A Comprehensive Review on the Potential Use of Metal-Organic Frameworks for Carbon Capture Applications

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Received November 28, 2024
Accepted May 14, 2025
Electronic access May 31, 2025

With climate change occurring at exponential and unprecedented speeds, the increase in carbon emissions over the last few decades has been extremely detrimental to our Earth and its environment. The global average temperature is reaching an all-time high, and action must be taken to tackle such issues before the irreversible effects start to take a toll on humanity. Thus, Carbon Capture and Sequestration (CCS) methods were innovated to mitigate the amount of carbon production in fuel and other industries. In recent years, the use of Metal-Organic Frameworks (MOFs) has been further developed and proven effective in carbon dioxide separation and storage, potentially opening a new door for environmental scientists. However, after much research, MOFs are still lacking maturity for industrial establishment, which is the major issue that this paper is addressing. In this comprehensive review, we have documented the highest-performing MOFs in the current industry, effective MOF optimization/chemical tuning, and possible large-scale implementations for this new type of porous structure. MOFs such as the HKUST-1 with its efficient open-metal sites, and the Lewis-Basic Site containing IRMOF-3 as well as numerous amounts of others are deeply investigated. Furthermore, a particular emphasis on the methods of industrial applications is discussed.

Introduction

Our globe is currently facing significant challenges, with climate change being the major threat and cause of such an extreme environment. This past decade, our earth has had record high temperatures that have never been seen before in the last 1000 years, and the rapidly increasing carbon footprint is to blame. If the current situation continues in the near future, global warming is likely to reach 1.5 C by 2030 to 2052. [1] With the constant need for energy to power our cities, cars, factories, and more, humans have been overexploiting and even abusing energy sources to an irreversible point. Although inherently this does not appear as such an issue, there has been no sustainable and efficient energy source implemented yet, causing most industries to rely on fossil fuels. Made from fossilized plants and animal remnants, this source of energy is one of the cheapest yet most damaging and pollutant-emitting fuel sources in use. It is estimated that 89% of carbon emissions have originated from fossil fuels, and such numbers are only going to get worse [2]. From producing carbon dioxide as a byproduct to releasing tons of ash into the air, fossil fuels have been one of the largest contributors to the global warming scheme. The burning of fossil fuels remains the leading source of all carbon emissions and can be found responsible for the enhanced greenhouse effect, thus leading to climate change. This irrevocable effect has changed the terrain of numerous forests, killed millions of marine animals, and has been causing our ice caps to melt, potentially flooding our lands. With the ozone layer collapsing, ocean water pH rising at rapid speeds, and the average temperature of our earth increasing, the production of carbon dioxide via fossil fuels must be stopped. However, studies have shown that a realistic phase-out of fossil fuel reliance is harder to implement than described, and would take at least 1-2 decades before a visible decrease in temperature [3]. On top of that, this was hypothetically calculated under the assumption that another viable energy source is actually founded, and is able to efficaciously power all of humanitys needs. Therefore, the complete abolishment of fossil fuels is not exactly feasible in our current society and needs a new alternative. In the recent decade or so, scientists have innovated a new pathway for removing carbon dioxide from the atmosphere, and that is to capture it at the source. Carbon capture technology has been under experimentation since 1972 [4], yet it has never been introduced at an industrial scale for practical usage. By filtering the gas produced by fossil fuel emissions and isolating the carbon dioxide, researchers have been able to find various ways to transport and store this harmful gas. CO2 is commonly injected into underground oil reserves and acts as a compound that assists with oil recovery. Even though most techniques have failed to be effective at a larger scale, one technique that practices adsorption has been at the center of discussion recently. This potential-bearing, nanomaterial-made substance is known as Metal-Organic Frameworks (MOFs), the future of carbon capture. The first permanent porous lab-created MOF was synthesized in 1995, by Professor Omar O. Yaghi and his co-authors [5]. Consisting of metals/metal clusters and organic linkers, this minuscule material brings many advantages such

as versatility, high porosity, chemical tunability, and compatibility. All of these traits among many more are what provide metal-organic frameworks its large potential. When connected by many other ligands and metal particles, MOFs have been specifically synthesized for carbon capture and have proven to be successful numerous times. Unfortunately, MOF technology still contains lots of restrictions and requires extensive amounts of research before being implemented into society. For future applications of metal-organic frameworks, recording current research and attempts is an extremely important step in innovation. As a result, this meticulously documented review article summarizes carbon capture and sequestration methods, the current status of MOF technology as well as possible practices. To begin, we start by going in-depth on carbon capture chemistry, which is necessary for background knowledge. To follow up, a section detailing all of the common MOF modification techniques for carbon efficiency is encapsulated. Moving on, we will propose multiple implementation plans for MOFs to get industrialized and used to save our globe from carbon dioxide. Last but not least, we will highlight challenges that may be faced on the way and in the near future of MOFs.

Method

Several procedures were followed to maintain a high quality literature review process, with the combination of an eligibility criteria, search strategy, and a clear scope. In terms of the inclusion of a referenced paper, we required the source to stem from a peer-reviewed journal with a significant impact factor, while articles from predatory or non-reputable journals are excluded. Research containing empirical data, or experimental results yielded by respective professors were also looked highly favorably upon. These scholarly articles were all retrieved through Google Scholar, as well as PubMed, which are two trustworthy and effective databases that collaborated well with our search strategy. Most of the papers originated from scientific journals such as but not limited to: Nature, Energy & Environmental Science, and Journal of Material Chemistry. Our search strategy mainly consists of using keywords combined with boolean operations and filters to efficiently retrieve high quality scholarly papers. This comprehensive search utilized a wide range of key terms, including: MOFs, carbon capture, synthesis, adsorption, and environment. With the help of boolean operations (and, or, not), these terms were able to be combined for a more effective search. On the contrary, filters were placed to limit the time period of review articles, and also put in place to remove unwanted paper formats such as opinion pieces, and non-peer-reviewed articles. The recommended time period for papers regarding MOFs and their synthesis is any paper between the year 2000 and 2025, while historical articles range from 1990s to present day.

Carbon Capture

Intro to CCS

Since its debut on the global stage in March of 1992 during the First International Conference on Carbon Dioxide Removal[6], Carbon Capture and Sequestration (also known as CCS) has been a crucial stepping stone in saving our planet from emissions. Derived from its name, CCS is a technology which allows polluting industries to remove, filter, and store the toxic carbon dioxide gas produced. This groundbreaking technique allows our society to still thrive on high emission gasses, while at the same time being able to mitigate our carbon footprint. As a result, CCS provides a way for clean energy emission without doing a complete phase-out of fossil fuels or any other unsustainable energy sources. After such an innovation was shared, many contributing nations have started collaborating on research, such that there are now 22 global CCS demo projects currently undergoing testing[7]. With the United States of America in the lead holding 7 projects, many other more economically developed countries (MEDCs) such as China have also established their own CCS demo projects.

In a simple picture, Carbon Capture essentially works by separating CO2 from the harmless gasses emitted when generating energy by burning fuels such as coal. Moving on, Carbon Dioxide (or any solution that carries it) is then extracted, compressed, and transported to a deep underground oil/gas reserve. Lastly, it will be injected into the geological formation and left there for benefits to the reserve, such as oil recovery[8]. This allows oil or gas industries to access such fields while also eliminating pollutants, making it auspicious for both sides. However, there are still numerous limitations to CCS technologies which will be dissected deeply in section 4. The following subsections will go through in further depth the different techniques used to capture CO2 and discuss its advantages, disadvantages, and plausibility.

Carbon Dioxide Absorption

Being the most researched and advantageous technique, especially during post-combustion capture, chemical absorption is one of the most commercialized CO2 capture methods[9]. By utilizing chemicals such as K2CO3 and Na2CO3, this type of capture results in highly effective CO2 absorption efficiency of 80100%, adaptability to low-pressure conditions, and capability to produce high-purity CO2 (up to 99%)[10]. Moreover, absorption can be practiced in various ways including but not limited to using: amine based chemicals, Alkaline Solutions, Ionic Liquids, and Ammonia (NH3). However, amine-based chemicals are still the preferred absorbent because of their high reactivity, selectivity, and regeneration rates. This simple process takes around two steps to complete in what is known as the Two-Phase System, one of the most reliable absorption techniques. In the first phase of absorption, CO2-containing gas (such as any factory emissions) is sent into a packed bed absorber column, where it will react with chemical solvents. This will result

in an intermediate compound, which essentially is a CO2-rich chemical absorbent. This compound will then be transferred into a stripper where heat is applied, leading the absorbent to release CO2 and regenerate the solvent. This phase is known as the Regeneration phase and it provides industries with a way to reproduce the solvent for more absorption in the future [11].

As mentioned previously, one of the most common practices of absorption is to utilize amine based chemicals because of its high percentage of yields. Derived from ammonia (NH3), amines are extremely similar other than the fact that one or more hydrogen molecules has been replaced by an organic compound such as the re-occurring nitrogen. By reacting such chemicals with carbon dioxide gas, the amines take the role of a weak alkaline solution, neutralizing the acidic nature of CO2. This forms carbamate (R-NHCOO), which then forms bicarbonate once it reacts with the moisture of the air. [12]. Carbon Dioxide is then filtered and removed via the Two-Phase System, and the amine based chemicals are regenerated for another round. Although they are still currently under investigation, Amine compounds such as Ethanolamine (MEA), Diethanolamine (DEA), and Methyldiethanolamine (MFEA), have been extremely successful in many different projects, resulting in excellent results. However, absorption also comes with many obstacles and challenges that must be tackled before industrial implementation.

