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A Review of CO_2 Adsorption From Ambient Air (Direct Air Capture)

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ABSTRACT

Direct Air Capture (DAC) has risen in the past decade as a promising choice to remove CO_2 directly from ambient air. Although there are many technologies like pre-combustion, post-combustion and oxy-combustion to mitigate the emissions of CO_2, there is still a need for a better or a complementary technology in controlling these emissions. Even though, there are many options for adsorbents that can be used, metal-organic frameworks (MOFs), which are hybrid materials with a crystalline structure, tunable pores, and high surface area, have risen as a promising candidate. Functionalizing MOFs with amine groups will greatly enhance their capacity towards CO_2, like mmen-M_2 (dobpdc) (M=Mg, Fe, Mn, Zn, Co). These adsorbents show S-shaped adsorption isotherms and have a very high affinity to CO_2 under atmospheric conditions, due to the cooperative insertion of CO_2 into mmen-M_2 (dobpdc) that leads to their unique adsorption isotherms. The energy required to regenerate these materials using small heat variations makes a better choice than aqueous amines. This mechanism has been studied by using X-Ray Diffraction (XRD) and spectroscopy experiments. Furthermore, a thermodynamic study has been reviewed to understand the mechanism through which CO_2 is inserted into the diamine bond. These materials are a promising choice for the removal of CO_2 directly from the atmosphere and require more future research.

1. Introduction

There is a growing acceptance that global warming is real and that human activity is partly responsible for it. As industrial life has thrived, greenhouse gas emissions have also thrived with it. Carbon dioxide, which is an important greenhouse gas, has experienced a steady increase in its atmospheric concentration from 280 ppm into 400 ppm, since the start of the industrial revolution as a direct result of the burning of fuels and power generation [1], [3-5]. Although the subject still under debate, some strongly advocate that present concentrations of carbon dioxide do play a major role in the warm-up of the earth's atmosphere, resulting in the reduction of the sea ice at the poles and the increased water levels [1, 2]. For example, Figures (1) and (2) respectively show the most recent results related to both the Arctic sea ice extent and the global (both land and ocean) temperature index from the National Snow & Ice Data Center (NSIDC). In both cases, the graphs show that we have reached unprecedented records. If human activity is to be indicated as playing a major role in the presently observed trends, then the causes that lead to present CO_2 concentrations need to be addressed. Recently, for example, the Intergovernmental Panel on climate change (IPCC) have suggested that emissions need to be reduced by 30-60 % in the next 35 years [6]. Although there are many types of research going towards the development of technology for using renewable energy sources such as solar, wind, geothermal, etc., fossil fuels are still providing almost 80% of the world's need for energy. Today, depending on how CO_2 emissions are generated, CO_2 removing processes have been defined according to three different categories: those that are pre-combustion, those that are post-combustion, and those that are oxy-combustion.

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Nomenclature

DAC	Direct air capture	*IAST*	Ideal adsorption theory
MOFs	Metal-organic frameworks		

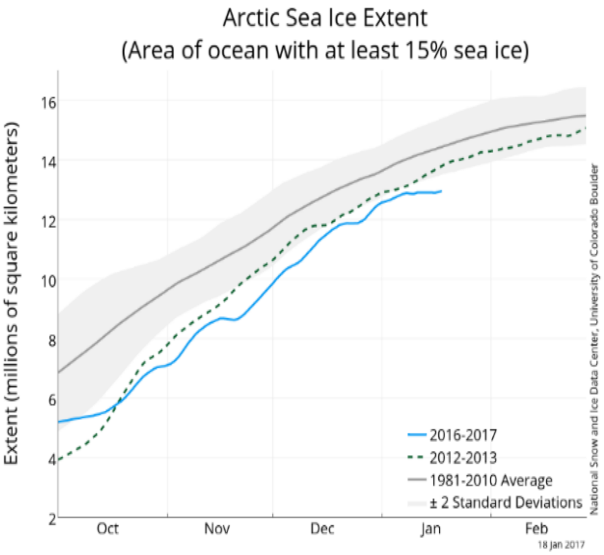

Figure (1): Arctic sea ice extent as of January 2, 2017, along with daily ice extent data for four previous years[7]

