4), CO_2 is not strongly attracted to the surface of graphene and adsorption is dominated by stronger gas-gas interactions for CO_2. This is due to the large quadrupole moment of CO_2 molecules, resulting in a two monolayer coating (0.0267 g CO_2/g SWCNH). It is interesting to note that in spite of the different nature of SWCNH and SWCNT, they show similar CO_2 adsorption charateristics, akin to graphite where strong quadrupole interactions between CO_2 molecules lead to hysterestis on adsorption curves (Bienfait et al., 2004; Terlain and Larher, 1983). On SWCNT bundles, the CO_2 coverage was found to be 0.8 mmol/g (0.352 g CO_2/g of 1.7 nm diameter SWCNT) at 130K with an isosteric heat of adsorption close to that for the basal plane of graphite, about 22.5kJ/mol (Bienfait et al. 2004). The adsorbed layer of CO_2 is stablized due to entropic effects in the grooves and in the interstitial channels in the SWCNT bundle. For hydroxylated poly(ethyleneimine) modifed 3D-porous graphene scaffolds, the largest CO_2 uptake was found to be around 4.13 mmol/g (0.181g CO_2/g of carbon) measured in simulated ambient air under 1 atm of dry CO_2 for the sample with an averaged pore size of 15 nm (Liu et al. 2015).

2.5.3 Hetero-atom Activated Carbon

In the context of hetero-atom activated carbon, an analogous class of structurally similar materials is boron nitride nanomaterials (BN). However, in boron nitride nanomaterials, which include nanosheets and nanotubes (BNNT), nitrogen is a primary part of the material structure, whereas in carbon based nanomaterials, it is typically a low concentration dopant. Due to the difference in electronegativity between B (2.04) and N (3.04) atoms, the electrons on BN nanomaterials are not delocalized, leading to asymmetric charge distribution. Recent first principles density-function theory calculations showed that if the surface of a BN nanomaterial is negatively charged, the CO_2 could be physically or chemically adsorbed on the surface (adsorption energy ~ 67 kJ/mol). The highest adsorption energy is expected for a BN nanosheet (70 kcal/mol) and BNNT (77 kcal/mol) with (5, 5) unit cell symmetry, which have a charge density equivalent to two electrons (Sun et al., 2013). Reduction of BNNT (negative charging of nanotubes) increases their reactivity towards reaction with NH_2 radicals by a factor of five compared to neutral nanotubes (Shin et al. 2015). Unlocking reactivity of reduced BNNTs could provide a pathway for development of hybrid coatings to improve CO_2 capture. A concept of electrocatalytically switchable CO_2 capture on graphitic carbon nitride (g-C_4N_3) was modeled using first principles calculations for negatively charging surfaces with one and two electrons (Tan et al., 2015). Negative charging of g-C_4N_3 can lead to significant enhancement of CO_2 capturing ability with estimated CO_2 capture capacity up to 42.3 wt.%, and adsorption energy of about 88 kcal/mol (Tan et al., 2015). Previously it was shown through *ab initio* calculations that CO_2 chemisorption in boron-rich BNNT is almost independent of the tube diameter (Choi et al., 2011a). Design of carbon-based and similar nanomaterials adsorbents with high surface area, small pore size, and surface modification enabling high selectivity for capturing CO_2 from a

dilute gas mixture at various humidity levels remains challenging. However, recent results for designing new hierarchically-structured carbon adsorbates or analogous materials suggest that breakthroughs might be possible for this class of adsorbents in the near future.

2.6 Supported Amine-Sorbents

Many of the materials discussed above that offer both high CO_2 capacities and tolerance to humidity contain amines as the key CO_2 binding sites. The presence of highly basic amine groups on the surface of the supported systems results in a strong affinity for binding with CO_2. Moreover, the ability of these materials to operate at near ambient conditions, their tolerance to humidity, and mild temperature regeneration make them attractive as air capturing sorbents (Choi et al., 2009; Didas et al., 2015; Choi et al., 2011b). Moreover, Prakash and co-workers recently reported the use of a polyamine; pentaethylenehexamine (PEHA), for directly converting CO_2 from air into methanol (Kothandaraman et al., 2016). In this work, they demonstrated that by using PEHA and a ruthenium-based homogeneous catalyst, 79% of CO_2 captured directly from air was converted into methanol. Conversion of atmospheric CO_2 to methanol using amines is highly significant because of methanol's potential use as an alternative fuel in fuel cells and hydrogen storage (Carbon dioxide captured from air can be directly converted into methanol fuel, 2016). Supported amine-adsorbents based on primary, secondary, or tertiary amines are one of the most developed and promising classes of materials for directly capturing CO_2 from air (Didas et al., 2015). Compared to MOFs and MOPs, the preperation of traditional supported amine-adsorbents based on porous oxide supports functionalized with amines is simple and relatively inexpensive (Didas et al., 2015). Supported amine adsorbents have been previously classified into three types based on their synthesis: Class 1 adsorbents consist of polymeric or oxide supports (typically silica) that are physically loaded with amine-

