Crystal Engineering of Hybrid Ultramicroporous Materials for Study of Direct Air Capture of Carbon Dioxide

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Abstract

Global atmospheric CO$_2$ levels are currently 409 ppm, an increase of 130 ppm since the pre-industrial era. Efficient mitigation strategies combined with advanced carbon capture technologies are required to address this global threat. Direct air capture (DAC) offers an attractive proposition that would facilitate onsite technologies that use CO$_2$ as a feedstock, eliminating the need for storage and transportation. Currently, CO$_2$ scrubbers based on aqueous alkanolamine solutions and amine grafted mesoporous materials are being used for DAC, but they suffer from high regeneration energy.

CO$_2$ selective physisorbents have the potential to reduce energy costs of DAC but have until recently not exhibited appropriate selectivity and hydrolytic stability. Crystal engineering, defined as “the field of chemistry that studies the design, properties and application of crystals” has recently enabled the design of a new generation of physisorbents with the pore size and pore chemistry suited for DAC. Specifically, hybrid ultramicroporous materials (HUMs) with inorganic anion pillars that offer strong electrostatics and tight binding sites for CO$_2$ can offer precise control over pore size/chemistry to afford order of magnitude improvement in the carbon capture performance of physisorbents.

A pyrazine based HUM, (Zn(pyrazine)$_2$SiF$_6$)$_n$, SIFSIX-3-Zn, reported in 2013 was found to exhibit a new benchmark for CO$_2$/N$_2$ selectivity (> 1800). The primary objective of this study is to prepare and characterise a platform of related HUMs by systematically varying the metal node or the inorganic pillar in order to develop HUMs with the following characteristics: a) high thermal and hydrolytic stability, b) better DAC performance and c) cost-effective synthesis (high yield/low waste). A secondary objective is to gain insight into the reasons for the exceptional carbon capture performance of HUMs.
Chapter 1 reviews the deployment of state-of-the-art CO₂ capture technologies in the context of addressing the global issue of greenhouse gas (GHG) emission-regulation. It comprehensively reviews the present and emerging technologies available for trace capture of CO₂, and its eventual role in mitigating atmospheric CO₂ emissions. Prompted by diverse functionalities, CO₂-selective sorption performance for literature-reported MOFs over other relevant competing gases have been discussed, prior to the evaluation of trace carbon capture capacity for a few. This follows an attempt to systematically decipher the crystal engineering principles aimed at the design of efficient CO₂-sorbents. Discussion on importance of pore size and pore chemistry and their influence on selectivity for CO₂ over other competing gases, thermal and hydrolytic stability, and high isosteric heat of adsorption ($Q_{st}$) for CO₂, relevant to DAC of CO₂ concludes the chapter.

Chapter 2 focuses on the assessment of DAC performance for CO₂ by porous materials. In this regard, four different types of materials represented by prototypical compounds, an amine-grafted mesoporous silica (chemisorbent), a zeolite (inorganic physisorbent), HKUST-1 and Mg-MOF-74 (MOF physisorbents), and [Ni(pyrazine)$_2$(SiF$_6$)$_3$], SIFSIX-3-Ni, a Hybrid Ultramicroporous Material (HUM physisorbent) were studied for their DAC performance. Quantification of CO₂ and other vapours (i.e. H₂O) adsorbed by the sorbents under different atmospheric conditions relevant to DAC was obtained by Temperature-Programmed Desorption (TPD) combined with Thermogravimetric Analysis (TGA) and Mass Spectrometry (MS). All the sorbents were found to be capable of carbon capture from CO₂-rich gas mixtures, but competition and reaction with atmospheric moisture significantly reduced their DAC performance. SIFSIX-3-Ni, a HUM outperformed all the other physisorbents with a DAC capacity of 4.07 litres of CO₂ per kilogram of material and was second only to amine-grafted mesoporous silica (a chemisorbent), in terms of its performance. However, lower regeneration temperature for
SIFSIX-3-Ni relative to amine-grafted mesoporous silica makes it the preferred candidate for DAC of CO₂. Stability of sorbents towards moisture, a critical parameter towards the assessment of DAC performance was also studied using the standard, industry-accepted accelerated aging protocol (45 °C and 75% relative humidity).

Chapter 3 highlights the role of fine tuning the HUMs by varying the inorganic pillar to yield sorbents with enhanced stability and improved trace carbon capture performance. In this context, a new HUM [Ni(pyrazine)₂(TiF₆)]ₙ, (TIFSIX-3-Ni), was obtained by the use of TiF₆²⁻ as the inorganic pillar instead of SiF₆²⁻ used in SIFSIX-3-Ni, and NbOF₅²⁻ used in [Ni(pyrazine)₂(NbOF₅)]ₙ, NbOFFIVE-1-Ni. Sorption properties, DAC performance, thermal and hydrolytic stability of the three isostructural analogues were studied to understand the correlation between the choice of inorganic pillar and the resultant properties. TIFSIX-3-Ni and NbOFFIVE-1-Ni performed the best with benchmark DAC capacity of 9.09 and 9.42 litres of CO₂ per kilogram of material respectively. This study indicates that increased electrostatics generated by highly polarized inorganic pillars such as TiF₆²⁻ and NbOF₅²⁻ in HUMs are most effective at improving Qₜ and overall CO₂ adsorption performance of the sorbents.