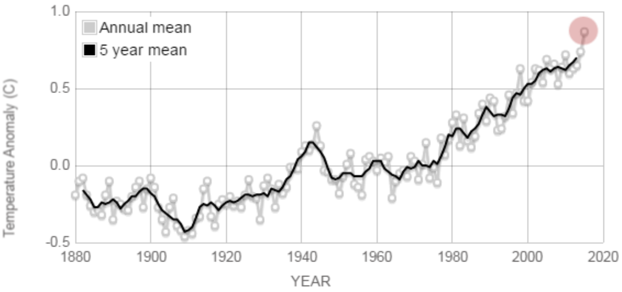

Figure (2): Global Land-Ocean Temperature Index[7]

In pre-combustion processes, CO_2 is removed from a stream before its conversion into the flue gas. This method is typically used in industries involved in the production of natural gas, H_2, and syngas [1],[6], and [8], such as gasification, sweetening, steam reforming, and water gas shift reaction. In post-combustion processes, CO_2 is removed from streams with no energetic value or flue gas, which, as the term indicates, is carried out mostly after a combustion process has taken place [1], [6], [8], and [9]. This type of processes is intended for downstream processing of fuel-based energy and power generation units typically found in the industry and power plants. However, CO_2 removal processes meant for the cemented steel and aluminium industry can also be included in this category. Finally, in oxy-combustion processes, nitrogen is excluded from the combustion processes via oxygen purification resulting in a flue gas consisting mainly of CO_2 and water vapor [1], [6].

In addition to these three categories, there are other more recent approaches to CO_2 capture. One of such approaches is the direct air capture (DAC), wherein CO_2 is captured directly from the air at ambient conditions [3], [11]. The concept, which was proposed by Lackner [10], has been attracting significant attention in recent years. Although this technology is considered in its infancy, it shows promise mainly because of its location flexibility as units can be incorporated in any place [1], [10-12]. Further, ambient air is rather free of SO_x and NO_x [10], which usually react with adsorbents irreversibly. On the other hand, the major limitation of DAC is the small concentrations of carbon dioxide, resulting in significantly low collection rates and very small yields and throughputs when compared to the more traditional ways of collection mentioned earlier. Despite this, it is worthwhile reviewing the present efforts toward the development of this technology. This is the intention of the present work.

Solid adsorbents are being widely proposed as an alternative to aqueous amine solutions due to the lower energy required for desorbing CO_2 [4]. The metal-organic frameworks (MOF) are excellent candidates for DAC because MOFs are porous solids that are promising alternatives to due to their large surface area, tunable pores, availability of open metal sites and their high likelihood to be produced on an industrial scale[4],[13-15]. The adsorption capacity of these adsorbents towards CO_2 at ambient pressures can be improved significantly by introducing alkyl diamines into the pores of unsaturated sites of these adsorbents [16]. Functionalization of metal-organic framework MOF with alkylamine can greatly enhance its adsorption capacity towards CO_2 [14], [16,17]. McDonald introduced synthesized two MOF Zn and Mg; dobpdc4-=4,4'-dioxido-3,3'-biphenyldicarboxylate via solvothermal and microwave method which is reported in the literature [17,18]. Then the MOF was functionalized by introducing N, N'-diethyl ethylenediamine (mmen) to afford Mg_2(dobpdc)-(mmen)1.6(H_2O)0.4 (mmen-Mg_2(dobpdc)). After the materials had been synthesized, powder X-ray diffraction was performed to get information about the dimensions of the unit cell of these materials. The amount heat of adsorbed CO_2 (mmol/gm) was calculated at a temperature range of 25,50 and 75°C using Longmuir-Freundlich eq. while the isosteric heat of adsorption was calculated using the Clapeyron Eqn. Also, the purity and CO_2 selectivity were calculated [17]. The sample was regenerated to 150 under vacuum for one hr, then followed by thermodynamic analysis and gas cycling using thermogravimetric analyzer TGA at a flow of 15% CO_2 in N_2 atmosphere flowing at a rate of 25ml/min and ramp rate ranging between 5-10 °C. Other physical measurements were also performed to get extended information about the sample.