Studies have shown that scaling this system up to 25-30 billion tons of CO2 would prove to be a massive barrier because of the demanding energy and heat requirements. It is estimated that heat requirements reached a high of 4200 MJ/ton CO2 captured for a 400 MW power station [13]. Unfortunately, due to the current carbon emission volume, such limitations render this process ineffective and unable to be easily applied. On top of that, the large volume of absorbents needed may even prove to be a safety hazard for our environment. As a consequence, outlets or wash circuits are a must-add when addressing the degradation products. To conclude, although amine-based chemicals have shown the best yields data-wise, it is still under research and is facing too many restrictions to be commercialized in the current time frame.

Membrane Capture

In this environmentally friendly and efficient technique of Carbon Capture, scientists manipulate different chemical membranes to separate CO2 from non-polluting gasses. This method comes with several advantages including a high packing density, versatility in current applications, and a high separation efficiency that is still undergoing experimentation. Membranes can vary from many different structures yet must follow two strict requirements to maximize carbon capture effectiveness. Each three of these membrane classes: polymeric membranes, inorganic membranes, and mixed matrix membranes should possess high permeability as well as high selectivity if put to the test [14]. Although this process has many different methods of capture, membrane separation techniques generally work via gas permeation. As pollutant/excess gas containing CO2 is emitted, a membrane will be set up so that the gas mixture passes through it. However, the membrane would selectively only allow Carbon Dioxide to pass through due to factors such as membrane pore size, gas molecule size, or kinetic diameter. This generates a net which slows or stops non-toxic gasses from mixing with the CO2, allowing it to be captured, compressed, and stored away effectively. Operational parameters such as pressure, heat, or specific membrane properties also can contribute to yield efficiency.

Polymeric membranes have always been the center of attention when discussing possible membrane classes to implement because of their recently innovated enhanced transport properties [15]. On the other hand, inorganic membranes display exceptional separation performance, making them another great option for the near future. Nevertheless, one other class of membranes that has been standing out in the recent decade is the mixed-matrix membranes (MMMs). This newly developed membrane combines the two advantages of polymeric and inorganic membranes mentioned above to create a superior material that is fused with potential. Because of its different priorities, the morphology of MMMs should be made distinct to ensure preferential gas transport is through the inorganic phase rather than the polymer phase. To further add on, MMMs can also be classified into three different types: liquidpolymer, solidpolymer, and solid-liquid polymer. The Solid-Polymer MMMs class has caught the attention of numerous scientists in the past years, and many companies have started investigating the different uses of solid fillers. From traditional fillers such as zeolites to novel approaches such as Metal-Organic Frameworks, there has been a proven spike in gas permeability of up to 7 times [16]. With the evident efficiency of Mixed-Matrix Membranes (especially Solid-Polymer MMMs), there is no doubt that membrane capture technology will very likely be implemented shortly. Nonetheless, great technologies also bear many challenges such as sustainability, stability, and capacity limitations. At this current time, MMMs, polymeric and inorganic membranes are still quite unstable for large-scale applications but have lots of potential for a massive project. Many of the current issues can be taken forward with more experimentation, and many studies believe that it will be a feasible option in a short amount of time.

Carbon Dioxide Adsorption

The process of adsorption via porous materials is a relatively new technique in the CCS field yet brings one of the highest promises compared to other paths. By utilizing substances such as zeolites, carbon-based adsorbents, metal oxides, and supported amines, adsorption provides a sustainable, energy-efficient, and rapid way to capture and store carbon dioxide. Moreover, another type of adsorbent known as metal-organic frameworks (which were briefly discussed in the introduction)

has been taking the CCS community by storm with its vast development potential. Adsorption is completed with a simple process, where gas (containing CO2 in this scenario), comes in contact with any of the above adsorbents which act like a filter. These substances are either specifically customized or naturally found to have characteristics that adhere to CO2, and as a result, would let the non-toxic gasses pass through, yet contain CO2 on their surface, effectively separating them[17]. Not only is this technique straightforward, it also yields a higher purity of CO2, requires less heat energy to operate, and bears high future development compared to absorption and other approaches.

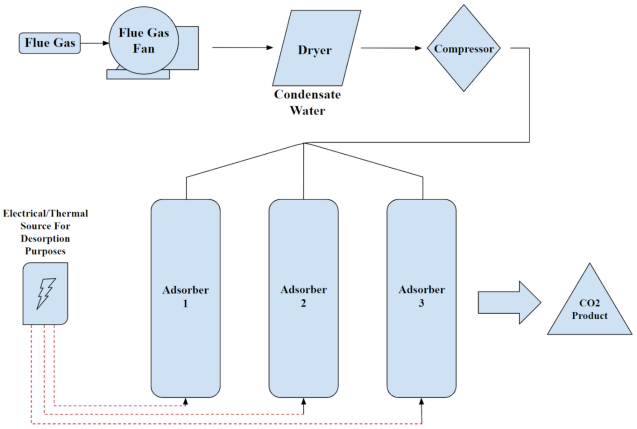

Fig. 1 A schematic diagram of a basic CO2 adsorption process adapted from Songetal.,2019

The most traditional and common substance used in adsorption processes is known as zeolites, which have high carbon dioxide selectivity, stability as well as a low cost.[18]. Being first coined by the Swedish mineralogist Axel Fredrik Cronstedt in 1756[19], this alkali-heavy substance has a unique porous structure that uses its mesopore surface to effectively adsorb CO2. As zeolites are a type of mineral substance, they must be synthesized before being used in laboratory work as naturally found zeolites prove ineffective in terms of CO2 yield. First created in 1950, the main commercial zeolite that has been proven to be functional multiple times is Zeolite 13X, along with its other synthesized variants[20]. By implementing a process known as hydrothermal treatment, zeolite 13X can become custom variants such as 13X-B, 13X-K, and the commercially available 13X-C. Many of these, such as the 13X-K, have been synthesized with substances that contain a specific pore volume, BET diameter, and other factors that have been created to target carbon dioxide capture. To further add on, scientists have also been experimenting with 3D-printed zeolite monoliths and amine-grafted zeolites, innovating multiple promising products. However, CO2 adsorption does not reach its full potential without the use of Metal-Organic Frameworks.

Table 1 A Comparison of Current Existing CO2 Capture Technologies

Technology	Advantages	Disadvantages	Maturity
Amine Absorption	High CO2 intake, consistent effectiveness, suitable for large scale absorption.	Extremely high energy demand, requires a large volume for work, expensive and costly, unable to be upscaled any further.	Commercially implemented and heavily researched.
Membrane Capture	Low energy consumption, compact design, environmentally friendly.	Limited selectivity, unstable at a large scale implementation, capacity constraints on membrane.	Currently ongoing research at an early stage.
Zeolite Adsorption	High CO2 selectivity, energy efficient, effective and rapid adsorption.	Limited stability, highly costly, ineffective in moist environments.	Commercially implemented in small scaled separation.
MOF Adsorption	High selectivity and intake rate, tunable mechanics, low energy requirement.	High synthesis cost, relatively new technology.	Currently ongoing research at an early stage.

Metal-Organic Frameworks (MOFs)

An Introduction to MOFs

Originally discovered in 1965 from chemical waste, lab-synthesized MOFs were not truly innovated until the 1990s by Professor Omar M. Yaghi[21]. As mentioned briefly above, MOFs are organic compounds formed by metal ions or clusters that harmonize with organic ligands to form dimensional structures. They are a unique class of crystalline porous structures and have been used in multiple fields outside of CCS such as catalysis, enzyme immobilization, drug delivery, water capture, and sensing. With that said, MOFs are commonly classified into 3 different classes (measured by pore size), and that are microporous, mesoporous, and macroporous MOFs[22]. Each of these types is classed from the smallest size to the largest, and their characteristics can heavily influence its performance in CCS. However, to be even more precise, MOFs are also split into 5 more detailed classes, which include Isoreticular MOFs, Zeolitic Imidazolate Frameworks, Porous Coordination Networks, Porous Coordination Polymers, University of Oslo (UiO) MOFs. Each of the corresponding groups are simply just different MOFs binding with specific materials such as metal oxides, quantum dots, or carbon compounds. Although these areas are pretty crucial for the classification of MOFs, from a CCS perspective, the pore diameter classes are more impactful

when discussing carbon dioxide yield rate and more. In recent years, numerous MOFs have been synthesized, and many of the commonly used carbon capture MOFs include: MOF-2, MOF-5, ZIF-8, PCN-11, and more, which will all be dissected in later sections.

MOFs and their advantages

As mentioned briefly above, Metal-Organic Frameworks are a relatively new technique in the CCS industry, yet is one that have the best chance of practicality in the near future. With many different superior characteristics such as high CO2 yield, predictable structures, and high compatibility, MOFs are a one-of-a-kind material that must be precisely synthesized. One of its main advantages comes from its chemical tunability and how such nanomaterials can be customized so that they easily uptake CO2. In addition, its high porosity and surface area allow it to adsorb CO2 better than any other material, beating out zeolites, membranes, and absorption amines. Over the past years, many scientists have begun looking into metal-organic frameworks and have developed multiple working prototypes such as MOF-5 [Zn4O (benzenedicarboxylate)3] and ZIF-8 [Zn(methyl imidazolate)2][23].

