CLIMATE CHANGE MITIGATION USING METAL-ORGANIC FRAMEWORKS FOR DIRECT AIR CAPTURE OF CO_2

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Rising atmospheric CO_2 levels must be addressed to avoid the inevitable environmental harms of climate change. Carbon capture and sequestration (CSS), separating CO_2 from other gases at anthropogenic point sources, has been a research interest in this area. Recently, carbon capture directly from the atmosphere, direct air capture (DAC) has been posited as a possible alternative. There are certain advantages to this, as only 47% of CO_2 emissions are addressable by conventional CCS, and it has the potential to decrease atmospheric concentrations, rather than simply slow the rate. There are unique challenges, however, as air concentrations are much more dilute, making the process more expensive. Currently, metal-organic frameworks (MOFs) seem the most promising sorbents for this process, although they face disadvantages such as high regenerability costs. This review will summarise progress in this area, focusing on chemisorption via alkylamine-appended MOFs and physisorption by MOFs bound with hexafluorosilicate anions, and will suggest further areas of research.

Introduction

CO_2 has been a primary target for climate change mitigation, having risen from pre-industrial levels of 280 ppm to current levels of 400 ppm (NOAA/ESRL), and will likely cause significant environmental harms if not addressed. An important mid/long term strategy is carbon capture and storage, or CCS (IPPC, 2014). This is gas separation of CO_2 from other gases such as N_2 and CH_4, and storage for further use. Conventionally, this operates at large anthropogenic point sources to prevent the gas reaching the atmosphere – this area is where most of the research has been conducted and many argue the technology, though expensive, will soon become necessary to reach mitigation targets (Riahi *et al.,* 2015). However, it is estimated that only 47% of CO_2 emissions sources are addressable by conventional CSS (EEA, 2007), the rest coming from diffuse sources such as small isolated industry plants and transport. This has led some research interest into the more controversial field of CO_2 capture straight from the atmosphere, or direct air capture (DAC).

There are numerous recognised advantages to DAC. As well as capturing emissions from diffuse sources, air capture belongs to the negative emissions group of technologies, which can potentially *decrease* current CO_2 levels, in contrast to conventional capture, which can only slow the rate of release (Choi *et al.,* 2011). For this reason it has been posited as a fall-back option in case countries do not reach the necessary targets, and can be implemented anywhere, not just at selected point sources. Finally, it has applications beyond climate change mitigation, electrolyte function in fuel cells (Kordesch *et al.,* 2000), anaesthesia (Dosch, 2006), and air purification in space shuttles (Ernsting, 1999) being some examples.

There are, however, serious obstacles facing its implementation. The current process is very expensive (Socolow *et al.,* 2011), because atmospheric CO_2 levels of 400 ppm (0.04%) are hundreds of times lower than post-combustion flue streams of 10-15% and pre-combustion (for natural gas) of up to 35% (D'Alessandro *et al.,* 2010). The sorbent (material used to capture the CO_2) therefore faces larger obstacles than for conventional capture and must be extremely efficient to be practicable. It is estimated that for the current sorbents a 10-metre high DAC system would need to be 30 km long to capture the emissions from one 1000 mW coal power plant. Since it is thought that sorbent is the biggest contributor to the high cost (Socolow *et al.,* 2011), the need for new materials if the technology is ever to become usable is clear.

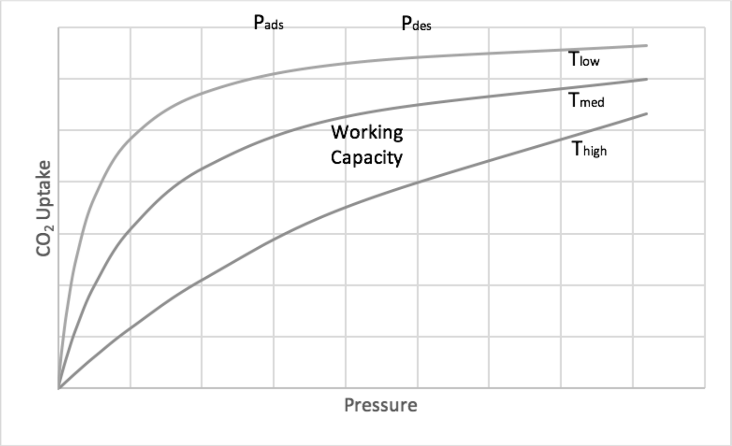
Among the most promising class of materials for future DAC is MOFs. These are highly crystalline, porous materials made of metal centres linked together by organic ligands, called "linkers", have very high surface areas and are easily tunable. Although MOFs began being used for DAC well after solid-supported amines, which have been discussed from at least 2009 (Lackner, 2009), the rate of progress has been quicker. They currently perform as well and sometimes better, although there has so far been no satisfactory study comparing performance in terms of overall cost. This review summarises the progress of MOFs for the purpose of DAC and will provide an explanation of the main properties that underlie their success. There are two broad classes – alkylamine-functionalized MOFs, which have been the main focus until recently, and MOFs that adsorb via physiadsorption, a more recent and very promising method.