Chapter 4 elaborates the facile synthesis method to synthesize HUMs in gram-scale, by mechanochemistry. In this regard, a rapid, solvent free and energy economic method using dry solid grinding approach was developed to efficiently synthesize HUMs. Ten HUMs, six previously reported ([Zn(pyrazine)₂(SiF₆)]ₙ, SIFSIX-3-Zn; [Co(pyrazine)₂(SiF₆)]ₙ, SIFSIX-3-Co; [Fe(pyrazine)₂(SiF₆)]ₙ, SIFSIX-3-Fe; SIFSIX-3-Ni; TIFSIX-3-Ni and NbOFFIVE-1-Ni) and four new HUMs ([Zn(pyrazine)₂(TiF₆)]ₙ, TIFSIX-3-Zn; [Co(pyrazine)₂(TiF₆)]ₙ, TIFSIX-3-Co; [Zn(pyrazine)₂(NbOF₅)]ₙ, NbOFFIVE-1-Zn; and [Co(pyrazine)₂(NbOF₅)]ₙ, NbOFFIVE-1-Co) were obtained using the mechanochemical method. Sorption properties,
thermal and hydrolytic stability of mechanochemically synthesized HUMs were compared to the ones obtained via conventional method, so as to verify their phase purity and confirm the structural integrity. Further carbon capture performance and physical stability of all the ten variants were systematically studied to understand the structure-property relationship in isostructural HUMs. Ni\textsuperscript{2+} variants performed the best in terms of CO\textsubscript{2} uptake and also exhibited higher degree of stability which could be attributed to the stronger Ni-N bonds.

Chapter 5 addresses the role of strong electrostatics offered by inorganic pillars and narrow pores in the context of DAC of CO\textsubscript{2}. The DAC performance of ten physisorbents, four HUMs, SIFSIX-3-Cu, DICRO-3-Ni-i, SIFSIX-2-Cu-i and MOOFOUR-1-Ni, five microporous MOMs, DMOF-1, ZIF-8, MIL-101, UiO-66 and UiO-66-NH\textsubscript{2}, and an ultramicroporous MOM, Ni-4-PyC, was investigated. The amounts of sorbates (CO\textsubscript{2} and H\textsubscript{2}O) adsorbed by the physisorbents under different atmospheric conditions relevant to DAC was quantified by TPD coupled with TGA and MS. All the physisorbents exhibited high CO\textsubscript{2} adsorption capacity and strong interaction with CO\textsubscript{2} under dry conditions. However, under moist conditions, their CO\textsubscript{2} capture performance significantly reduced owing to competition with water. Microporous and ultramicroporous MOMs devoid of inorganic pillars exhibited negligible CO\textsubscript{2} uptake upon exposure to DAC conditions, emphasising the importance of strong electrostatics created by the presence of inorganic pillars. Furthermore, one observes significant reduction in CO\textsubscript{2} sorption performance of interpenetrated HUMs, DICRO-3-Ni-i and SIFSIX-2-Cu-i, under DAC conditions. This highlights the fact that the mere presence of inorganic pillars does not facilitate enhanced CO\textsubscript{2} sorption performance. The disposition of inorganic pillars lining the pore walls is equally crucial in terms of creation of strong electrostatics. Indeed, SIFSIX-3-Cu, that fulfils these two factors along with the presence of ultramicropores, exhibits high CO\textsubscript{2} uptake (7.18 L/kg) under DAC conditions. While SIFSIX-3-Cu lacks stability towards humidity precluding its practical utility, it provides valuable
insights regarding improved design strategies for the development of advanced functional materials for DAC of CO₂.

**Chapter 6** explains how modular nature and amenability to crystal engineering makes HUMs the only class of potential sorbents that can offer viable solutions for DAC of CO₂. The findings detailed herein afford better understanding of structure-property relationship and how subtle changes in pore size and pore chemistry can enhance the carbon capture performance of sorbents even in the presence of moisture. Also, these studies leads to development of new design principles which can be used in the future to develop advanced sorbents with improved performance for myriad applications. With facile synthetic strategy in place, the chapter emphasises the need to further explore and develop HUMs in terms of higher technological readiness levels for the implementation of DAC of CO₂ at industrial scale.

**Chapter 7** outlines some of the potential usage for captured CO₂ and how DAC could enable the existing industrial processes using CO₂ as feedstock. The chapter further discusses some of the potential applications of HUMs. It concludes by highlighting the yet unaccomplished objectives in context of HUMs and how their achievement would advance the field of research on HUMs to higher technological readiness levels.
Declaration

The substance of this thesis is the original work of the author, under the supervision of Prof. Michael J. Zaworotko, and due reference and acknowledgement has been made, when necessary, to the work of others. No part of this thesis has been submitted to this or any other university.

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This thesis was defended on the 24th of April, 2018.

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Dedication

To my family for their understanding, support and encouragement...
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**Figure 5.1** Ten physisorbent materials were evaluated in this study. Elements C, O, N, Si, F, Cu, Cr, Ni, Mo, Zn and Zr are represented by grey, red, blue, yellow, pink, salmon, dark red, sky blue, orange, brown and purple, respectively; H atoms have been omitted for clarity. The dark green net represents the second interpenetrated network in SIFSIX-2-Cu-i and DICRO-3-Ni-i

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Chapter One. Introduction

1.1 Global Warming and Carbon Dioxide Capture

Global warming, defined as recent warming of the Earth’s surface and lower atmosphere, is considered to be the outcome of strengthening of the greenhouse effect. First discovered by Joseph Fourier in 1824, the greenhouse effect is a process in which radiations reflected from the earth’s surface get absorbed by some atmospheric gases, termed as greenhouse gases (GHGs). The absorbed radiations are then re-emitted in all directions including surface and lower atmosphere, consequently transferring the energy back to the surface. This phenomenon has helped in maintaining the earth temperature habitable and warmer compared to what it would have been just based on direct heating from sun.