containing small molecules or polymers. Class 2 adsorbents contain amine moieties (small molecules) covalently bonded to a solid support; and class 3 adsorbents are comprised of a solid support covalently bonded to polymeric amines prepared by *in situ* polymerization of the support surface, resulting in a large number of active CO_2 capturing sites on the surface (Jones et al., 2011; Goeppert et al., 2012; Choi et al., 2009; Choi et al., 2011b; Bollini et al., 2011). Among class 1 adsorbents, poly(ethyleneimine) (PEI) -based sorbents typically show the highest capacity for capturing CO_2 directly from air (Goeppert et al., 2012; Goeppert et al., 2011; Chaikittisilp et al., 2011). Class 1 adsorbents are easy to prepare and show excellent ability to adsorb CO_2 directly from air; however, due to the lack of chemical bonds between the support and the active adsorbent, these materials can sometimes undergo leaching and instability during regeneration (Goeppert et al., 2010). Class 2 type supported amine sorbents are more stable and were first reported for direct air capture by Belmabkhout *et al* (Belmabkhout et al., 2010). Pore-expanded mesoporous silica (PE-MCM-41) was functionalized with 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (TRI) and the functionalized material (TRI-PE-MCM-41) showed high adsorption capacity (0.98 mmol/g) at low CO_2 concentrations (400 ppm) at 25 ^{o}C. Wurzbacher *et al.* grafted [*N*-(2-Aminoethyl)-3-aminopropyl]trimethoxysilane (AEAPTMS) onto silica gel beads, and reported extracting CO_2 from dry and humid air at 97% purity using a combination of pressure and temperature swing adsorption methods (Goeppert et al., 2012; Wurzbacher et al. 2011). The adsorbent showed good stability over 40 consecutive adsorption/desorption cycles with a CO_2 capture capacity of 2 mmol/g per cycle. The development of class 3 adsorbents was based on combining the high nitrogen loading present in class 1 adsorbents, with the high stablity and low volatility of class 2 absorbents (**Figure 9**) (Choi et al., 2012; Didas et al., 2015; Choi et al., 2011b; Choi et al.,

2011c). A recent report using a class 3 absorbent based on a hyperbranced aminosilica (HAS) shows CO_2 capture capacity from ultra dilute sources such as ambient air to be about 1.7 mol CO_2/ kg sorbent for the highest amine containing material; 42 wt% aminopolymer (Didas et al., 2015).
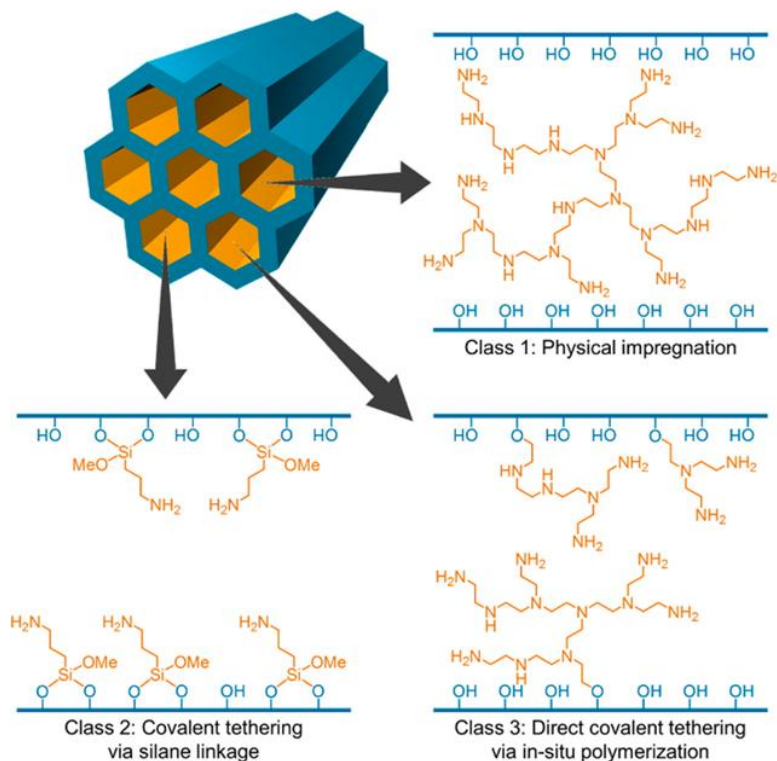
Figure 9. Representation of the three classes of amine adsorbent materials.