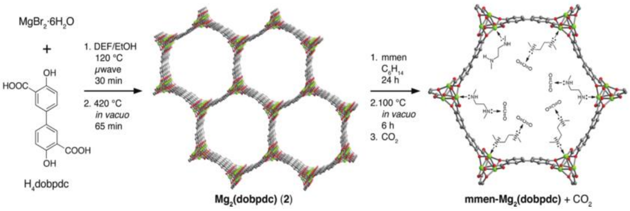

Figure (3): Synthesis of mmen-Mg_2(dobpdc) (mmen = N, N′-dimethylethylenediamine;dobpdc4^-=4,4′-dioxido-3,3′-biphenyldicarboxylate). Green, red, and gray spheres represent Mg, O, and C atoms, respectively; H atoms are omitted for clarity. Amine-appended CO_2 adsorbent Mg_2(dobpdc)(mmen)1.6(H_2O)0.4 (right)[17]

After performing the experiment, it was seen that the functionalized MOF had a capacity 15 times higher than that of the unmodified MOF, the modified MOF adsorbed 2mmol/gm at 0.39 mbar and 3.86 mmol/gm at 1 bar, which shows a remarkable affinity towards CO_2. Although the modified version of MOF has a higher adsorption capacity towards CO_2 than unmodified MOF at low pressures than at higher pressures,20 mmbar, due to large density difference [17]. The calculated heat of adsorption was less at lower coverage and increased until it reached a value of -71 KJ/mol, which is an indication of chemical adsorption due to the formation of the C-N bond of a carbamate that is probably formed. This is also proved by performing infrared spectroscopy, which shows an apparent loss of 3316 cm-1 due to NH stretch. The presence of amine groups is necessary to stabilize the formed carbamate [17]. The slow desorption at room temperature is an indicator of the formation of the ammonium carbamate since the latter desorb CO_2 at room temp. But is not conclusive [17]. Further investigation for the role of the neighboring amines is required. The S-shaped isotherms are not expected in these materials due to the material has strong adsorption of CO_2 as well as large pores, which means that CO_2 should have been adsorbed on the mmen before being greatly adsorbed on the other weaker sites [17]. This can be hypothesized that the CO_2 adsorption on the mmen is not favored at low concentration of CO_2 in the pores due to need to chemically adsorb CO_2 which will require reorganization of the amines which will be associated with large positive entropy and as the thermal motion increase so as the minimum chemical potential that is required for the reorganization or the amines increase with it as can be seen from the shift in the isotherms at higher pressures and temperatures [17]. This hypothesis went through the further investigation as will be explained later [4]. The selectivity of the mmen2 towards CO_2 is studied in comparison with N_2 and O_2, and the result was underestimated due to the inability to use ideal adsorption theory (IAST), which is a mathematical model developed by Myers is independent of the experiment results and actual data [17], [19,20]. These materials showed a very high selectivity towards CO_2, on the other hand, they were able to achieve 96% purity under direct air capture conditions [17].Although this purity under actual conditions of operation in the adsorbent bed will be affected by different factors, but in adsorbent bed of 80% void volume the purity of CO_2 will be over 90% [17]. The renewability of these materials have showed a great promise in reducing the regeneration energy because even though 1.05mmol/gm were adsorbed only after flowing air at atmospheric conditions for an hour, no loss in capacity was noticed after regenerating the sample with N_2 at 150°C for 30 min and repeating the cycle for 10 times 17]. These materials also have fast kinetics, even though polyethyleneimine impregnated silica gel was able to achieve 2.4 mmol/gm adsorption capacity, but it took almost 4 hours while mmen2 was able to achieve 1.05 mmol/gm in one hour. In conclusion, these materials show high selectivity and capacity towards CO_2 under atmospheric conditions, but the mechanism at which CO_2 is adsorbed needs to be further investigated. McDonald et al. explained the mechanism that leads to the step-shaped isotherms is due to the cooperative CO_2 insertion to the metal amine bond [4]. X-ray diffraction at 100 K before and after five mbar CO_2 exposure on the mmen-Mn_2 (dobpdc) was performed to get structural information on how CO_2 binds with these materials. They found that full insertion of CO_2 occurs the adsorption of CO_2 on these metal sites into the Mn-N bond resulting in a carbamate with one O atom bound to Mn and the other O atom bonded to N atom from a neighboring mmen resulting in chains of ammonium carbamate. The x-ray helped them formulate a detailed mechanism to explain the adsorption of the CO_2 in these phase change adsorbents. In the presence of CO_2, the amine of the mmen molecule to act as strong base leading to deprotonation of the acid gas followed by nucleophilic CO_2 addition resulting carbamate formation in which the M (M=Mg, Mn, Fe, Co, Zn)-N bond and the formation of the M-O bond. This cooperative effect will propagate until 1D ammonium carbamate chain has been formed and this effect is the cause of the high CO_2 adsorption capacity due to full accessibility of CO_2 into the pores unlike other adsorbents in which the main mechanism gate opening that hinders the CO_2 into the pores due to the presence of flexible hydrogen bonding functional groups[4].