There are a range of different properties important for assessing materials. The most important are identified by Huck *et al.,* (2014) in calculating parasitic energy (a cost-based metric), and include adsorption capacity (of CO_2, measured in mmol of CO_2 adsorbed per gram of material), regenerability (related to the isoteric heat of adsorption, as desorption is essentially the reverse of this value), selectivity of CO_2 uptake versus other gases, and working capacity (measured by comparing uptake isotherms as the amount of CO_2 that can be released following adsorption). Each of these will be incorporated into the discussion as necessary.

Mechanism of Alkylamine-functionalized MOFs

The functionalization of MOFs was performed for other purposes, including post-combustion air capture before it was used for DAC, and the mechanism of functionalization has been long understood (McDonald *et al.,* 2011). Upon synthesis of certain MOFs, some solvent molecules, often DMF or H_2O, become coordinated to the metal centre. These can be removed, usually by heating around 400 °C (McDonald *et al.,* 2012), leaving what are called coordinately unsaturated sites (CUS), usually pentavalent metal centres. Sometimes entire one-dimensional pore channels can be lined with these CUS spaces, and in conventional MOF carbon capture these areas are the sites of adsorption, as the central metal is a strong lewis acid (D'Alessandro *et al.,* 2010). For DAC, these CUS have been exploited to allow alkylamine-functionalization. After expelling the solvent molecules the MOF is placed in an organic solvent with the desired alkylamine, and the CUS are functionalized, to varying degrees depending on the framework. The diamines chosen are highly basic and coordinate strongly to lewis acidic metal centres, leaving one amine end free.

The mechanism of reaction between the amine and CO_2 differs from that of the aqueous amines currently in use for carbon capture and from the solid-supported amines reported to work well for DAC. Early reports suggested a 1:1 amine:carbon reaction stoichiometry, whereas the usual mechanism forming a carbamate species showed a 2:1 ratio, where one nucleophilic amine attacks the partially positive carbon atom and another acts as a base to abstract the N-H proton (Planas *et al.,* 2013). This was originally thought to be due to a mechanism where a second CO_2 molecule was attacked by an amine hydrogen-bonded to the first carbamic acid, forming a bis-carbamic acid complex, giving a 2:2 stoichiometry. However, the evidence was indeterminate and this mechanism could not adequately explain the "step" in reported isotherms, giving a sigmoidal curve in contrast to the usual Langmuir-type isotherm (an important consequence of which is higher achievable working capacities – see figure below). Recently another mechanism was proposed, explaining the step and supported by DFT calculations and IR data. (McDonald *et al.,* 2015)



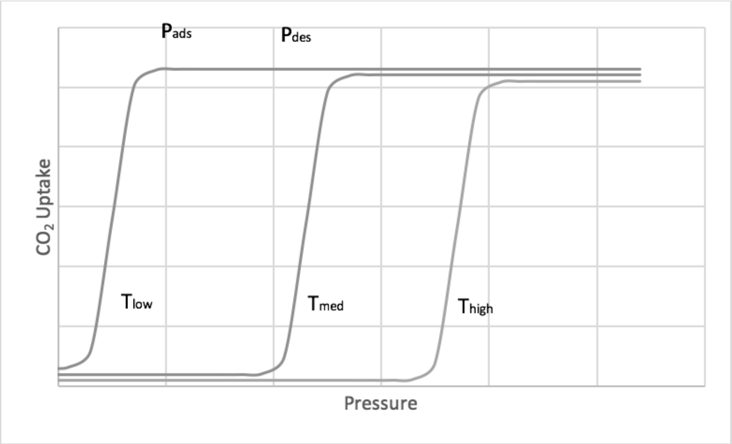


Figure 1. *Comparison of Langmuir isotherms (top) with sigmoidal isotherms(bottom). Adapted from McDonald et al., 2015*

In this proposed mechanism the incoming CO_2 molecule inserts into the amine-metal bond. In the presence of CO_2 an uncoordinated amine end will abstract the acidic N-H proton of a metal-bound neighbour along the c-axis (down the MOF channels), which then forms a carbamate with the incoming CO_2 molecule. This is stabilised by the recently protonated ammonium countercation. The M-N bond will break and the M-O bond will be formed. The rapid rise in uptake is now explained – the ion-pairing interaction destabilizes the mmen ligand (the particular diamine ligand used for this study, and the mechanism is thought to be the same for other amine-appended MOFs) and weakens the M-N bond, leading to an increase in the rate of CO_2 insertion. This continues in a chain reaction across amines along the c-axis, each new interaction weakening the neighbouring M-N bond.