However, since the dawn of industrialisation, the natural balance of GHGs has been altered, primarily due to anthropogenic escalation in atmospheric GHGs such as carbon dioxide (CO$_2$), nitrogen dioxide (NO$_2$), water (H$_2$O), and methane (CH$_4$). Extensive use of fossil fuels to meet ever-increasing energy demands combined with other human-based activities has led to an accumulation of more than 2.4 trillion tons of CO$_2$, a primary constituent of GHGs. As a result of this, global atmospheric CO$_2$ levels has reached 408 ppm in 2017, an increase of 130 ppm since the pre-industrial era as shown in (Figure 1.1). The repercussion of increased carbon footprint is prominently visible across the globe, regardless of the sources of this emission. Over the last decade, earth’s mean temperature rose by 0.8 °C from the pre-industrial era, and if the same rate of CO$_2$ emission persists, it is expected to rise by 1.5 - 5.5 °C causing catastrophic effects. As per the modelling studies performed by various research groups, an increase of more than 2 °C in average atmospheric temperature would raise the global sea-level by 0.2 to 1.5 meters leading to inundation of many low lying cities of the world. Due to widespread global concern regarding climate change, leaders
from 196 countries met together at the Paris agreement to discuss global warming and iterated the necessary steps required to promote sustainable living.

1.1.1 Paris Climate Accord

On the 12th of December 2015 at the Paris Agreement, the World’s first all-inclusive climate agreement on greenhouse gas emissions, 196 countries signed the agreement and vowed “to take all necessary steps relevant to keep the global temperature rise well below 2 °C above pre-industrial levels and to pursue efforts to limit the temperature increase even further to 1.5 °C”. The member countries also agreed to, “a)increase the ability to adapt to the adverse impacts of climate change and foster climate resilience and low greenhouse gas emissions development, in a manner that does not threaten food production, and b) make finance flows consistent with a pathway towards low greenhouse gas emissions and climate-resilient development” for a better and sustainable future.

![Graph](image)

**Figure 1.1.** Simulated transient warming (°C) as a function of cumulative emission of CO₂ (X-axis). The decades in which each additional trillion tons of CO₂ got emitted and the corresponding atmospheric CO₂ concentrations are shown on the top.
Swaying away from traditional environmental meetings where specific targets are set, the Paris climate accord encouraged every participant country to unanimously determine their plans, to coherently mitigate global warming and execute the plans within a reasonable timeframe. All the specific targets set-up in previous agreements were discarded as it was understood that no country could be forced to follow a particular path. However, each country was motivated to set a target exceeding the previous one. With the current global CO₂ being more than 2.4 trillion tons (Figure 1.1) and expected to double up by 2050, particular emphasis was placed on carbon negative strategies (CNS) and the immediate need for global peaking of greenhouse gas emissions to achieve the set target. All these aims have been penned in article 2, “enhancing the implementation,” of the United Nations Framework Convention (UNFCCC) and new strategies to achieve them are expected to roll-out in the upcoming 2020 edition.

1.1.2 CO₂ Capture and Storage

In spite of numerous agreements on climate change and advancements to harness alternative energy sources, future energy landscapes predict an enduring demand in the sector of fossil fuel-derived energy (66%-75% of the global primary energy mix in 2050). As the global population is estimated to reach ca. 9 billion by 2050, the projected climate and energy framework implies substantial complexity to impede the mitigation of anthropogenic CO₂ emissions, considering the enormous scale of the problem, its associated costs and interweaved dependence on energy production. Industrial scale deployment of CO₂ capture and storage (CCS) is regarded as the most environment-friendly, state-of-the-art technology to mitigate anthropogenic CO₂ emissions, until the gap is bridged between our current energy framework and a greener future via alternative energy sectors. Developed in the early 1930s, CO₂ scrubbing from fossil-fuel driven point sources e.g. fossil-fuel based power
plants is regarded as a near-term capture technology since these point sources can be retrofitted with post-combustion CO\textsubscript{2} capture systems.

CO\textsubscript{2} scrubbing is highly CO\textsubscript{2} capture-selective owing to the reaction of aqueous amine solutions with CO\textsubscript{2} to form carbamates. At present, 17 large-scale CCS facilities are operating worldwide, while 4 will be operational by 2018. These 21 facilities have a combined CO\textsubscript{2} capture capacity of 37 million tonnes per annum (Mtpa).\textsuperscript{16} IEA forecasts that to achieve near-future CO\textsubscript{2} emission goals, this needs to increase to around 4 billion tonnes in 2040 and 6 billion tonnes in 2050.\textsuperscript{11} From the perspective of these ambitious CO\textsubscript{2} emissions reduction targets, CCS technologies alone will be unable to sustain the growing energy demand in Europe and beyond. To realize a long-term solution to this crisis, CCS has to be developed in synergy with renewable green technologies, such as wind or solar. Also, instead of the focus of CCS technologies being anchored upon CO\textsubscript{2} capture from point sources, e.g. fossil power plants, cement industry, and refineries, for carbon capture and utilization (CCU), CO\textsubscript{2} can be utilized as a carbon source for chemical production and as a readily available feedstock gas for use in polymer industry and greenhouses.