MOF Synthesis

Synthesis describes the process in which Metal-Organic Frameworks are created, and this varies through many different techniques that each have their advantages and disadvantages. MOF synthesis is a cornerstone in CCS-related MOF technologies because this is the phase in which a large percentage of chemical tuning takes place. This makes this process undeniably the most important step during MOF implementation. In this following subsection, we will go over the 5 main techniques used for synthesis and delve into the chemistry behind each procedure

Microwave-Assisted Method

Discovered in 1946 by P.L. Spencer at the Raytheon Corporation when a chocolate bar was accidentally melted in his pocket during a microwave radar application experiment, microwave heating has been an approach used to commonly heat food and can be found in many modern-day households[24]. Other than that, microwave-assisted synthesis has been mainly used in pharmaceutical industries but has slowly been introduced to CCS as it bears the potential to prepare nanoporous inorganic materials. By using a microwave, this method of MOF synthesis is one of the most efficient and fast-paced ways of synthesizing a solution. This approach is extremely effective and has a high chance of success because the microwave itself guarantees a uniform spread across the solution, shortening the cycle of synthesis.

The Microwave Assisted Method (MWAM) functions by utilizing microwaves to activate and therefore synthesize MOFs upon absorption of the MW. In the first phase of MWAM, MOF activation is needed, which essentially describes the process in which unwanted solvents found in the porous structures as well as open-metal sites (OMSs) are eliminated. The three main mechanisms behind MW MOF activation are dielectric polarization, ionic conduction, and dipolar rotation. All of these orbit around the same principle, and that is to use the irradiation from microwaves to rid the trapped molecules commonly found in pores. Dielectric polarization is the interaction between the solution and electric fields of the microwaves, and Ionic conduction is the movement of ions under the influence of microwaves. Lastly, the most important mechanism is dipolar rotation, where the oscillating electric field of the microwaves comes in contact with polar molecules in the solution. This excites the dipoles and dielectric solids in such particles, causing rapid rotation, thus increasing the thermal energy[25]. This heat energy is then used for the activation procedure and effectively eliminates all excess solvents. In comparison to traditional MOF activation practices which are known for damaging the MOF frameworks with their high temperatures, MW Activation is a much safer yet similarly efficient method. Moving forward, the rapid and volumetric heating of microwaves speeds up the synthesis process and eventually leads to the creation of MOFs.

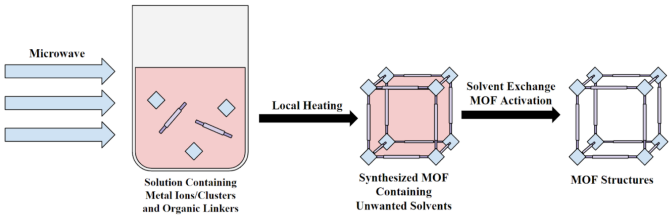

Fig. 2 Microwave-Assisted Solvothermal Synthesis of MOF Structures[26]

Being one of the first MOFs synthesized via the MWAM, Cr-MIL-100 was produced under a temperature of 220 degrees Celsius for 4 hours[27]. However, the method was later revised and improved to last for an 1-hour duration only. The following MOFs were all successfully synthesized using the MWAM and have shown some promising characteristics. To start, the well-known MOF-199 (HKUST-1) ([Cu3(BTC)2] [BTC = 1,3,5-benzenetricarbox-ylate]) was created using microwaves and is known for its high chemical stability and pore volume. It was synthesized within 30 minutes and resulted in a 77% yield along with large homogenous crystals. Such volume of crystals was recorded because of MOF-199s extensive crystallization time, which even led to the occurrence of Ostwald Ripening. Unfortunately, the MWAM resulted in less hydration compared to the solvothermal-produced MOF-199 but is still a successfully synthesized project. Other MOFs that fall under the MWAM category include but are not limited to: UiO-66, Crystalline Zr-MOF, and Transition Metal MOFs. All of these MOFs showed great crystalline structures, encouraging absorption capacity and yield rates when interacting with carbon dioxide.

Electrochemical Method

Different from the MWAM, the electrochemical method (ECM) utilizes electricity to synthesize MOFs from chemical solutions. The main form of ECM that will be discussed here is anodic dissolution, as it is the most commonly used and effective technique. Pioneered by Mueller and colleagues, this method comes with many advantages such as precise control over MOF characteristics as well as regulation[28]. All chemical tuning of the electrochemical solution is able to happen in real time and this is important as it can help scientists easily adjust and track the synthesis process. On top of that, because no metal salts are involved during the process of anodic dissolution, the final product is not influenced by metal precursors, resulting in extremely consistent MOF features[29]. During Anodic Dissolution (or Anodic Electrosynthesis), a current, which in this case is an anodic potential, is applied to the metal electrodes inside of the solution. As a result, the metal oxidizes and dissolves into the solution and forms metal ions that will later be used in MOF synthesis. Near the electrode surface, the previously created ions react with the organic ligands and form a thin layer of MOFs. Although method deposition on the cathode is avoided through the use of protic solvents, hydrogen (H2) is created in the process[30]. After synthesis, the MOFs go through a phase similar to MOF activation where unwanted solvents are eliminated through heat and vacuum treatment. This concludes the basis of the electrochemical method via anodic dissolution.

The first synthesized MOF through the ECM is HKUST-1 (MOF-199) which was mentioned in the microwave-assisted method sector of this paper because it can also be created by microwaves. This was patented and reported by BASF in 2005 and consists of using bulk copper (Cu) plates as anodes in an electrochemical cell[28]. On the other hand, the solvent used was H3BTC (Trimesic Acid) dissolved in methanol which, along with the copper anode, experienced a voltage of 12-19 V and a currency of 1.3 A for a duration of 150 minutes. This was a standard anodic electrosynthesis procedure and led to the formation of octahedral crystals (averaging 0.55 m in size) that could be found in a dark blue powder after MOF activation. It contained a large surface area of 1820 m/g, proving this project to be successful in regions of CO2 yield and the quality of MOFs. Because of this, scientists have been continually synthesizing MOFs through this method and to this day have produced many effective MOFs such as the ZIF-8, Al-MIL-100, Al-MIL-53, and Al-MIL-53-NH2, many of which are famous in the CCS world[30].

Solvothermal Method

One of the simplest and most convenient approaches of synthesis, the creation of MOFs via the solvothermal method (STM or ST) is a consistently seen way of producing MOFs in the field of CCS. Being the undisputed traditional style of MOF synthesis, the solvothermal method comes with many advantages as well as disadvantages. As it only requires primitive equipment (which will be further explained later on), the solvothermal/hydrothermal method can be easily scaled to a high degree of production, such that big industries may be able to implement it. To further add, most of the successful ST-created MOFs all contain three characteristics, and that is high crystallinity, purity, and versatility. STM is able to synthesize a wide range of different MOFs because of its ability to adapt to any organic linker/metal cluster and oftentimes guarantee great yield success. Versatility can also be seen in its solvents as STM can incorporate a large variety of chemicals that can synergize well with the other necessary compounds. On the contrary, the simplicity of the STM also gives a major downside. The two main disadvantages of this method are the extremely long operational time (up to 4 days) combined with the ability to regulate the crystal growth[31]. These are devastating factors that significantly impact the quality of MOFs and should be tackled immediately.

Innovated in 1995, when the worlds first MOF was synthesized by Professor Omar M. Yaghi, hydrothermal/solvothermal methods are the earliest recorded approaches to MOF synthesis[32]. On a small laboratory scale, ST synthesis utilizes electric heating in apparatus such as vials or NMR tubes. Inside, metal clusters/ions as well as organic ligands are dissolved in solvents such as water or Dimethylformamide HCON(CH3)2 (DMF). A long heating process between 12-72 hours with vastly contrasting temperatures of 80-220 degrees Celsius is then applied to such a solution and allows the compounds to commence in self-assembly. Once complete, the newly synthesized MOFs go through solvent exchange and washing via heat and vacuum treatment, removing all unwanted solvents stuck in between the porous structures. The MOF is now synthesized and ready for CCS and/or other uses.

Numerous MOFs were created via the STM and this includes the MOF-5, IRMOF-3, [Cu2(hfbba)2(3-mepy)2] (Cu-F-MOF-4B), as well as MOF-74[33]. Being one of the most effective MOFs at carbon capture, the MOF-5 was initially synthesized using a diffusion method which unfortunately resulted in a low yield. The method was then adjusted to the high-yielding solvothermal method that involves heating Zn(NO3)24H2O and H2BDC in the solvent DEF at 105C[31]. Similarly, the IRMOF-3, which contains Zn4O clusters linked by BDC-NH2 was synthesized in DMF/DEF at 90C for 24 hours, resulting in a highly effective MOF. Most STM-produced MOFs are synthesized in similar ways, providing scientists with an easy and solid method of MOF synthesis.

Sonochemical Method

By utilizing powerful ultrasound (20 kHz10 MHz), sonochemical synthesis (SC) is a recent advancement in MOF technology and provides one of the most elegant approaches to the creation of MOFs. In order to generate energy for synthesis, SCM operates through acoustic cavitation, which essentially is the growth

and collapse of pre-existing microbubbles under the influence of ultrasound[34]. This unique process can generate thermal energy of up to 5000C and pressures up to 1000 atm in an extremely small and localized area, allowing for an extremely rapid synthesis duration. Other than its efficient speed, the use of ultrasound as a source of energy is also much more simple in comparison with traditional sources of energy. Moreover, sonochemical synthesis gives scientists the opportunity to have precise control over crystal size and is very effective during phase-selective synthesis.

To test this method, various traditional MOFs were synthesized using ultrasound, including MOF-5, HKUST-1 (or MOF-199), and MOF-177. MOF-5 was created under a time of 30 minutes and involved using 1-methyl-2-pyrrolidone (NMP) in a horn-type reactor, which successfully synthesized high-quality crystals. With their size being around 525 m, sonochemically synthesized MOF-5 demonstrated higher yield rates compared to conventional methods such as solvothermal. Similar results can also be seen in MOF-177 as it achieved a yield rate of 95.6% in just under 40 minutes[35]. By utilizing the tritopic organic linker BTB and the solvent NMP (which seems to synergize well with ultrasound), high-quality crystals sized around 510 m were synthesized and a large BET surface area of 4898 m/g was also created. This allowed MOF-177 to be exceptionally efficient during CO2 adsorption as it recorded an all-time high of 1315 mg/g at 30 bar and 298 K, a decently high intake rate. Although the sonochemical method should be further investigated and developed before being implemented, it provides one of the fastest synthesis speeds as well as yield rates compared to any other method.