This proposed mechanism suggests some improvements and reveals limitations for such MOFs – amine bonds tethering it to the surface must be coordinate and not covalent, to allow for M-N breakage, so this mechanism is therefore likely to be unattainable in amine-functionalized silica sorbents, and neighbouring amines must be suitably aligned, so the mechanism will occur with only a limited set of MOFs with appropriate CUS placement. It is predicted that the position of the step, and therefore working capacity, may be changed by altering the linker ligands between each neighbouring amine group, the sterics of the M-N bond, and the strength of the M-N bond by changing the central metal.

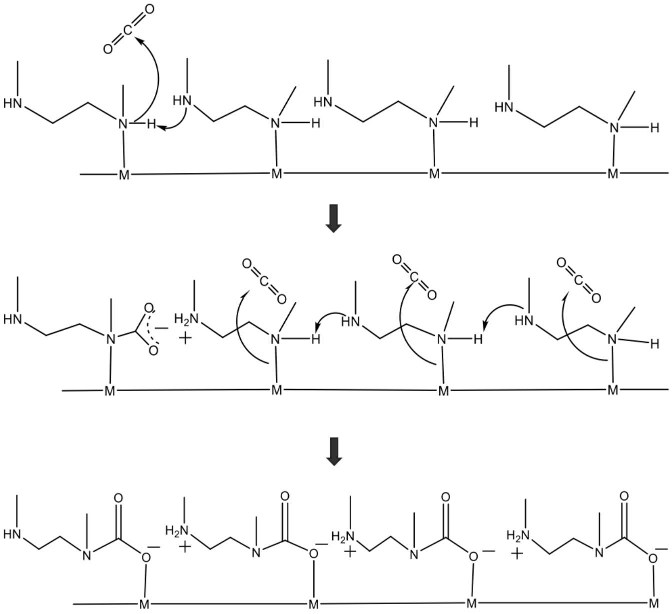


Figure 2. *Overview of proposed alkylamine-functionalized CO2 adsorption mechanism. Adapted from McDonald et al., 2015*

Improved performance from alkylamine-functionalization

Two such structures suitable for DAC were reported in 2012, one by Choi *et al.,* (2012), using Mg-MOF-74. This MOF is composed of Mg(II) metals centres linked with 2,5-dioxido-1,4-benzenedicarboxylate ligands. After synthesising Mg-MOF-74 and expelling the solvent molecules the MOF was functionalized with ethylene-diamine (en or ED) ligands. Analysis of this with dry simulated air streams with CO_2 concentrations at 390 ppm showed it to have exceptional properties, unprecedented for DAC with MOFs. Performance was measured over 4 adsorption-desorption cycles using temperature swing. ED-Mg-MOF-74 had an adsorption capacity from 1.51 mmol/g-1.55 mmol/g with no significant change over the four cycles, higher than non-functionalized Mg-MOF-74 (which also suffered a 20% drop in adsorption capacity) and close to the final value of PEI-silica at 1.65 mmol/g, which suffered a 29% drop from 2.36 mmol/g. There was no reported isoteric heat of adsorption, so it is difficult to assess the regeneration cost – however it is likely to be higher than the non-functionalized framework, as most other reports shows.

Even better results were reported for mmen-Mg_2-(dobpdc) (McDonald *et al.,* 2012). This MOF is an analogue of Mg-MOF-74 with extended linker ligands (4,4'-dioxido-3,3'-biphenyldicarboxylate) which increased the pore space from 11 Å to 18.4 Å. As with ED-Mg-MOF-74 the alkylamine was added via a post-synthetic pathway, giving the final structure, shown below. The material's adsorption capacity was measured using temperature swing over 10 adsorption-desorption cycles, giving an adsorption capacity of 2 mmol/g and no apparent degeneration of the MOF, close to the first use of PEI-silica gel of 2.4 mmol/g. The MOF has the advantage of better reaction kinetics – it takes PEI-silica 200 minutes to reach $4.6\%_{mc}$, while mmen-Mg_2-(dobpdc) reaches the same value after only 60 minutes. The material also performed well in purity of CO_2 sequestered and selectivity over N_2, with values of 96% and 49,000 respectively. However, the materials still suffer from a high isoteric heat of CO_2 adsorption at -71 kJ/mol compared to the value of -47 kJ/mol for the non-functionalized Mg-MOF-74, making the regeneration process energy-intensive – as noted earlier, cheap regenerability is key to the viability of new air capture materials.