1.1.2.1 Point-Source CO\textsubscript{2} Capture

A point source of CO\textsubscript{2} can simply be defined as a single localized emitter of CO\textsubscript{2} such as fossil fuel based power plants, or industrial process plants manufacturing steel and cement. Currently, capture of CO\textsubscript{2} from point-source is preferred over CCS strategies as localized emitters offer an opportunity to develop CO\textsubscript{2} capture plants for producing and storing high purity CO\textsubscript{2}, due to the large volume of emissions. The key technologies for point source CO\textsubscript{2} capture are: a) pre-combustion capture, b) oxy-fuel technologies (capture during combustion and), c) post-combustion capture. (Figure 1.2)
A. Pre-Combustion

Pre-combustion technologies involve removal of CO$_2$ before combustion. In a typical process, a suitable feedstock is created either by steam reforming (reaction 1) or gasification (reaction 2) of fuels such as coal, coke or oil residues to yield syngas (carbon monoxide (CO) + hydrogen (H$_2$)). Further, CO (a significant component of syngas) undergoes water gas shift reaction in the presence of water (reaction 3) to produce a stream primarily composed of H$_2$ and CO$_2$. Capture of CO$_2$ from shifted syngas stream is more facile than post-combustion capture due to enriched CO$_2$ concentration in the stream ranging from 15% - 60%. Additionally, removal of CO$_2$ leads to H$_2$-rich stream, which can be used for electricity production. Though CO$_2$ enrichment in the stream facilitates the carbon capture process, pre-combustion technologies are lagging behind because of the considerable cost and infrastructure associated with it.$^{18,19}$

![Figure 1.2. Point-source CCS-process families: technology alternatives for CO$_2$ capture in the power generation sector.$^{17}$](image)
\[ C_xH_y + xH_2O \rightarrow xCO + \left( x + \frac{y}{2} \right) H_2 \]  

(1)

\[ C_xH_y + \frac{x}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2 \]  

(2)

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  

(3)

**B. Oxy-Fuel Combustion**

Oxy-fuel technologies are based on the use of oxygen (O\(_2\)) as the primary oxidant instead of air during the combustion of carbon-containing fuels. Use of O\(_2\) as the oxidant reduces the volume of flue gas and concomitantly increases the CO\(_2\) concentration in the stream (up to 90\%).\(^{20,21}\) CO\(_2\) being the primary component in the stream and moisture as the bulk impurity, demoisturization, drying, and compression can generate a pure CO\(_2\) stream which can be used as an industrial manufacturing feedstock. However, the potential of these processes is yet to be achieved due to the cost factor associated with the air separation process required to generate a pure O\(_2\) stream.\(^{20,21}\)

**C. Post Combustion**

Post-combustion CO\(_2\) capture also known as “end of pipe” or “amine scrubbing” process removes CO\(_2\) from the flue gas released after combustion. It is the most preferred CO\(_2\) capture strategy as no further modification is needed to the existing combustion facility, but it relies heavily on liquid amines such as monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA) dissolved in water to capture CO\(_2\).\(^{22,23}\) Despite their efficiency in capturing CO\(_2\), post-combustion processes also suffer from some drawbacks. Low CO\(_2\) concentrations in the stream (ca 4\% - 15\%) and desulfurization as a pre-requisite makes the process more challenging.\(^{24}\) Further, the corrosive properties of liquid
amines and energy-intensive regeneration processes associated with such chemisorbents make post-combustion processes a costly affair and demands alternative technologies.

1.2 Carbon Negative Strategies

Capture of CO₂ from point sources alone will not suffice to achieve the goals of the Paris climate accord. As per new data released, if we were to limit the rise of global average temperature to 1.5 °C over pre-industrial levels with a > 50% chance, no more than 210 Gt of CO₂ should be released into the atmosphere by the end of century.³ However, with a current emission rate of 40 Gt of CO₂ per year and no mitigation strategy in place, we are likely to deplete the allotted quota by 2021, and even with a mitigation strategy we will only be able to last till 2026.³ Considering the current scenario of CO₂ emissions and the lifespan of CO₂ in the atmosphere (30-95 years), an attempt to achieve the target would either require emissions to steeply decline or introduction of carbon-negative strategies (CNS) to make up for the excess CO₂ released. The former being improbable, we need to spend more time and resources to develop CNS. This will facilitate the process of minimizing the carbon footprint build over the years and also assist in restoring the carbon cycle in a shorter timescale.³ Bioenergy with carbon capture and sequestration (BECCS),²⁵ Biochar²⁶ and direct air capture (DAC)²⁷ are some of the prominent CNS approaches to have emerged in the last decade. Thanks to minimal land footprint and high technical potential as compared to other CNS, DAC has garnered interest over the last few years.²⁶,²⁷

1.2.1 Direct Air Capture

While all the point-source carbon capture technologies are aimed at reducing CO₂ content from flue gas streams before being released to the atmosphere, DAC aims at scrapping out existing CO₂ from the atmosphere to reduce the atmospheric CO₂ concentration. First coined by Lackner in 1999,²⁸ DAC has experienced enormous growth in the last decade with researchers focusing their work towards the development of new
materials and processes for this technology. Contrary to point-source capture technologies which are solely aimed at removing CO\textsubscript{2} from stationary sources, DAC has the potential to address both mobile as well as the fixed CO\textsubscript{2} sources. DAC technologies are not location-specific and hence can promote the development of on-site technologies that use CO\textsubscript{2} as feedstock, thus eliminating the need for storage and transportation. Absence of contaminants such as SO\textsubscript{x} (acidic oxides of sulphur), NO\textsubscript{x} (acidic oxides of nitrogen), and mercury that degrades the efficiency of sorbents used in flue gas processes, further facilitates the DAC process.