Table 2 Comparison of referenced MOFs

MOF Name	Synthesis	Advantages	Disadvantages	CO2 Capture Rate
MOF-5	Solvothermal & Sonochemical Method	High surface area and porosity.Effective for CO adsorption.	Long synthesis time (solvothermal)	812 mg/g at 298 K, 40 bar[36]
ZIF-8	Electrochemical Method	High chemical and thermal stability. Large pore volume.	Susceptible to framework collapse under pressure	547 mg/g at 298 K, 40 bar[37]
HKUST-1 (MOF-199)	Microwave, Sonochemical, & Electrochemical Method	High chemical stability. Large homogeneous crystals. Fast synthesis (30 min with MWAM).	Decrease in hydration with microwave synthesis	183 mg/g (4.16 mmol/g) at 298 K, 1 bar[38]
UiO-66	Microwave Method	Exceptional thermal and chemical stability.High crystallinity.	Lower yield with microwave assisted method compared to solvothermal	97 mg/g (2.2 mmol/g) at 298 K, 1 bar[39]
MOF-177	Sonochemical Method	Extremely high surface area. Fast synthesis time. High yield (95.6%).	Requires specialized ultrasound equipment for effective synthesis	1315 mg/g at 298K, 30 bar

MOF Adsorption Chemistry

Constructed by joining metal clusters (otherwise known as secondary building units or SBUs) and organic linkers, metal-organic frameworks utilize reticular synthesis to create open crystalline frameworks[40]. These ultra-high surface area structures are the backbone behind gas adsorption, and their porous characteristics are significant and impactful factors on CCS. A MOF's ability to capture carbon essentially relies on its adsorption mechanism, whether that be physical or chemical. On the physical side of the spectrum, a process known as physisorption takes place, and MOFs rely on their pores to capture and trap CO2 molecules through weak Van Der Waal electric forces[41]. This type of adsorption is not as powerful as pure chemical bonding and therefore is reversible. On the contrary, chemical adsorption utilizes its active sites (explained more in detail in the following section) to interact with CO2 through covalent or ionic bonding - although ionic is less seen. By sharing electrons, chemisorption allows the MOF to capture CO2 much more effectively, resulting in higher selectivity rates and capacity. Moreover, functional groups created through chemical tuning and synthesis (e.g., amines, and hydroxyls) can also chemically interact with CO2 and can form bonds relatively easily. However, chemical adsorption requires 40 to 400 kJ mol 1 (reaction heat) to operate, whereas physisorption only needs 1040 kJ mol 1[42], meaning its energy requirements are much larger. As this study provides only a brief overview of MOF chemistry, a more in-depth coverage of molecular modeling and adsorption mechanisms lies beyond its intended scope. For an in depth level of chemistry, please refer to a study conducted by Hiroyasu Furukawa, The Chemistry and Applications of Metal-Organic Frameworks[43]. All in all, chemisorption and physisorption both carry their own unique advantages and disadvantages and are suitable for different types of MOFs in different circumstances.

Metal-Organic Framework Optimization

Introduction

One advantage of MOFs is their strong chemical tunability and their many customizable variations that can be made during or post-synthesis. This allows lots of its factors and characteristics to be optimized for CO2 yield/adsorption. This section will dive into multiple techniques for MOF customization and its many benefits.

Open Metal Sites (OMSs)

Open Metal Sites, also known as Coordinatively Unsaturated Metal Sites, are usually located on a MOFs multimetallic secondary building units and are one of the crucial components to improving CO2 capture rates. The first report on OMS and its linking to gas adsorption was proposed by Professor Yaghi, and was first used for hydrogen uptake[44]. Being one of the strongest binding sites in a MOF, the activation of OMSs is a crucial factor in applications like catalysis sensing and gas sorption. However, the most impacted region is undeniably in the process of gas separation, hence why OMSs are so significant during CCS. On top of that, OMSs also bring more advantages to MOFs such as interactions with olefins, producing metal-olefin complexes, and can even assist in post-functionalization. The interaction between CO2 molecules with OMSs is through a process known as lone pair donation, leading to a strong yet mostly physisorption interaction. This helps in both efficient CO2 capture and easier regeneration of the adsorbent. Although HKUST-1 was one of the earliest examples of OMS activation, MOF-74 shows the OMS effect especially well because of its extremely high CO2 adsorption rates in dry conditions, as well as its efficient selectivity. With an open Mg+ (manganese) site, the OMS on MOF-74-Mg (CPO-27-Mg, Mg2(dobdc)) is called upon via thermal activation and allows CO2 to preferentially bind onto it. Differing from the predicted bond angle of 180 degrees, CO2 bonds at a 160.5-degree angle because of its end-on orientation, helping the molecule gain more flexibility. This factor, along with the benefit of OMSs allows MOF-74 to become a benchmark MOF in the CCS field. Moving on, a MOF that was previously mentioned above, HKUST-1, also reflects the impact of OMSs in various ways including high yield percentage and uptake efficiency. By containing Cu2+ binding sites that become available after thermal activation, HKUST-1 hosts multiple CO2 adsorption sites that by neutron diffraction and PXRD studies attract carbon dioxide more easily due to electrostatic forces[45]. In 2005, an uptake speed of about 10 mmol g1 at 42 bar was recorded for HKUST-1, which was way above average and displays the significance of open-metal sites[46].

Lewis Basic Sites (LBSs)

Other than OMSs, organic linkers containing Lewis Basic Sites (LBSs) can highly impact carbon adsorption in MOFs. These openly accessible sites are extremely vital for developing reactive heterogeneous catalysts as well as enhancing selective CO sorption via acid-base interactions. Inspired by the successful aqueous amine solutions[47], LBSs were traditionally synthesized through pure chance, and an artificial and intentional design was not created until later. In recent studies, scientists were able to incorporate Lewis Basic Sites into MOFs during synthesis by fusing multitopic functional bridging ligands and metal ions[48]. On top of that, LBSs also carry many useful advantages such as a fully customizable geometry of MOF channels, synergy with OMSs, and decent performance in humid conditions (a common weakness in MOFs).

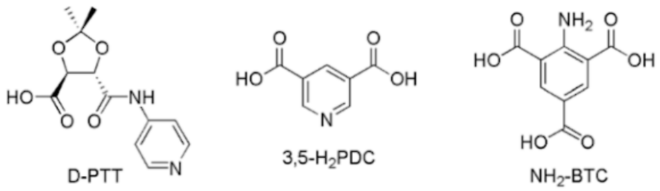

Fig. 3 Three notable Carboxy-based Lewis Basic Ligands and their structures[49]

One common example of a Lewis Basic Site containing MOF is the IRMOF-3, an efficient and highly effective MOF in the CCS field. Sharing a similar structure and being isoreticular to the renowned MOF-5, the IRMOF-3 utilizes 2-aminoterephthalic acid (NH2-H2BDC) as the organic linker, with the amine groups acting as the Lewis Basic Site. This strongly enhances its adsorption abilities and strengthens its interaction with CO2. During a test at 298 K, IRMOF-3 exhibited a CO2 uptake capacity of approximately 14.7 mmol g over a pressure range up to 12.3 bar, which is +0.7 than that of MOF-5[50]. This superior result was due to the improved binding affinities provided by the Lewis Basic Sites. Another MOF that is commonly discussed is IRMOF-74-III-CH2NH2, which contains alkylamine functional groups in its organic ligands that allow for covalent bonding with CO2. Through its bonding process, it creates carbamic acids and ammonium carbamates, and this is all facilitated via the LBS. However, what makes this MOF unique is that scientists have managed to add two alkylamines per organic linker, resulting in a 100% increase in adsorption rate[51]. This proves that many MOFs that contain alkylamine LBSs can all be propelled twofold through the smart use of Lewis Basic Sites.

Pore Size

MOFs are a porous structure, and this is a large reason why they have such a vast surface area that allows gas adsorption. The size or diameter of the pores on a MOF is one of, if not the most crucial element in increasing carbon dioxide adsorption yield, as separation relies on these holes to trap the gas molecules. Porous structures are classified into these 3 categories, which include macropores, mesopores, and micropores, each sorted through diameter size. Starting from the largest, their sizes are as follows: macropores ¿ 50 nm, mesopores in the range of 2.050 nm, and micropores ¡ 2.0 nm[52]. Extensive studies have shown that micropores, in general, are more beneficial for carbon capture, and that when more restrictive pores result from interpenetration, the binding energy of CO2 increases. While larger pores may be more useful in gas transportation and diffusion, smaller

diameters bring many benefits such as stability and improved selectivity that must be kept in mind during large-scale applications[53]. Synthesized via the solvothermal method (STM), MOF Co(pz)(BPTC)0.5dmfEtOH4H2O has a microporous structure and has shown to have effective carbon dioxide uptake during testing. The total pore volume on this MOF is 0.95 cm3 g -1, showing great synergy with the crystalline structure, as well as displaying solvent-accessible volume. On the other hand, a similar MOF known as Co(bipy)- (BPTC)0.5solvent contains a much larger total pore volume (1.31cm3 g -1) yet has lower adsorption rates compared to MOF Co(pz)(BPTC)0.5dmfEtOH4H2O. At 273 K, Co(pz)(BPTC)0.5dmfEtOH4H2O has the ability to adsorb 89cm3 g1 and possesses a high affinity for CO2 molecules[54] which is 34cm3 g1 more than the second MOF. The results indicate that the total surface area of a MOF does not impact the adsorption rates as much as the pore size and that the most optimal slit pore size for CO2, H2, and CH4 uptake would be 6 (Angstroms) as it has stronger interactions with gas.