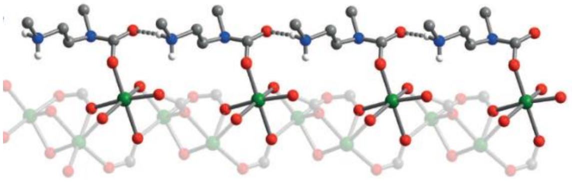

Figure (4): Powder X-ray diffraction structures of mmen-Mn_2(dobpdc), A portion of the crystal structure of the final configuration of CO_2 adsorbed within mmen-Mn_2(asdobpdc), depicting the formation of an ammonium carbamate chain along the pore surface. Green, gray, red, blue, and white spheres represent Mn, C, O, N, and H atoms, respectively; some H atoms are omitted for clarity [4].

They also performed infrared spectroscopy to confirm their conclusion on the adsorption mechanism. The results of the spectra are shown in figure (5) below:

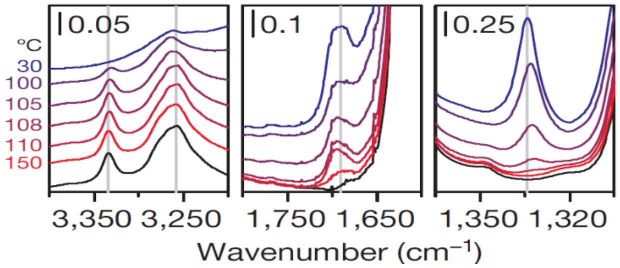

Figure (5): Infrared spectra on dosing an activated sample of mmen-Mg_2(dobpdc) (black) with CO_2 and cooling from 150 °C to 30°C (red to blue) under 5% CO_2 in N_2. The three different regions show bands corresponding to N–H (left), C–O (center) and C–N (right) stretching vibrations[4]

In the infrared spectra, the adsorbent was cooled under constant pressure from 150 to 30°C at a rate of 1 degree per minute under 5% flowing CO_2 in the N_2 environment. The N-H bond that could be noticed for the higher temperatures at 3,258 and 3,334 cm-1 is resulting from the presence of the mmen ends. The breaking of the N-H bond due to the presence of CO_2 (C=O at 1,690 cm-1) and the formation of amine N-H bond of the carbamate can be observed even at high temperatures. The infrared showed that the forming of ammonium carbamate is what gives the S-shaped isotherm for CO_2 adsorption. They also performed near-edge X-ray adsorption fine structure of the nitrogen K-edge mmen-Mg_2(dobpdc) under CO_2 pressure, and they were able to prove their proposed mechanism[4]. According to tat mechanism, the different metal amine strength offers different isotherm step position as they demonstrated by synthesizing different compounds of M_2(dobpdc) (M=Mg, Mn, Fe, Co, Zn, Ni) and performed adsorption for various temperatures ranging from 25-75°C. The detailed method of volumetric adsorption isotherms calculation and equations are mentioned in detailed in literature [21] . The results showed that Mg, Mn have the highest step position isotherms due to their long amine bond length

(~2.45,2.35 A° respectively) and they are suitable for adsorption CO_2 from natural gas under pressure as low as 0.05 bar. The only metal that didn't have the stepped shape isotherm is Nickel but instead had a regular Langmuir isotherm due to the high stability of the Ni-mmen bond preventing the cooperative effect from taking place.