According to a nuclear regulatory commission (NRC) report, we need to rethink our strategy towards capture and long-term storage of CO\textsubscript{2}, as there are environmental risks and uncertainties associated with it including long-term monitoring, leakage, potentially induced seismicity and cost. This provides a motive to develop new DAC technologies that can enhance the use of CO\textsubscript{2} as feedstock and act as an alternative to CCS. Additionally, with more than half of emissions originating from mobile sources, it has become vital to look at technologies other than point-source capture and simultaneously develop alternative technologies to enable the mapped time frame of the recently concluded climate agreement. The environmental community has suggested the development of DAC and traditional flue gas capture technologies in parallel, targeted at optimization of the CO\textsubscript{2} scavenging process.

Though DAC of CO\textsubscript{2} appears to be a promising CNS, its implementation on an industrial scale presents a scientific challenge of the highest order. With CO\textsubscript{2} partial pressure being only 0.0004 bar in the air, a large volume of air needs to be processed in order to collect a meaningful amount of CO\textsubscript{2}. Design and size of the absorber for DAC is another important issue that needs to be addressed. For the same sorbent, the driving force in DAC of CO\textsubscript{2} would be 300 fold less than when compared to removal of CO\textsubscript{2} from flue gas. Thus, the volume of sorbent required for DAC of CO\textsubscript{2} would be hundreds of times the volume of
sorbent required for CO₂ removal from flue gas. Low concentration of CO₂ in the air and large volume of sorbent requirement makes the process costly. However use of CO₂ selective sorbents can mitigate the problem as discussed in the next section.

1.3 Sorbents for Direct Air Capture of Carbon Dioxide

1.3.1 Aqueous Alkali Sorbents

In 1999, Lackner envisioned the use of aqueous calcium hydroxide, Ca(OH)₂, solution for DAC of CO₂. Ca(OH)₂ solution reacts rapidly with CO₂ to form calcium carbonate, CaCO₃, (reaction 4) and is an effective sorbent as it can capture CO₂ even at very low concentrations (partial pressure of 0.0004 bar). Though it possesses strong binding affinity for CO₂ due to an energetically favoured chemical reaction, the use of Ca(OH)₂ solution for DAC is limited by the energy penalty associated with the complete cycle. CaCO₃ generated during the process needs to be separated, dried and calcined at 700 °C to generate CaO which is associated with an energy investment of 179 kJ/mol (reaction 5). Moreover, calcination of CaCO₃ generates a concentrated stream of captured CO₂ which requires a second sorbent thus adding to the cost.

\[ \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad \Delta H^\circ = -109 \text{ kJ/mol} \quad (4) \]

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad \Delta H^\circ = +179.2 \text{ kJ/mol} \quad (5) \]

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \Delta H^\circ = -64.5 \text{ kJ/mol} \quad (6) \]
Kraft’s process is another well-known solution based process for DAC of CO\textsubscript{2} capture (Figure 1.3).\textsuperscript{32} Contrary to Ca(OH)\textsubscript{2} solution used by Lackner, it uses caustic solutions such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) and is as efficient as the former (reaction 7). Moreover, it forms a highly soluble carbonate, unlike CaCO\textsubscript{3} formed during the use of Ca(OH)\textsubscript{2} solution, which reacts with Ca(OH)\textsubscript{2} to regenerate the caustic solution used in the capture process (reaction 8). With CaCO\textsubscript{3} being the by-product during the regeneration of caustic solutions, the calcination process cannot be skipped, accounting for the energy intensiveness of the overall process (reaction 9-10).\textsuperscript{33} The high energy input coupled with the employment of two different sorbents for efficient DAC of CO\textsubscript{2} limits the use of solution based processes and demands new sorbents.
Absorber:

\[ 2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \quad \Delta H^\circ = -109.4 \text{ kJ/mol} \quad (7) \]

Causticizer:

\[ \text{Na}_2\text{CO}_3 + \text{Ca} (\text{OH})_2 \rightarrow 2\text{NaOH} + \text{CaCO}_3 \quad \Delta H^\circ = -5.3 \text{ kJ/mol} \quad (8) \]

Calciner:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad \Delta H^\circ = +179.2 \text{ kJ/mol} \quad (9) \]

Slaker:

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \Delta H^\circ = -64.5 \text{ kJ/mol} \quad (10) \]