Table 3 A Comparison of Surface Area and Their Effects on CO2 Uptake

	MOF Co(pz)(BPTC)0.5dmfEtOH4H2O[54]	MOF Co(bipy)-(BPTC)0.5solvent[54]
Pore Volume (cm^3g^{-1})	0.95	1.31
Surface Area (m^2g^{-1})	703	870
CO2 Uptake (cm^3g^{-1})	89	55

As CO2 has a kinetic diameter of 3.3, molecular sieves in general with a 6 pore diameter would be the most optimal due to it providing a crucial balance between accessibility and confinement. Theoretical models, such as the Density Functional Theory (DFT) and Grand Canonical Monte Carlo (GCMC) simulations, show that a pore size of around 6 maximizes van der Waals interactions while maintaining sufficient accessibility. This length has been proven to be extremely effective for MOFs in a variety of different researches, including those of Yaghi in 2005, where the MOF created an optimal environment for host guest interactions with CO2[55].

Framework Adjustments

Frameworks are a MOFs backbone, and they contribute to a lot of its characteristics, results, and interactions with gasses and especially the environment. In order to maximize the potential of metal-organic frameworks, scientists have begun diving into the field of tuning frameworks so that it is optimal for CCS. In this subsection, we will discuss the two major breakthroughs that are flexible and hydrophobic water resistant frameworks.

Flexible Frameworks

By offering stretchability as well as foldability, flexible frameworks have been crucial to the modern developments in separation membranes and porous structures, including MOFs[56]. Flexible frameworks often have linkers that allow for rotational or vibrational movements, and this is what allows the crystalline structure to vary so easily. Moreover, accessible and well-defined pores also further enable flexibility, as the structural arrangement of the MOF easily shifts according to any guest particles. Unfortunately, such versatility comes with downsides when in contact with external stimuli such as high heat or pressure. This is when excessive dynamic disorder occurs, which involves local movements of atoms or molecules from their ideal positions, causing the framework to be unstable[57]. Although this is a downside to the MOF structure, it can also bring a major benefit under a certain stimulus known as gated pressure. Gated pressure is a specific amount of pressure that can activate the framework, instead of damaging it, and this can allow a drastic increase in CO2 adsorption rate. The Langmuir and Freundlich adsorption models can be used to help understand this increase in CO2 uptake. According to this theory, adsorption capacity depends on the surface area and available binding sites, and with the flexible frameworks, the number accessible binding sites increase, therefore leading to higher uptake in comparison to a rigid MOF framework. This is the major benefit of flexible frameworks. Certain MOFs such as the IRMOF-116 all contain topological characteristics that allow flexible frameworks, and they exhibit high CO2 yield because of this attribute[58].

Hydrophobic Frameworks

Many MOFs are often susceptible to H2O, as well as humid environments, which leads to a high decrease in CO2 adsorption rates[59]. This issue has been consistently seen in MOFs such as MOF-5, ZIF-8, and even the HKUST-1, which although are primitive MOFs, still show the common weakness found in multiple porous structures. To combat this problem, hydrophobic frameworks were introduced and this enabled MOFs to be water-resistant and tackle humid conditions. As MOFs are commonly used in solutions that contain H2O, having a hydrophobic framework would be an incredible advantage for applications in the near future. Recent studies have shown that by incorporating ligands that are perfluorinated or contain fluorinated or alkyl side chains during the synthesis process, MOFs are able to gain hydrophobicity, and an example of this can be seen in MOFF-1 (Cu2(OFBPDC)2(MeOH)2). This MOF was created via the solvothermal method and used a combination of H2OFBPDC with Cu(NO3)2, both of which are perfluorinated ligands. After testing, this MOF demonstrated high water contact angles (up to 151), which indicates strong hydrophobicity[60]. Another notable superhydrophobic MOF is FMOF-1 (Ag4Tz6), which

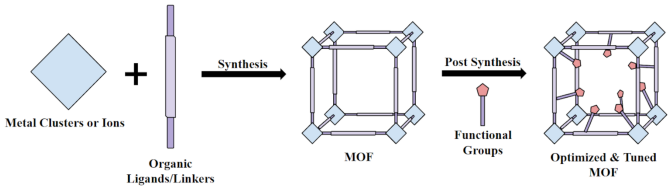

Fig. 4 A simple scheme describing the Post Synthetic Modification Process[64]

was able to sustain its structure after a prolonged period of time in water. By incorporating CF3 groups in its internal pores, FMOF-1 displayed insignificant water uptake, thus proving its hydrophobicity.

Post Synthetic Modification (PSM)

As derived from its name, Post Synthetic Modification describes the tuning of MOFs after the synthesis stage, and is commonly created through the formation of covalent bonds with the organic frameworks. First published in a paper by Hoskins and Robson in 1990, scientists inferred that a MOFs structure could be modified by the exchange of guest molecules and thus creating the backbone of PSM[61]. Although this seems like a basic interaction, it took various scientists more than a decade to finally implement this through covalent modification, making PSM a relatively new technique[62]. Numerous advantages to CO2 adsorption and MOF characteristics are a result of PSM and this includes a more diverse range of functional groups, simple purification of modified products, a tunable MOF structure[63], as well as new CO2 adsorption sites. Essentially, PSM accomplishes the following additions: adding new functional groups (amines), modification/insertion/exchange of organic linkers, and cation exchange(in anionic MOFs). However, this technique can only be utilized if a MOF already contains established OMSs, specific functional groups, and a large pore diameter[51].

Conducted by O. M. Yaghi and co-authors, the amine-bearing IRMOF-3 was used to generate sulfonate and alkylamine groups via ring-opening reactions[64]. These groups were created by placing IRMOF-3 in CHCl3 and treating it with either 1,3-propanesultone or 2-methylaziridine at 45 degrees Celsius. Both compounds yielded similar results, and 1,3-propanesultone transformed around 57% of original amine sites into sulfonate groups[65]. This grants IRMOF-3 many benefits such as stronger acid-base interaction with CO2, flexible frameworks, overall stability, and more. Another successful example of a PSM-affected MOF is the MIL-100 and 101. Conducted in Ferey laboratories, a Post Synthetic Modification test was run on MOFs MIL-100 and MIL-101, which are 3D MOFs constructed by combining Cr(III) trimers that are then bridged by BTC and BDC (BDC = 1,4-benzenedicarboxylate) ligands[66]. MIL-101 was treated with various multifunctional organic amines such as ED in toluene to create ED-MIL-101 and this increased its activity rate by almost 3-fold (96% vs 31.5% unmodified). This would possibly significantly impact CO2 adsorption rates, and therefore achieve excellent yield.

Comparison of Optimization Techniques

Throughout the various optimization techniques mentioned in the previous sections above, many of these methods are able to accelerate a MOFs carbon dioxide uptake by quite a margin, with its adsorption capabilities increasing. In comparison to other enhancement strategies, Lewis Basic Sites are, without a doubt, the most dominant in terms of CO2 uptake performance due to its acid -base interactions. Its ability to bind strongly onto carbon dioxide makes the addition of these openly accessible sites crucial for high performing metal-organic frameworks. However, OMS-based MOFs, along with those that undergo pore size optimization methods, are also strong contenders for significantly increasing CO2 intake. Other than its adsorption statistics, another field in which these modifications must be evaluated is their effectiveness in wet, humid conditions. While crafting hydrophobic frameworks is definitely the priority in these circumstances, LBSs are also able to achieve chemically stable CO bonds in wet conditions, and many PSM techniques can also enhance water resistance and selectivity in MOFs. On the contrary, flexible frameworks are less competent in moist environments due to its susceptibility to structural instability in the vast presence of water. Open metal sites also experience a dramatic lowering in efficiency as H2O competes with the carbon dioxide for the same binding sites. All in all, in terms of the overall proficiency of these optimization methods, lewis basic sites and post-synthetic modifications would be the most impactful on MOFs as they have great tunability, water resistance, and increase in CO2 adsorption.

Industrial Applications of MOFs

Pre Combustion Carbon Capture

During Pre Combustion Carbon Capture, the fuel sources, such as gas, coal, or fossil fuels are decarbonated, so that the emissions will be free of CO2[67]. Being one of the most plausible current CCS technologies, pre-combustion carbon capture has many benefits such as its small amount of equipment needed, well-developed systems, and easier CO2 separation[68]. This sets it above the other capture methods in the current status quo, and many power plants are being implemented to support this technique. The decarbonization process is rather simple and follows three main steps, which all revolve around the production of syngas. In the first step, our fuel (coal for example), is gasified at extremely high temperatures and pressures, which releases syngas that contain CO, CO2, H2, and H2O. Secondly,

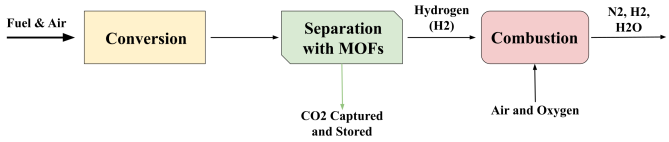

Fig. 5 An illustration of Pre-Combustion Carbon Capture using MOFs

the water-gas shift reaction is then utilized, increasing H2 and CO2 production in the syngas. Lastly, Metal-Organic Frameworks are used in gas separation, removing the unwanted CO2 or H2 from the released gas. To further add on, the leftover gas can be combusted and released back into the atmosphere as nitrogen, oxygen, or water vapor. This completes the decarbonization process, resulting in zero carbon emissions from the fuel. However, this method comes with a few disadvantages that must be tackled in the near future. Because of the instability of MOFs under variable-like circumstances, a large-scale industrial-sized application is still rendered impractical at the moment. On top of that, pre-combustion carbon capture with MOFs is not as cost-effective as other traditional methods (such as amines), which is an issue that must be urgently addressed.