Jones *et al.* detailed the design of class 3 type HAS sorbents *via* surface immobilization of polymeric chemisorbents via ring-opening polymerization of aziridine over mesoporous silica (Choi et al., 2012; Didas et al., 2015; Choi et al., 2011b; Choi et al., 2011c). However, higher amine-containing Class 3 materials have slower adsorption kinetics due the blocking of pores,

which hinders CO_2 diffusion within these materials (Didas et al., 2015). In addition to HAS-type sorbents, another strategy that has been reported that uses an aminopropyl-functionalized mesoporous silica support, to polymerize Z-protected L-lysine *N*-carboxyanhydride (Lunn and Shantz, 2009; Chaikittisilp et al., 2011). In a related approach, Qi *et al.* prepared linear polyamines grafted to a porous silica sponge that displayed exceptionally high CO_2 sorption capacities (Qi and Giannelis, 2014). These supported-amine sorbents are advantageous because they can be regenerated at temperatures between 70-120 ^{o}C or lower if vacuum is applied (Wurzbacher et al., 2011; Serna-Guerrero, 2010). However, for the practical appliction of these materials, the long-term stability will also need to be considered. Currently, two modes of degradation have been identified for these materials (Li et al., 2010a; Li et al., 2010b; Heydari-Gorji, et al., 2012; Sayari et al., 2012; Gebald et al., 2013). The first mode of degradation involves amine oxidation, with primary amines being the most stable under oxidation and other expected conditions (Didas et al., 2012; Bollini et al., 2011; Calleja et al., 2011; Heydari-Gorji et al., 2011). The second mode involves degradation of the support system. A loss of porosity was reported for amines supported on highly porous, thin-walled silica upon exposure to steam conditions (Serna-Guerrero et al., 2010). Recent reports have shown that amine-supported basic alumina materials are a more stable CO_2 sorbent than conventional silica-supported materials under silimar conditions (Bali et al. 2014). However, commercially available alumina supports have lower porosity than their silica counterparts, requiring a balance between stability and active amine-content when steaming is used for desorption (Didas et al., 2015). High porosity, steam-stable sorbents could have some advantages (Wilfong et al., 2015).

Supported amine-sorbents, which are related to MOFs, carbons, zeolites, etc., can be viewed as one of the most developed "air-capturing" agents. Nonetheless, the development of practical

adsorbents for direct air capture applications is still in its infancy. The practical applicability of these materials will be determined by their CO_2 capture/release efficiency, long-term stability under the process conditions and the overall cost and safety of the deployed system. To this end, there are still many fundamental research challenges that must be overcome to fully optimize and evaluate these materials for direct air capture. The CO_2 adsorption properties of supported amino-polymers have been linked to morphological and dynamical characteristics of the polymeric phase, but are not fully characterized. Utilization of modeling and simulation approaches can help bridge this gap in terms of providing a fundamental understanding of the structural and dynamic properties of these systems, which in turn can be used to design systems with enhanced carbon capture capabilities (Barkakaty et al., 2016; Carrillo et al., 2015; Holewinski et al., 2015). We also note that compared to alkylamine-based sorbents discussed here, other nitrogen-containing basic moieties such as amidines that typically have higher basicities than amines (Alkhabbaz et al., 2014) are under-explored and might offer potential as more efficient materials for capturing CO_2 directly from air (Endo et al., 2004). For example, Heldebrant and coworkers reported the use of amidine/guanidine based structures as the first examples of CO_2-responsive solvents that could capture CO_2 directly from air (Heldebrant et al., 2008). Recently, Furusho *et al.* has shown that polymers containing amidine groups have higher CO_2 fixing efficiencies than PEIs (Furusho and Endo, 2013), which are reported to have the highest capacities to capture CO_2 directly from air among all the to-date studied amines (Goeppert et al., 2012; Goeppert et al., 2011; Chaikittisilp et al., 2011). However, unlike the synthesis for amine-based polymers, synthesis of amidine-based polymers is a cumbersome process. Recently, a facile synthesis of amidine-based polymers by post-polymer modification of poly(2 vinyl-4,4-dimethylazlactone) (PVDMA) has been reported (Barkakaty et al., 2016). To