1.3.2 Solid Sorbents

Wide range of operational temperature (from ambient air to 700 °C), reduced waste during cycling and ease of handling makes solid sorbents more preferential for DAC as compared to liquid sorbents.\textsuperscript{34} Over the last decade, a number of solid sorbents have been considered for DAC such as, solid alkali oxides and carbonates,\textsuperscript{35-39} supported alkali carbonates\textsuperscript{40-43} and organic-inorganic hybrid sorbents.\textsuperscript{35-39} Efficient solid sorbents for DAC of CO\textsubscript{2} must exhibit high CO\textsubscript{2} uptake at partial pressure comparable to that of CO\textsubscript{2} in the air (0.0004 bar). They must have high selectivity for CO\textsubscript{2} over N\textsubscript{2} (S\textsubscript{CN}) and H\textsubscript{2}O (S\textsubscript{CW}) as they are the main competing gases in the air. Efficient DAC of CO\textsubscript{2} from air requires S\textsubscript{CN} > 2000 (; in air, CO\textsubscript{2} (400 ppm, 0.04%) over N\textsubscript{2} (ca. 80%), CO\textsubscript{2}:N\textsubscript{2} = 1:2000) and S\textsubscript{CW} > 100. Apart from high uptake and selectivity, moderate heat of adsorption for CO\textsubscript{2} (Q\textsubscript{st}) (40-60 kJ/mol) is equally important for the energy economic capture processes. Moderate Q\textsubscript{st} ensures low regeneration energy conditions, thus minimising the energy penalty associated with the CO\textsubscript{2} capture process.
Along with good sorption properties (i.e. high uptake capacity, moderate CO$_2$ $Q_{st}$ and high selectivity), other factors also play a crucial role in the selection of the sorbent for DAC of CO$_2$. Amongst them, economic criteria is the most important one and have to always be taken into account, not only with regards to the costs of synthesis but also to the size of the equipment (i.e. the volume of the adsorbent needed). Robust sorbents exhibiting good physical (thermal and stability towards humidity) and chemical stability are preferred as they ensure long shelf-life and promotes wide range of working conditions (i.e. temperature, humidity and composition of the gas). To summarize, an ideal sorbent for DAC of CO$_2$ should have high CO$_2$ uptake capacity at low pressure, high selectivity for CO$_2$, fast adsorption/desorption kinetics, good mechanical properties, high hydrothermal and chemical stability, as well as low costs of synthesis.

A. Bulk Alkali Carbonates

Solid inorganic bases including alkaline oxide, hydroxides and carbonates such as calcium oxide (CaO), Ca(OH)$_2$, sodium oxide (Na$_2$O), NaOH, sodium carbonate (Na$_2$CO$_3$) and KOH have been widely studied for DAC of CO$_2$ owing to their strong chemical reactivity with CO$_2$. Steinfeld was the first to report the use of solid CaO and Ca(OH)$_2$ for DAC of CO$_2$. He studied the DAC performance of these materials using a thermogravimetric analyser (TGA) with 500 ppm of CO$_2$ under both dry and wet conditions. Optimum carbonation reaction was observed in the temperature range of 300 °C - 450 °C and under wet conditions, while no reaction occurred at temperatures below 300 °C. Improved performance under wet conditions was attributed to the adsorption of CO$_2$ on the surface by hydroxide (OH$^-$) groups. Steinfeld also examined Na-based thermochemical cycles instead of Ca-based ones, however, they proved to be inefficient due to the slow carbonation rate. Further, with an energy input of 10.6 MJ for every mole of CO$_2$ captured with capture process occurring at 375 °C and calcination of carbonate at 875 °C, Ca-based thermochemical cycles require
higher energy input than alkali solution based scrubbing process. Heating of ambient air to 375 °C contributes towards the high energy requirement and has inspired the scientific community to look for alternatives.35,38,39

B. Supported Alkali Carbonates

In an attempt to increase the efficiency and reduce the operational cost associated with alkali carbonates, supported alkali carbonates were developed and studied for DAC. Solid supports used in supported alkali carbonates enhance the exposed alkali surface area and hence improve the carbonation rate. Przepiorski studied the DAC performance of porous carbons doped with CaO and magnesium oxide (MgO) for 2000 ppm of CO₂ under both dry and wet conditions.40 Similar to solid CaO, performance of doped porous carbon also improved under humid conditions. Enhancement in performance under humid conditions was attributed to the formation of a water film on the surface which acted as a trap for CO₂ and mediated the reaction of CO₂ with the sorbent material. Proven to be efficient in removal of CO₂ from flue gas, Veselovskaya and Jones investigated composites of potassium carbonate (K₂CO₃) and γ-alumina (γ-Al₂O₃) for DAC of CO₂.41 The K₂CO₃/γ-Al₂O₃ composite used by Veselovskaya et al. had potassium loading equivalent to 21-23% of K₂CO₃ and can capture 4.0-4.9 wt % of CO₂ when exposed to ambient air. Further Christopher W. Jones used γ-Al₂O₃ impregnated with 5 and 10 wt % potassium (AlK5 and AlK10) for DAC studies and compared its performance with benchmark amine-based γ-Al₂O₃ sorbents. At 400 ppm CO₂, AlK5 and AlK10 had an uptake of 0.86 and 0.78 mmol/g and was slightly lower than the benchmark material Al_PEI35, which had an uptake of 0.95 mmol/g. A number of other studies using K₂CO₃/Y₂O₃, K₂CO₃/activated carbon, K₂CO₃/zeolite 5A, have also been carried out for DAC of CO₂.42,43 The results clearly demonstrate the synergistic relationship between the alkali carbonate and the solid support regarding capture of CO₂, at conditions
relevant to DAC. However high regeneration conditions and the cost factor precludes their use for DAC of CO₂.