4-pyridylcarboxylatebased ultra-microporous MOF [Ni-4PyC, Ni9(-H2O)4(H2O)2(C6NH4O2)18.solvent] is a successful pre-combustion CCS MOF, which proved effective results[69]. This nickel-based framework structure contains a BET surface area of 945 m/g, with high N2 and CO2 adsorption capacities at low temperatures. With a CO2 uptake of 11 mmol/g at 195 K (273 K and 303 K at higher temperatures), PALS measurements combined with the density function theory confirm that this MOF has an ultra-microporous character and bears spherical pore sizes of 3.9 to 4.4 [70]. This data indicates that it performs exceptionally well in high temperatures as well, making it an overall versatile MOF that shows lots of promise. To add on, more experiments were conducted on MOF [Ni-4PyC, Ni9(-H2O)4(H2O)2(C6NH4O2)18.solvent], to check its efficiency under high pressure. According to GCMC simulations, the predicted CO2 uptake of this MFO was 8.2 mmol/g at 10 bar and 298 K which perfectly aligns with the experimental results. Its exceptional CO2 saturation capacity and selectivity make this MOF a great future prospect for pre-combustion carbon capture with metal-organic frameworks.

Post Combustion Carbon Capture

Opposite from Pre Combustion, Post Combustion Carbon Capture relies on separating CO2 from the flue gas before being emitted into the atmosphere. Flue gas is essentially exhaust gas from the burning of fuels and is commonly (but not always) made up of 73-77% N2, 15-16% CO2, and 5-7% H2O[71]. Pre-combustion is the most widely used technique for CCS, as its basic properties allow it to be retrofitted upon already existing power plants[72]. This makes it much easier for industries to apply this method as they do not need to spend extra investments on new projects. By packing MOFs into adsorption columns or beds, and sending the flue gas through these special units during treatment, the porous structures of a MOF are easily able to separate CO2 from the exhaust gas. Regeneration units are also established to commit desorption of the MOFs, allowing for them to be reused for more emissions. Post-combustion, unfortunately, comes with a few disadvantages, including instability of MOFs, high and hard-to-deal-with CO2 volumes, and low water stability in specific MOFs. These downsides all significantly impact the adsorption rate and effectiveness of CCS operations.

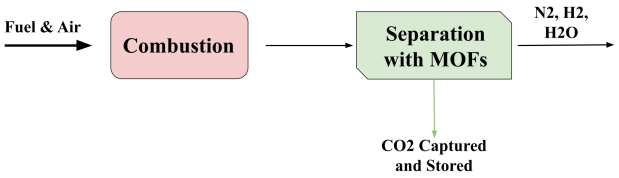

Fig. 6 An illustration of Post-Combustion Carbon Capture using MOFs

Synthesized by Yaghis group, the prominent MOF-74 has displayed efficacious CO2 yield during post-combustion, and remains the most encouraging MOF for this method of capture. One of its variants, the magnesium-based MOF-74-Mg synthesized by Matzger and co-authors, is an isostructural MOF that utilizes the benefits of Mg to produce high carbon yield efficiency[73]. Showing an uptake of 296K at 0.1atm, which is double that of any MOF-74 series, MOF-74-Mg performs spectacularly well under post-combustion circumstances. Some other potential MOFs include dptz-CuTiF6[74], SIFSIX-3-Cu, and NbOFFIVE-1-Ni[75] which are being heavily researched currently. All in all, post-combustion carbon capture via MOFs is one of the most feasible methods alongside pre-combustion, and can be implemented in the near future if all issues are resolved.

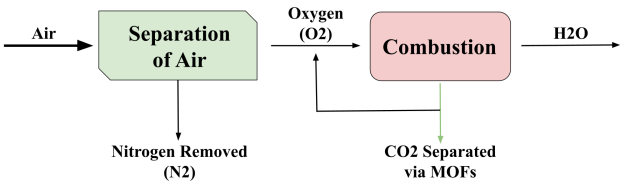

Fig. 7 An illustration of Oxy-fuel Combustion Carbon Capture using MOFs

Oxyfuel Combustion Carbon Capture

In comparison to Pre and Post Combustion Carbon Capture, CCS via Oxyfuel Combustion is a relatively new technology that relies on pure oxygen instead of air to burn fuel. By burning pulverized coal or carbon-based fuels in such an environment, flue gas that contains mainly water vapor and CO2 is released and separated for carbon capture[76]. This method comes with many advantages such as high CO2 concentration due to the lack of nitrogen, the absence of nitrogen oxide, as well as high capture rates. Its yield rates have been proven to be much higher than other methods, (reaching a high of 95%), yet has not seen any large-scale application. The reason behind this is because of its costly operation price, which needs pure oxygen, and highly complicated gas separation techniques[77]. Oxygen generation is commonly implemented through two techniques, the most renowned of which is cryogenic separation. This method requires compressing air and cooling it under cryogenic temperatures (-150 degrees Celsius), causing it to liquefy. This liquid is then distilled and oxygen is separated from other gasses such as Nitrogen. As a result, this creates high-purity O2 that is then used for oxyfuel combustion. The other technique is known as pressure swing adsorption (PSA), which utilizes zeolites and carbon-based materials to generate oxygen[78]. Unfortunately, this method is too impractical and can only be used at a medium-level scale. As oxy-fuel combustion is still a relatively new technique, not many MOFs have been tested as a means of separation for this method. Effectively innovated by Liu et al, PIF-1 and ZIF-8 are the only notable MOFs that have undergone Oxy-fuel combustion[79]. Both composite membranes demonstrated great thermal stability and had an above-average carbon dioxide yield. However, the energy requirements needed to efficiently build oxyfuel-targeted power plants are still too high, making this method of carbon capture insufficient for the time being.

Direct Air Capture

Unlike the previous three methods, Direct Air Capture (DAC), which was first introduced in 1999, involves capturing carbon dioxide from ambient air, rather than flue gas that is released from the burning of fuels[80]. This technique is more passive but still requires either solvents or sorbents to capture the CO2 at lower concentrations (around 400 ppm)[81]. While the solvents are usually aqueous organic amines that have been discussed in section 1.1.1, the sorbents range from a variety of different compounds such as activated carbons, zeolites, and MOFs. The major advantage that DAC has over the other techniques is its efficient scalability. As it only requires ambient air that can be found in the atmosphere, DAC is extremely easy to implement in places all over the globe and requires less energy than processes such as oxyfuel capture. A report from the 2021 International Energy Agency (IEA) indicates that there are currently 19 DAC sites in operation in numerous countries and that their combined CO2 uptake is around 0.01 million tons annually[82]. Since there are already various fully functioning DAC plants up and running, it shows great potential for the further establishment of MOFs as a replacement for the physisorbents used at the moment.

To utilize MOFs in a DAC system, the ambient air must be first pulled into contactors, where the CO2 is then adsorbed onto the sorbent (MOFs). Once it is fully adsorbed, a desorption phase occurs, which removes residual air, and adds steam to heat the sorbent (80C to 120C) for regeneration.

Amine Functionalized MIL-101(Cr) has been one of the most successful MOFs in the DAC field. Synthesized with a modified recipe from Hatton et al[83], MIL-101(Cr) has been grafted with two different amine-loaded compounds, TREN, and PEI. By activating the MOF and then adding either one of these compounds heated at a specific temperature (110 C for TREN, 150 C for PEI), scientists were able to add these amines onto the MOF as a functional group. This has been proven to be useful during DAC, and has shown greater carbon dioxide yield on average. However, after multiple tests on MIL-101(Cr) - TREN (grafted), its stable cyclic adsorption capacity of 0.35 mmol/g was considered to be too low for industrial/large-scale application. On the other hand, the PEI-800 loading of 1.01.1mmol/g MOF (85 wt %) displays a promising result for Carbon Dioxide Adsorption for MOFs in the DAC industry[84]. Moreover, the combination of an effective MOF could propel DACs success rate, making it implementable soon. All in all, direct air capture is currently an underdeveloped and small-scale project that may have lots of potential in the future.

Challenges and Limitations

Capacity

One of the major challenges of MOF application is the capacity of CO2 that is captured, transported, and stored. The volume of space that can be issued for Carbon storage is often misleading and extremely confusing to establish, which leads to many problems regarding oil reservoirs, Oil and Gas companies, and CO2 injection in general. Successful storage requires the

Table 4 CO2 Uptake in Direct Air Capture of MIL-101 in Relation to Time

Time (Minutes)	MIL-101 (Cr)-PEI-0.97 (mmol/g)	MIL-101 (Cr)-PEI-1.32 (mmol/g)	MIL-101 (Cr)-PEI-1.76 (mmol/g)
25	0.42	0.27	0.29
50	0.7	0.52	0.58
75	0.93	0.76	0.8
100	1.04	0.95	0.98

rate of CO2 injection into a secure reservoir to match the rate of supply from associated facilities that have CO2-capture technology installed, which is highly unlikely in the current status quo[85]. Moreover, injection rates are expected to decline quickly after a few years of carbon storage, due to unfavorable geological conditions, pressure build-up[86], and extractive activity. The importance of dynamics in the area of capacity and storage is paramount, and many of these issues must be addressed before large-scale implementation should occur.