the best of our knowledge, the PVDMA functionalized polymer has a higher selectivity, and CO_2 fixing efficiency, than previously reported polymers (Furusho and Endo, 2013) including PEI and aliphatic poly(amidine) (Barkakaty et al., 2016). Thus like amines (Kothandaraman et al., 2016; Carbon dioxide captured from air can be directly converted into methanol fuel, 2016), amidines (Barkakaty et al., 2010; Barkakaty et al., 2011) are also interesting candidates to explore as carbon capture materials because the captured CO_2 can be utilized for *in situ* chemical transformation into compounds that can be used as building blocks for producing high-utility products. Therefore development of novel base supported systems with higher CO_2 uptake/release efficiencies, longer shelf-lifes and better scope for reducing the cost of carbon capture with efficient *in situ* utilization of CO_2 as a chemical feedstock, holds promise for potential direct air capture CO_2 utilization technology.

3. Outlook and Conclusions

Practical applications of direct air capture has already been successfully implemented in submarines and spacecraft equipped with closed-circuit breathing systems (CCBSs) (Goeppert et al., 2012; Ranjan and Herzog, 2011; Huang et al., 2009; Satyapal, 2001). For example, NASA reported that a poly(methacrylate)-supported PEI/poly(ethyleneglycol) (PEG)-based sorbent was capable of reversibly capturing and removing CO_2, maintaining an acceptable CO_2-level in a seven person spacecraft (Goeppert et al., 2012; Huang et al., 2009). However, theororetical calculations suggest that capturing CO_2 from air require about 3.4 times more energy than what is needed to capture CO_2 from flue gas if the separations were completed in a reversible manner (Ranjan and Herzog, 2011). The extensive adoption of air capture / negative emission technologies will depend on various factors including high sorption capacities, high sorption and desorption kinetics, high selectivity, long-term stability, flexibility, high surface areas, ease of

synthesis, scalability, and cost. Inorganic strong bases such as NaOH, KOH and Ca(OH)$_2$ show high capacities for capturing CO_2 from air but suffer from high energy penalties for regenaration. Most of the zeolites and MOFs are sensitive to moisture and hence not suitable candidates for direct air capture. However, recent studies in MOFs and activated carbon based materials indicate that strategic methods to control the pore size distribution with suitable functionalization are key factors for designing new materials in this category. For MOPs, functionalization with strong CO_2-philic functional groups such as amines have been identified as a potential strategy to enhance the ability of these materials for direct air capture.

Incorporation of sorbents that operate by unique mechanisms may also offer new ways of achieving cost effective DAC. As an example, a moisture-swing sorption process developed by Lackner *et al.* for capturing CO_2 from ambient air using anionic exchange resins is a method that relies on a different, possibly hybrid ad/absorption mechanism for DAC. In this method, the sorbent binds CO_2 under (relatively) dry conditions and releases it when hydrated. This method is correlated with changes in the hydration energies of the resin surface and therefore the sorption/release of CO_2 can be predicted and controlled as a function of humidity and temperature (Wang et al., 2013). Recent work on the improvement of adsorption kinetics showed that reducing the size of the sorbent particles can substantially improve the rate of ad/absorption under lower temperature conditions (Wang et al., 2016). In another example, a recent report of a new class of functional porous materials that combines the fluidity of a liquid with permanent porosity of porous solids might have potential application for directly capturing CO_2 from air (Giri et al., 2015). These materials consist of cage molecules, having well-defined pore size, and are highly soluble in solvents with molecular sizes that are larger than the size of its pores thereby prohibiting the solvent molecules to penetrate into its molecular cage. These materials

combine the benefits of free-flowing liquids used in conventional flow process for carbon capture and lower energy requirements for adsorption-release cycles in solid well-defined porous adsorbents. Boron-nitride nanomaterials are another class of porous materials that offers potential opportunities for developing novel materials for future applications in air capture technologies.