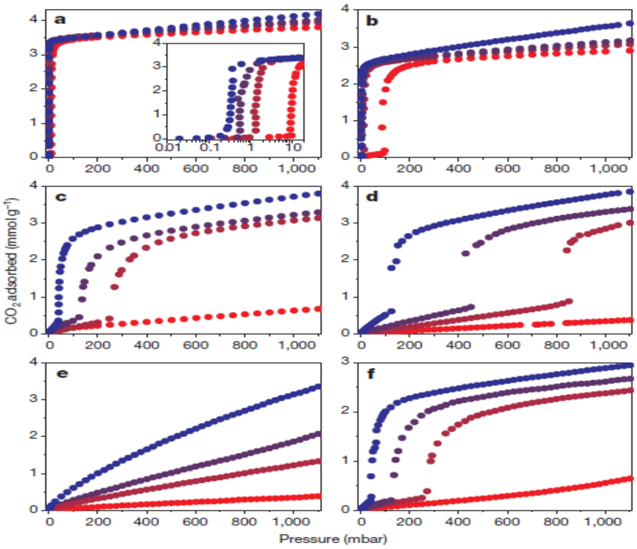

Figure (6): Carbon dioxide adsorption isotherms at 25 C (blue), 40°C (blue-violet), 50°C (red-violet) and 75°C (red) for mmen- Mg_2(dobpdc) (a), mmen-Mn_2(dobpdc) (b), mmen-Fe_2(dobpdc) (c), mmen-Co_2(dobpdc) (d), mmen-Ni_2(dobpdc) (e) and mmen-Zn_2(dobpdc) (f)[4].

It is not just the adsorption capacity that is important but also the working capacity (the amount of CO_2 removed from the adsorbent) on performing regeneration in pure CO_2 over ten cycles of adsorption in which mmen-Mg_2(dobpdc) and mmen-Mn_2(dobpdc) were exposed to 15% CO_2 in N_2 atmosphere at a constant pressure and temperature ranges from 100 to 150°C for mmen-Mg_2(dobpdc) and 70 to 120°C for mmen-Mn_2(dobpdc) , the working capacity was 13% for mmen-Mg(dobpdc) and 10% for mmen-Mn_2(dobpdc) with no loss in the adsorption capacity over these ten cycles. The regeneration step is energy conservative in which it requires (2.2-2.3) MJ/kg CO_2 captured, unlike other commercial adsorbents like aqueous amines.

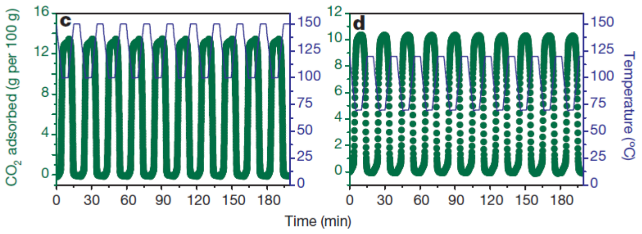

Figure (7): Cycling data for a pure temperature swing process involving adsorption from a simulated coal flue gas (15% CO_2 in N_2) at 100°C in mmen-Mg_2(dobpdc) (c) and 70°C in mmen-Mn_2(dobpdc) (d), followed by desorption at 150 and 120°C, respectively, using a flow of 100% CO_2[4]

Wu et al. performed a study on these same adsorbents (mmen-M_2 (dobpdc)) to further understand the thermodynamic mechanism of CO_2 adsorption on these materials [22]. They performed an experiment for three different temperatures 298, 323, and 348 °K using a calorimetry apparatus.