Fortunately, there are many ways to tackle the obstacles at hand. Firstly, establishing institutional capability among industries such as Oil and Gas (O&G) companies can be extremely beneficial in setting up relations, and plans for carbon dioxide storage. In order to achieve the target results, determining feasible CO2 storage options is a major step, and involves balancing geological, engineering, commercial, and sociopolitical factors that can influence CCS efficiency. As a consequence, carbon capture industries must put out great collaborative efforts with O&G industries, because they have a more extensive knowledge base on these topics. On top of that, regulations, infrastructure, and legislation regarding oil usage or carbon capture must be familiarized from both sides. Geological storage has been utilized for decades[87], yet a sustainable, long-lasting, and successful project has yet to be developed. CCS companies should enforce Dynamic Capacity Assessments on any prospective regions, and local O&G industries must help with geological conditions, as they are equipped to provide insight on potential carbon injection implementation.

Current MOF Challenges

Other than capacity-related issues, MOFs are still a relatively new and underdeveloped technology that can pose some problems. Although MOFs have been through lots of advancements and general improvements, many still contain stability issues, poor yields in humid environments, optimization needs, and more. Humidity and performance in water are still the largest issues that MOFs face, and consistently display low CO2 selectivity in the presence of H2O, serving as a large issue for numerous environments. To target this issue, hydrophobic frameworks (as mentioned in 3.5.2) have been slowly undergoing development, and have shown some promising results. Another common complication is the adsorption of the wrong glasses because of the flue gas composition. Polar gasses, that take up around 5-7% of exhaust gas, can sometimes be preferentially adsorbed over CO2[88], resulting in an extremely low carbon yield. However, this is not a crucial problem at hand as many MOFs such as MOF-808[89], ZIF-8, and MIL-101 have been demonstrating great thermal and chemical stability and a solid adsorption success rate. As time goes on, these MOFs along with many more should be well prepared for carbon capture uses in the near future.

Industrial Comparisons

In comparison to current standard carbon capture and sequestration procedures, such as large scale amine absorption plants, MOFs definitely lack in terms of research maturity, as well as a feasible upscaling strategy. To become a mechanism that is able to adsorb thousand tons of CO2 on a daily basis, metal organic frameworks must be reproduced at an extremely high level, with it being used at a vast scale. Unfortunately, there are currently a few economic barriers that lie within its way, including a high cost and energy usage during its synthesis process. For instance, the production of MIL-160 has been estimated to be around 55$ per kilogram, whereas traditional amine-based sorbents, such as monoethanolamine (MEA), are generally more cost-effective, with prices typically around $1 to $2 per kilogram[90]. Although future projections predict that MOFs can lower its price to around 10 dollars per kilogram, at its present state, the production price is extremely unrealistic, and is simply too much to be upscaled to an industrial level. Moreover, synthesizing these frameworks also require large amounts of energy, as the common solvothermal and hydrothermal procedures operate under high temperatures, leading to the possible productions of more carbon dioxide during its process. Occasionally, small amounts of toxic byproducts can also be produced by the heavy metals and use of organic solvents, which can have a negative impact on the environment. Amine capture plants also suffer from these issues, as one plant produces 184,000 kg of CO2 per hour due to their electricity use, which often breaks even with the amount captured. Such excess pollution that is produced is yet another limitation that poses itself in front of all existing carbon capture technologies, and will definitely be mitigated with time.

Conclusion

Metal-organic frameworks are one of the most promising carbon capture adsorbents in the current industry, as they brim with overflowing potential. Being an extremely effective catalysts for CO2 capture and conversion, their chemical tunability enhances interactions with CO2 and other substrates, making MOFs versatile in various environments. Through many of its synthetic

techniques (such as electromechanical and sonochemical being some of the more successful methods), MOFs can rely on numerous functional groups and properties to enhance their carbon dioxide yield rate. Open Metal Sites (OMSs), Lewis Basic Sites (LBSs), Pore Size, and Hydrophobic or Flexible frameworks are all crucial factors that can be tuned and used for increasing adsorption rates. Moreover, implementing the use of post-synthetic modification and MOF composites allows scientists to further dive into the ever-expanding potential of these porous structures, improving functionality and selectivity. However, possibilities of a large-scale application should very much be the current priority for scientists in the CCS field. With various capture techniques involving MOFs, post-combustion is the most feasible option at this stage because of its already existing plants, and the simplicity of implementation. Pre-combustion and direct air capture are also commonly seen, although these processes depend on the type of MOF that is being utilized since MOF types differ quite largely. Nevertheless, to properly introduce MOFs into large industries, many issues must be directed at and resolved first. This includes stability difficulties, susceptibility to water, carbon capacity limits, and large energy requirements. With many of these problems occurring consistently, researchers should definitely direct their future progress on chemically tuning these MOFs or building functional groups that can tackle these obstacles such as focusing on the reproducibility and long-term stability of catalysts. On top of that, the general carbon dioxide uptake should still be consistently improved, and experimentation with MOF composites or post-synthetic modification can also be a major step forward. Collaboration across industries (specifically oil and gas), disciplines, or even countries can ensure that many of the posed issues can be resolved and that regulations are to be established for the greater good of carbon capture. Through the detailed review above, it is without a doubt that MOFs are one of the top candidates for CCS adsorbents, and if strongly developed, can be extremely beneficial for the future of humanity. With CO2 emissions getting drastically cut down, the enhanced greenhouse effect slowly dissipating, and the ability to still generate large portions of energy for our globe, MOFs in CCS bring lots of upsides that can change the course of human history forever.

References

1 H. Yamada, *Polymer Journal*, 2020, **53**, 93–102.

2 Greenpeace Philippines, *How fossil fuel companies are burning our planet - Greenpeace Philippines*, 2023, https://www.greenpeace.org/philippines/story/61109/how-fossil-fuels-companies-are-burning-our-planet/.

3 D. Shindell and C. J. Smith, *Nature*, 2019, **573**, 408–411.

4 NationalGrid, *What is carbon capture and storage?. CCS explained — National Grid Group*, 2024, https://www.nationalgrid.com/stories/energy-explained/what-is-ccs-how-does-it-work.

5 D. Lv, W. Nong and Y. Guan, *Coordination Chemistry Reviews*, 2021, **450**, 214234.

6 B. L. Salvi and S. Jindal, *SN Applied Sciences*, 2019, **1**, year.

7 A. I. Osman, M. Hefny, M. I. a. A. Maksoud, A. M. Elgarahy and D. W. Rooney, *Environmental Chemistry Letters*, 2020, **19**, 797–849.

8 S. Fakher and A. Imqam, *Fuel*, 2019, **265**, 116944.

9 S. Y. W. Chai, L. H. Ngu and B. S. How, *Greenhouse Gases: Science and Technology*, 2022, **12**, 394–427.

10 D. Aaron and C. Tsouris, *Separation Science and Technology*, 2005, **40**, 321–348.

11 S. D. Peu, A. Das, M. S. Hossain, M. a. M. Akanda, M. M. H. Akanda, M. Rahman, M. N. Miah, B. K. Das, A. R. M. T. Islam and M. M. Salah, *Sustainability*, 2023, **15**, 5827.

12 A. A. Olajire, *Energy*, 2010, **35**, 2610–2628.

13 H. F. Svendsen, E. T. Hessen and T. Mejdell, *Chemical Engineering Journal*, 2011, **171**, 718–724.

14 C. Shah, S. Raut, H. Kacha *et al.*, *Chemical Papers*, 2021, **75**, 4413–4429.

15 Y. Han and W. W. Ho, *Chinese Journal of Chemical Engineering*, 2018, **26**, 2238–2254.

16 A. Katare, S. Kumar, S. Kundu, S. Sharma, L. M. Kundu and B. Mandal, *ACS Omega*, 2023, **8**, 17511–17522.

17 U. Khan, C. C. Ogbaga, O. O. Abiodun, A. A. Adeleke, P. P. Ikubanni, P. U. Okoye and J. A. Okolie, *Carbon Capture Science Technology*, 2023, **8**, 100125.

18 R. Gonzalez-Olmos, A. Gutierrez-Ortega, J. Sempere and R. Nomen, *Journal of CO2 Utilization*, 2021, **55**, 101791.

19 S. Kumar, R. Srivastava and J. Koh, *Journal of CO2 Utilization*, 2020, **41**, 101251.

20 H. M. Magee, *Nitrogen gas adsorption in zeolites 13X and 5A*, Walla Walla University, 2021, https://www.phys.ufl.edu/REU/2008/reports/magee.pdf.

21 M. Safaei, M. M. Foroughi, N. Ebrahimpoor, S. Jahani, A. Omidi and M. Khatami, *TrAC Trends in Analytical Chemistry*, 2019, **118**, 401–425.

22 X. Zhang, Z. Chen, X. Liu, S. L. Hanna, X. Wang, R. Taheri-Ledari, A. Maleki, P. Li and O. K. Farha, *Chemical Society Reviews*, 2020, **49**, 7406–7427.

23 J. M. Simmons, H. Wu, W. Zhou and T. Yildirim, *Energy & Environmental Science*, 2011, **4**, 2177.

24 J. Klinowski, F. a. A. Paz, P. Silva and J. Rocha, *Dalton Transactions*, 2010, **40**, 321–330.

25 P. T. Phan, J. Hong, N. Tran and T. H. Le, *Nanomaterials*, 2023, **13**, 352.

26 Y. Lee, J. Kim and W. Ahn, *Korean Journal of Chemical Engineering*, 2013, **30**, 1667–1680.

27 S. H. Jhung, J. H. Lee and J. S. Chang, *Microwave synthesis of a nanoporous hybrid material, chromium trimesate*, https://www.osti.gov/etdeweb/biblio/22748385, 2005, Accessed via www.osti.gov.