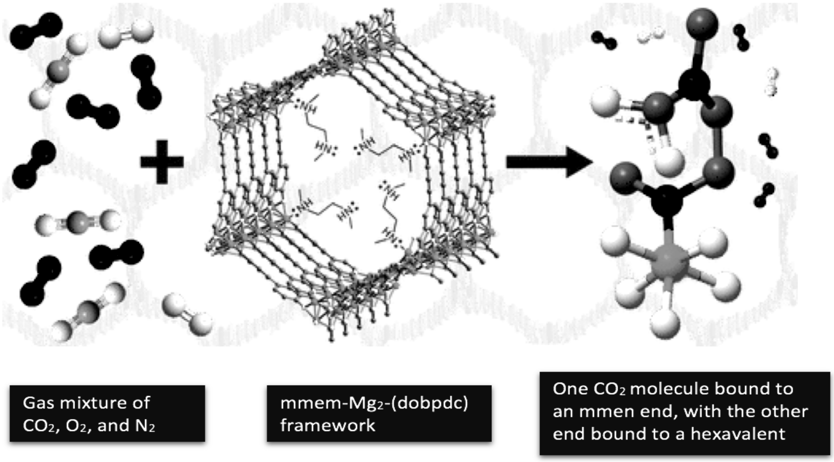


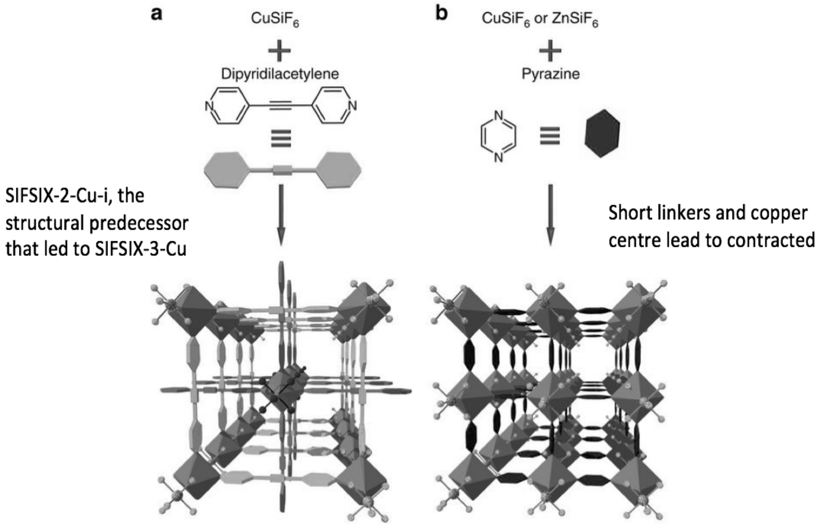
Figure 3. *Overview of CO2 adsorption by mmen-Mg2-(dobpdc). Adapted from McDonald et al., 2012*

The same strategy has since been used to the same effect on the same MOF framework, functionalized with different diamines. A very high-performing alkylamine-grafted MOF was reported by Lee *et al.,* (2014), called en-Mg_2(dobpdc). This is same MOF reported in McDonald *et al.,* 2012 but functionalized with en instead of mmen. This was measured to have a CO_2 adsorption capacity of 2.83 mmol/g, 1.4 times higher than that of mmen and with a lower isoteric heat of adsorption at -49-51 kJ/mol. It also showed superior selectivity over N_2 and purity of collected CO_2, at 70,000 and 97%. This study also reported that amine-functionalized MOFs are not greatly affected by humidity as was previously worried (Choi *et al.,* 2012 and McDonald *et al.,* 2012), showing both en-Mg_2(dobpdc) and mmen-Mg_2(dobpdc) having near perfect performance after capturing dilute CO_2 from humid air, while Mg-MOF-74 suffered a substantial decrease, probably because water molecules bound to CUS and were difficult to remove. However, on temperature swing analysis it showed a 6% reduction in adsorption capacity after 5 cycles – it is unsure why this degeneration occurred and is important to address.