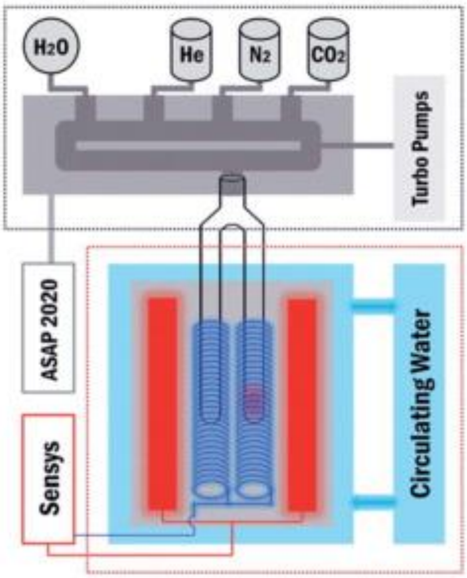

Figure (8): Adsorption calorimetry apparatus [22][23]

The material was put in a silica glass tube and subjected to vacuum for the day and a half at a temperature of 373 °K. the enthalpy of adsorption and the isotherms were recorded at the same time; this will help in determining the heat of adsorption as a function of the surface coverage. To fully explore the CO_2 adsorption mechanism on the mmen-Mg_2(doodc) the experiment were divided into three sets: firstly the adsorption and adsorption after regeneration under vacuum were conducted to investigate CO_2 reversibility, secondly after the second round on fresh mmen-Mg_2(dobpdc) the regeneration was done only by degassing without using heat to keep the chemisorbed amount of CO_2 and remove the physisorbed ones, finally the enthalpies of adsorption were measured at the experiment temperature range [22]. These materials have great reversibility with marinating the adsorption capacity towards CO_2 with no change in selectively since the isotherms and differential adsorption enthalpy overlaps. This makes them very cost-effective regarding the energy required for regeneration [22]. The third round represents the amount of CO_2 that is physisorbed on the surface, which can be removed by vacuum only, is five times less than the chemisorbed CO_2 [22]. The enthalpy and chemical potential of adsorption become less negative as the adsorption proceeds at higher temperatures due to weaker binding at the surface, and this leads to increased entropy. The explained that the CO_2 adsorption on mmen-Mg_2(dobpdc) falls into three regions: strong chemisorption, intermediate chemisorption, and weak physisorption. Most of the CO_2 is taken by the chemisorption, in which most of the active sites being occupied. Understanding the physical chemistry associated with the adsorption of CO_2 on these materials helps in enhancing these materials for industrial processes. Although increased adsorption towards CO_2 was observed in mmen-Mg_2(dobpdc) in the presence of water, further study for M_2(dobpdc) stability and adsorption need to be further investigated under humid atmospheric conditions [24] [25].

2. Conclusions:

Direct air capture is an interesting technology that has attracted significant attention in recent years and perhaps has to be taken more into consideration. The major appeal of this technology is its flexibility of location and the significantly low content of contaminants such as NO_x and SOx that it needs to deal with. Removing CO_2 using this technology is mostly held back today, however, by the expected cost of regeneration (i.e., high operating costs) and its inherent low yield (i.e., high capital costs) compared to traditional approaches. The cost of DAC can be greatly reduced by using solid adsorbents [20] that offer significantly higher working capacities around the partial operating pressures of carbon dioxide in the air with small swings of pressure or temperature. The functionalization of solid adsorbents with amines in recent efforts has shown to be correctly pointing in this direction [10][4]. MOFs impregnated with amines have shown great working capacities to adsorb CO_2 under dilute concentrations due to the cooperative insertion of CO_2 into the active metal sites causing S-shaped isotherms [4]. These materials also showed high reversibility by only having small temperature changes applied [4][10][17], while there has been much research effort towards improving the adsorption working capacity of MOFs, which makes DAC more of an attractive approach, there is still much to be done for the commercial competitiveness of those materials to show promise. Future efforts must be more significantly focused on the achievement of cheaper manufacturing and improved stability.

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