28 U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastr, *Journal of Materials Chemistry*, 2005, **16**, 626–636.

29 V. M, V. V. and G. Nageswaran, *Journal of the Electrochemical Society*, 2020, **167**, 155527.

30 Y. Lee, J. Kim and W. Ahn, *Korean Journal of Chemical Engineering*, 2013, **30**, 1667–1680.

31 D. Sud and G. Kaur, *Polyhedron*, 2020, **193**, 114897.

32 O. M. Yaghi and H. Li, *Journal of the American Chemical Society*, 1995, **117**, 10401–10402.

33 P. Pachfule, R. Das, P. Poddar and R. Banerjee, *Crystal Growth & Design*, 2011, **11**, 1215–1222.

34 M. Ashokkumar, *Ultrasonics Sonochemistry*, 2010, **18**, 864–872.

35 D. Jung, D. Yang, J. Kim, J. Kim and W. Ahn, *Dalton Transactions*, 2010, **39**, 2883.

36 W. Kukulka, K. Cendrowski, B. Michalkiewicz and E. Mijowska, *RSC Advances*, 2019, **9**, 17048–17054.

37 N. Missaoui and M. Bouzid, *Microporous and Mesoporous Materials*, 2023.

38 H. H. Do, I. Rabani and H. B. Truong, *Beilstein Journal of Nanotechnology*, 2023.

39 D. G. Madden, R. Babu, C. Çamur, N. Rampal, J. Silvestre-Albero, T. Curtin and D. Fairen-Jimenez, *Faraday Discussions*, 2021.

40 O. M. Yaghi, M. OKeeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714.

41 P. Pourhakkak, A. Taghizadeh, M. Taghizadeh, M. Ghaedi and S. Haghdoust, *Interface Science and Technology*, 2021, pp. 1–70.

42 M. Krlik, *Chemical Papers*, 2014, **68**, year.

43 H. Furukawa, *Science*, 2013.

44 B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras and O. M. Yaghi, *Angewandte Chemie International Edition*, 2005, **44**, 4745–4749.

45 R. A. Maia, B. Louis, W. Gao and Q. Wang, *Reaction Chemistry & Engineering*, 2021, **6**, 1118–1133.

46 A. R. Millward and O. M. Yaghi, *Journal of the American Chemical Society*, 2005, **127**, 17998–17999.

47 G. T. Rochelle, *Science*, 2009, **325**, 1652–1654.

48 H. Kim, S. Huh, D. N. Lee and Y. Kim, *Dalton Transactions*, 2018, **47**, 4820–4826.

49 Y. Kim and S. Huh, *CrystEngComm*, 2016, **18**, 3524–3550.

50 M. Ding, R. W. Flaig, H. Jiang and O. M. Yaghi, *Chemical Society Reviews*, 2019, **48**, 2783–2828.

51 R. W. Flaig, T. M. O. Popp, A. M. Fracaroli, E. A. Kapustin, M. J. Kalmutzki, R. M. Altamimi, F. Fathieh, J. A. Reimer and O. M. Yaghi, *Journal of the American Chemical Society*, 2017, **139**, 12125–12128.

52 B. Zdravkov, J. ermk, M. efara and J. Jank, *Open Chemistry*, 2007, **5**, 385–395.

53 A. C. Forse, K. A. Colwell, M. I. Gonzalez, S. Benders, R. M. Torres-Gavosto, B. Blmich, J. A. Reimer and J. R. Long, *Chemistry of Materials*, 2020, **32**, 3570–3576.

54 R. Wang, Q. Meng, L. Zhang, H. Wang, F. Dai, W. Guo, L. Zhao and D. Sun, *Chemical Communications*, 2014, **50**, 4911.

55 O. M. Yaghi, *Journal of the American Chemical Society*, 2005.

56 M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Mller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov and S. Minko, *Nature Materials*, 2010, **9**, 101–113.

57 S. Seth and S. Jhulki, *Materials Horizons*, 2020, **8**, 700–727.

58 L. Sarkisov, R. L. Martin, M. Haranczyk and B. Smit, *Journal of the American Chemical Society*, 2014, **136**, 2228–2231.

59 C. Wang, X. Liu, N. K. Demir, J. P. Chen and K. Li, *Chemical Society Reviews*, 2016, **45**, 5107–5134.

60 K. Jayaramulu, F. Geyer, A. Schneemann, . Kment, M. Otyepka, R. Zboril, D. Vollmer and R. A. Fischer, *Advanced Materials*, 2019, **31**, year.

61 B. F. Hoskins and R. Robson, *Journal of the American Chemical Society*, 1990, **112**, 1546–1554.

62 J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982–986.

63 Z. Wang and S. M. Cohen, *Chemical Society Reviews*, 2009, **38**, 1315.

64 D. Britt, C. Lee, F. J. Uribe-Romo, H. Furukawa and O. M. Yaghi, *Inorganic Chemistry*, 2010, **49**, 6387–6389.

65 K. K. Tanabe and S. M. Cohen, *Chemical Society Reviews*, 2010, **40**, 498–519.

66 G. Frey, C. Serre, C. MellotDraznieks, F. Millange, S. Surbl, J. Dutour and I. Margiolaki, *Angewandte Chemie International Edition*, 2004, **43**, 6296–6301.

67 Y. Tao and H. Xu, *Applied Thermal Engineering*, 2023, **236**, 121504.

68 J. Li, R. J. Kuppler and H. Zhou, *Chemical Society Reviews*, 2009, **38**, 1477.

69 S. Nandi, P. De Luna, T. D. Daff, J. Rother, M. Liu, W. Buchanan, A. I. Hawari, T. K. Woo and R. Vaidhyanathan, *Science Advances*, 2015, **1**, year.

70 M. Liu, A. G. WongFoy, R. S. Vallery, W. E. Frieze, J. K. Schnobrich, D. W. Gidley and A. J. Matzger, *Advanced Materials*, 2010, **22**, 1598–1601.

71 Q. Wang, J. Bai, Z. Lu, Y. Pan and X. You, *Chemical Communications*, 2015, **52**, 443–452.

72 J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *International Journal of Greenhouse Gas Control*, 2007, **2**, 9–20.

73 S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *Journal of the American Chemical Society*, 2008, **130**, 10870–10871.

74 W. Liang, P. M. Bhatt, A. Shkurenko, K. Adil, G. Mouchaham, H. Aggarwal, A. Mallick, A. Jamal, Y. Belmabkhout and M. Eddaoudi, *Chem*, 2019, **5**, 950–963.

75 P. M. Bhatt, Y. Belmabkhout, A. Cadiau, K. Adil, O. Shekhah, A. Shkurenko, L. J. Barbour and M. Eddaoudi, *Journal of the American Chemical Society*, 2016, **138**, 9301–9307.

76 M. A. Nemitallah, M. A. Habib, H. M. Badr, S. A. Said, A. Jamal, R. Ben-Mansour, E. M. A. Mokheimer and K. Mezghani, *International Journal of Energy Research*, 2017, **41**, 1670–1708.

77 T. Nenoff, D. S. Gallis, M. Parkes, J. Greathouse, M. Rodriguez, S. Paap, T. Williams and C. Shaddix, *Novel metal-organic frameworks for efficient stationary sources via oxyfuel combustion*, Sandia national laboratories technical report, 2015.

78 H. Luo, K. Efimov, H. Jiang, A. Feldhoff, H. Wang and J. Caro, *Angewandte Chemie International Edition*, 2010, **50**, 759–763.

79 Y. Liu, J. Zhang and X. Tan, *ACS Omega*, 2019, **4**, 16572–16577.

80 K. Lackner, H. Ziock and P. Grimes, *Carbon Dioxide Extraction from Air: Is It An Option?*, Los alamos national lab. (lanl), los alamos, nm (united states) technical report, 1999.

81 P. Boone, Y. He, A. R. Lieber, J. A. Steckel, N. L. Rosi, K. M. Hornbostel and C. E. Wilmer, *Nanoscale*, 2022, **14**, 16085–16096.

82 International Energy Agency, *Direct Air Capture - Energy System - IEA*, n.d., `https://www.iea.org/energy-system/carbon-capture-utilisation-and-storage/direct-air-capture`.

83 L. Bromberg, Y. Diao, H. Wu, S. A. Speakman and T. A. Hatton, *Chemistry of Materials*, 2012, **24**, 1664–1675.

84 L. A. Darunte, A. D. Oetomo, K. S. Walton, D. S. Sholl and C. W. Jones, *ACS Sustainable Chemistry & Engineering*, 2016, **4**, 5761–5768.

85 J. Lane, C. Greig and A. Garnett, *Nature Climate Change*, 2021, **11**, 925–936.

86 N. W. Bosshart, N. A. Azzolina, S. C. Ayash, W. D. Peck, C. D. Gorecki, J. Ge, T. Jiang and N. W. Dotzenrod, *International Journal of Greenhouse Gas Control*, 2017, **69**, 8–19.

87 R. Tarkowski, *Renewable and Sustainable Energy Reviews*, 2019, **105**, 86–94.

88 L. Liang, C. Liu, F. Jiang, Q. Chen, L. Zhang, H. Xue, H. Jiang, J. Qian, D. Yuan and M. Hong, *Nature Communications*, 2017, **8**, year.

89 H. Furukawa, F. Gndara, Y. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, *Journal of the American Chemical Society*, 2014, **136**, 4369–4381.

90 M. I. Severino, E. Gkaniatsou, F. Nouar, M. L. Pinto and C. Serre, *Faraday Discussions*, 2021.