C. Amine Functionalized Solid Sorbents

Solid-supported amine materials, also known as organic-inorganic hybrid sorbents, are one of the most widely investigated adsorbent materials for DAC of CO₂. They exhibit high CO₂ Q_{st} and high S_{CN} (> 2000). These desirable properties can be attributed to chemisorption that results in formation of strong chemical bonds between CO₂ and the amino group. First introduced by Global Thermostat in 2007, use of these materials was initially demonstrated by Jones and co-workers in 2008. Hyperbranched aminosilicas were used for the extraction of CO₂ from a simulated gas mixture mimicking atmospheric conditions. In 2010, Sayari and co-workers further illustrated the use of amine-grafted materials for DAC. Considered to be more efficient than supported alkali carbonates, the performance of these sorbents relies heavily on the amounts of free amine. As per the reaction mechanism proposed by Caplow and Danckwerts, capture of each CO₂ requires two free nitrogen atoms and hence these materials can achieve a maximum uptake of 0.5 mole of CO₂ per mole of N. The presence of free nitrogen being a primary requirement for the chemical reaction to proceed, only primary and secondary amines can be used under dry conditions.

This class of solid sorbents can broadly be categorised into three subclasses: a) class 1 sorbents, synthesized by impregnating amines into the pores of a support, b) class 2 sorbents, consisting of amines covalently bonded to the walls of porous materials and c) class 3 sorbents, where amine monomers have been polymerized in situ, resulting in polyamine structures tethered to the walls (Figure 1.4).

The first example employing a class 1 sorbent to address DAC of CO₂ was reported by Choi, Gray and Jones. They used a poly(ethylimine)(PEI)-impregnated oxide sorbent
obtained by impregnating commercial silica with 45% PEI to capture CO$_2$ from simulated air. PEI amine was preferred over others because of its properties such as low molecular weight, high amine density and good stability under temperature swing adsorption (TSA) or vacuum swing adsorption (VSA). The sorbent exhibited an exceptional uptake of 2.36 mmol/g in the first cycle, but its performance deteriorated gradually and was reduced by 30% after 4 cycles.

Subsequently, in a quest to obtain a better material with improved DAC capability, PEI was combined with a number of other silicas such as $\gamma$-Al$_2$O$_3$, mesoporous silica or Santa Barbara amorphous type material (SBA-15). An attempt to further enhance thermal and cyclic stability was also made where PEI was mixed with a number of additives such as aminopropyl organosilanes (APS), or tetrapropylorthotitanate (TT), (Figure 1.5). Based on the DAC results obtained for a PEI-impregnated oxide sorbent, Olah, Prakash and co-workers illustrated the use of PEI mixed with PEG for improved DAC performance. Working
along similar lines, Meth illustrated the use of 10% poly(ethylene glycol) (PEG), 42.5% PEI and 47.5% fumed silica as the optimum mix for enhanced performance (Table 1.1).

In order to evaluate the impact of covalently bonded amines for DAC (class 2 sorbents), Sayari functionalized PE-MCM-41 (pore expanded mobil composition of matter no.41) with diethylenetriamino organosilanes (DT) and tested it for DAC of CO₂. The sorbent exhibited an uptake of 0.98 mmol/g of CO₂ at 25 °C and 400 ppm. To assess the performance under practical performance conditions, dynamic breakthrough experiments were carried out and it revealed an uptake of 0.9 mmol/g for CO₂ and negligible uptake for O₂ or N₂, thus imparting high S_CN which is essential for DAC. However, due to the presence of both primary and secondary amines in DT, the contribution of different types of amine towards DAC performance was difficult to determine.

![Molecular structures of commonly used amines for class 1 and class 2 DAC sorbents.](image)

**Figure 1.5.** Molecular structures of commonly used amines for class 1 and class 2 DAC sorbents. [Reproduced with permission from reference 27].

Later, Jones and co-workers carried out a comprehensive study to understand the role of amine structures on CO₂ adsorption and ensuing DAC performance. Adsorbents
(organosilane) containing only one type of amine group and common loading was prepared and investigated. The study revealed an amine efficiency of 0.2 for primary amines and 0.07 for secondary amines. It was further illustrated that amine efficiency of primary amines can be enhanced to 0.3 by simply increasing the amount of organic loading. Better performance by primary amines as compared to secondary amines under DAC conditions was attributed to the entropic effect rather than the previously thought enthalpic effect, as both types of amine exhibit similar heats of adsorption at low loading conditions. Despite the proven efficacy of grafted amines for DAC, they suffer from their own drawbacks. The desorption stream produced by these sorbents is dilute and requires steam stripping for concentrating the stream. Sometimes, steam stripping can lead to the loss of tethered amine groups, thus reducing the sorbent’s efficiency.

In-situ polymerization of amine monomers yields polyamine structures tethered to the walls and offers another prospective sorbent for DAC. Categorised as a class 3 sorbent, its use for DAC was first illustrated by Jones and co-workers. They used aziridine, a 3-member cyclic compound containing nitrogen as monomer, to obtain hyperbranched aminosilica (HAS) sorbents with different loadings (Figure 1.6). During the process, maximum nitrogen loading of 9.9 mmol of N/g was achieved, a value better than most of the grafted samples. Further when tested for DAC, it exhibited a CO$_2$ uptake of 1.72 mmol/g at 25 °C, significantly higher than the previous reports of amine-grafted samples.

![Molecular structures of class 3 amine sorbents for DAC.](image)

**Figure 1.6.** Molecular structures of class 3 amine sorbents for DAC. 27
Table 1.1. DAC performance of class 1 and class 2 sorbents.