To date, supported amine-adsorbents are one of the most developed and promising materials for air capture technologies. These materials demonstrate high CO_2 capturing efficiency, tolerance to moisture and mild temperature regeneration. Moreover, a recent report on application of a polyamine for directly converting CO_2 captured from air into methanol emphasizes the potential of these materials for enabling the use of atmospheric carbon as a source of alternative fuels in the future (Kothandaraman et al., 2016; Carbon dioxide captured from air can be directly converted into methanol fuel, 2016). However, the current state of art for these materials suggests that further R&D is needed to improve their long-term stability for practical applications. The development of novel solid immobilized funtional groups such as amidines having higher stability and basicity than amines and the ability for utilization of the captured CO_2 as chemical feedstock may lead to the next breakthrough in this field. In the search for new breakthroughs, computation and molecular simulation are expected to play an important role in guiding experimental scientists in designing new materials with optimized structures for increased efficiency and stability to capture CO_2 directly from air.

The materials disccused in this article to develop carbon negative technologies are synthetic materials that employ chemical processes to capture CO_2 directly from air. Another noteworthy class of carbon negative materials that has gained significant attention is biochar. Biochar is a carbon-enriched solid material obtained by removing all of the volatile hydrocarbons and most of

the oxygen and hydrogen content in a biomass via heating in the absence or presence of a limited supply of oxygen (Tenebaum, 2009). Biochar materials have the potential to be carbon negative because of their ability to resist chemical and microbial degradation when deployed as a carbon storage medium, retaining a substantial portion of carbon fixed by plants through photosynthesis. Unlike ordinary biomass that adds carbon to the atmosphere via the natural process of biodegradation, biochar stores carbon in a more stable form. Global implementation combining biochar production and its storage in soil could have the potential to avoid net CO_2 emissions on the order of 1.8 Pg (1 Pg = 1Gt) CO_2-C equivalent (CO_2-C_e) annually, and of 130 Pg CO_2-C_e over the course of a century while preserving biodiversity, ecosystem stability and food security (Woolf et al., 2010).

 NASA and the National Oceanic and Atmospheric Administration (NOAA) have reported that 2014 was the Earth's warmest year since 1880 (NASA, NOAA find 2014 warmest in modern record, 2015). Recent reports suggested that 2015 was even warmer (Thomson, 2016). In the recent Paris agreement that was adopted by 195 countries on December 12th, 2015 at the twenty-first Conference of the United Nations Framework Convention on Climate Change (UNFCC), world leaders agreed to take necessary actions to limit the rise in the average global temperature below 2 ^{o}C by 2100 (Editorial, 2016). Therefore, the development of effective carbon capture technologies will be key to control future atmospheric CO_2 levels. Solomon *et al.* used Atmosphere-Ocean General Circulation Models (AOGCMs) and Earth System Models of Intermediate Complexity (EMICs) and reported that irreversible climate change will occur if the atmospheric CO_2 concentration increases from around 385 parts per million (ppm) to 450-600 ppm (Solomon et al., 2009). The current atmospheric CO_2 concentration is already very high, ~ 402 ppm (December 2015) (Earth's CO_2 Home Page, 2016), and as more than 50%

anthropogenic carbon emission comes from distributed sources, point source emission reductions alone will not be able to slow down the effects of global warming without considering additional "carbon negative" strategies such as air capture.

The cost of capturing CO_2 directly from air will be the key factor that determines whether negative carbon processes are deployed. However, as highlighted in this work, suitable technologies for capturing CO_2 directly from air still require significant research and development (R&D), and cost estimates of early technologies are often not accurate, as the cost can drop by orders of magnitude with mass production and further developments. Furthermore, a combination of air capture with suitable CO_2-conversion technologies will aid in further reducing the cost. Therefore, growth in R&D of new materials for capturing CO_2 from ultra-dilute sources coupled with model and computational aided design holds the key for future materials and technology to make "air capture" become economically feasible.

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