MOF tuning for maximum physiadsorption

More recently a method of DAC using MOFs has been suggested that has departed from methods up to that point which warrants some attention – tuning the pore size and other properties of MOFs to allow for maximum physisorption. There are some advantages to physisorption over the more common chemisorption pathways (Nugent *et al.,* 2013). Capture occurs via weak van der Waals bonds and so should have a lower isoteric heat of adsorption and therefore less energy-intensive regeneration, and since the use of amines is not necessary it avoids some other disadvantages, such as sorbent degeneration. Also preparation costs should be reduced, as activation of CUS and functionalization of amines is often performed at extreme temperatures. However they usually have lower adsorption capacities, which must be addressed if they are to become a viable future option for DAC.

CO_2 has a high polarizability, which has been exploited before in carbon dioxide capture technology, for example in zeolites (Morris *et al.,* 2010). The most promising MOF for DAC of this class so far is called SIFSIX-3-Cu (Shekhah *et al.,* 2014) and was optimised by contracting the pores to increase electrostatic van der Waals interaction between CO_2 and the SIFSIX pillars. Metal-organic structures with SIFSIX anions are often classified as metal-organic-materials (MOMs), the difference being they are not necessarily infinite crystal structures and may be supramolecular finite structures (Cook *et al.,* 2013) – however in the original paper reporting this material it was classified as an MOF, as well as in much of the literature discussing it (Huck *et al.,* 2014, Shekhah *et al.,* 2015). SIFSIX-3-Cu is also structurally and functionally similar to MOFs discussed so far, having one-dimensional pore channels in an infinite lattice, and therefore it can be considered an MOF. The material has hexavalent Cu centres, bound to pyrazine to form two-dimensional sheets which are pillared together with SiF_6^{2-} (the "SIFSIX" pillars) to form the 3-dimensional structure with square pore channels. The pore size here has been contracted to 3.5 Å from structurally similar predecessors by using short pyrazine linkers and Cu, which has a d^9 electronic configuration and undergoes Jahn-Teller distortion. F-CO_2 distance is short and four fluorine atoms point directly into the square channels, allowing for high charge density.



SIFSIX-2-Cu-i, the structural predecessor that led to SIFSIX-3-Cu

Short linkers and copper centre lead to contracted

Figure 4. *SIFSIX-3-Cu and structural analogue. Adapted from Shekhah et al., 2014*

This MOF shows very good properties for adsorption. At 400 ppm CO_2 it had an adsorption capacity of 1.24 mmol/g, showed high selectivity of carbon over N_2 and CH_4, and was not affected by humidity. Although it has a reasonably high isoteric heat of adsorption at -54 kJ/mol which suggests energy intensive regeneration, desorption was easily done under the mild conditions of a vacuum at 323 K. Indeed, a recent review (Huck *et al.,* 2014) using parasitic energy as a metric showed this MOF as the second most promising material overall for DAC, lagging just being the top-performing silica-supported amine (although it is important to note that this review did not assess any alkylamine-functionalized MOFs). It is suggested that further work based on the same framework but with different metals will improve efficiency – this emerging method of DAC by MOFs looks like a promising alternative to amine-functionalized MOFs.

Conclusion

It is important to note that DAC is still unlikely to be implemented for use over other climate change mitigation strategies, such as alternative fuels and conventional CCS from anthropogenic point sources, as the cost will probably have to be higher to be equally effective (Socolow *et al.,* 2011). It will most likely be used for novel uses such as air purification in confined spaces and anaesthesia, and possibly to decrease atmospheric levels of CO_2 if they become too high in the distant future. It is difficult to predict however as the area is still in its infancy, and technological advances may unexpectedly render it economical.

Technological advances so far have been impressive, particularly for MOFs. There is a good deal of further research necessary, however. First of all, all MOFs should be measured against each other and against other materials for DAC to see which is currently the most cost-effective and where further research should explore – a metric like parasitic energy used by Huck *et al.*, (2014) would be suitable. There are some specific improvements necessary – the high regeneration energy and synthesis cost of alkylamine-functionalized MOFs need to be addressed, although improved performance is likely as different ligands are tested with different frameworks. The proposed mechanism helps guide this, predicting that changing the distance of neighbouring amines and changing the central metal may improve performance. Also, all materials using this method have been based on Mg-MOF-74, as it was the MOF which showed highest performance for post-combustion flue streams (Huck *et al.*, 2014). However, trends of material efficiency often reverse for DAC (for example non-functionalized Mg-MOF-74 performs very poorly for DAC, with parasitic energies ten times higher than the best materials), so it is probable that another MOF not yet synthesised will perform better. For the physiadsorption method, fine-tuning the ligands and central metal again should improve performance – these materials need a higher working capacity to be viable. For both methods, future materials will probably not resemble current high-performing materials in terms of MOF used, but will function by the same principles and the research will rely on the lessons they offer to advance progress.

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