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<th>CO₂ (ppm)</th>
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<th>Adsorption capacity (mmol of CO₂/g of sorbent)</th>
<th>Amine efficiency (mmol of CO₂/mmol of N)</th>
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Motivated by the results obtained for aziridine, Jones in collaboration with Shantz polymerised Z- (l-lysine) over anaminopropyl grafted silica and subjected it to DAC studies. With amine content between 2.75 to 5.18 mmol of N/g, a value much lower than the aziridine based sorbent, the materials exhibited moderate CO\textsubscript{2} uptake with 0.6 mmol/g of CO\textsubscript{2} at 25 °C for the best performing lysine loaded sorbent. Though amine supported sorbents have proved their efficacy for DAC, new alternatives are required due to the drawbacks of these class of sorbents. High regeneration temperature (> 100 °C), loss of tethered amines during the sorption-desorption process followed by subsequent loss in performance and efficiency and high manufacturing cost involved in manufacturing these sorbents motivates researchers to look for new technologies.

D. Zeolites

Zeolites are crystalline, microporous aluminosilicate minerals commonly used as commercial adsorbents and catalysts. Type X and A zeolites modified by addition of cations are widely studied for CO\textsubscript{2} capture processes. Incorporation of cations into the zeolites leads to strong binding sites for CO\textsubscript{2} due to a strong interaction between CO\textsubscript{2} and the cations. Zeolite Na-X (or 13X), an example of cation modified zeolite, is considered to be one of the benchmark CO\textsubscript{2} physisorbents with moderate CO\textsubscript{2} \(Q_{st}\) (ca. 45 kJ/mol) and suitable for PSA regeneration, unlike chemisorbents. Benchmark \(S_{CN}\) (420) and high CO\textsubscript{2} uptake at low CO\textsubscript{2} partial pressures exhibited by Zeolite 13X can be attributed to the presence of sodium open metal sites and narrow pore channels. Promising CO\textsubscript{2} sorption properties makes zeolites an ideal sorbent for CO\textsubscript{2} capture applications.

Despite the high adsorption capacity and selectivity for zeolites exhibited by pure gas isotherms, its separation performance in real applications is handicapped due to the presence of water. Exposure to moist gases or humid conditions leads to reduced CO\textsubscript{2} uptake due to alteration of the electric field reducing the strength of interaction between the quadrupole of
CO₂ and the cations. The presence of even very small amounts of water greatly reduces the adsorption performance of zeolites. This high affinity toward moisture significantly impacts regeneration of zeolites and temperatures as high as 300 °C might be required to remove the strongly bound water molecules. High energy penalty associated with regeneration of zeolites diminished its potential for majority of CO₂ capture applications.

1.4 Metal Organic Materials

Metal-organic materials (MOMs) also known as porous coordination networks, (PCNs); porous coordination polymers, (PCPs); or metal-organic frameworks, (MOFs) are widely touted as energy-efficient alternatives to traditional amine based sorbent owing to their reversible binding-aided ease of regeneration. Research on MOMs has drawn huge attention in recent years largely due to the combination of permanent porosity and structural tunability. This dual combination of features allows MOMs to have emerged as a distinctive class of porous materials for studying a myriad of applications viz. gas separation, gas storage, catalysis, drug delivery, and sensing. Self-assembled from single metal ion or metal cluster nodes (molecular building blocks, MBBs) and multifunctional ligands, these crystalline materials essentially have potential void spaces which are amenable to design. Designed topologies (square lattice (sql), primitive cubic (puc), diamond (dia), and twisted boracite (tbo)) result from the appropriate choice of MBBs and ligands, while the modularity of both components permits systematic variation of pore size and pore chemistry in accordance with crystal engineering principles.

1.4.1 Crystal Engineering: a Systematic Approach

Crystal engineering, first coined by G. M. J. Schmidt, is defined as the field of chemistry that studies the design, properties and applications of crystals. Since, the advent of X-ray beams by W. C. Roentgen in 1895, and observation of x-ray diffraction by Max Von Laue in 1912 the single-crystal X-ray crystallographic structural determination has
represented an active area of research with the structure of table salt being analysed as early as 1914, whereas the growth of crystal engineering and crystal design were lagging far behind until 1988. Despite the general realization that diverse aspects of solid-state chemistry could only be resolved through an insightful exploration of structure-function relationships, John Maddox in his 1988 Nature editorial remarked “One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition.”\textsuperscript{99} This provocative comment exposed the situation and highlights an issue that continues to pose a challenge of immense scientific and technological relevance. As envisioned by Feynman, “What would the properties of materials be if we could really arrange the atoms the way we want them?”\textsuperscript{100}, such an exciting dream generally remains to be achieved, at least in terms of molecular self-assembly in the crystalline state. However, it has triggered a seemingly exponential growth in research activities related to crystal design and crystal engineering as their implications reach domains well beyond materials science, such as solvent-free synthetic chemistry and drug design and pharmaceutical development.\textsuperscript{101-109}

Through a series of seminal contributions focused upon using the Cambridge Structural Database (CSD)\textsuperscript{110} for analysis and interpretation of noncovalent bonding patterns in organic solids, Desiraju\textsuperscript{111-113} and Etter\textsuperscript{114,115} introduced the concept of supramolecular synthons\textsuperscript{113} and established hydrogen bonds as one of the most widely observed noncovalent interactions in the context of crystal engineering. These early studies to decipher H-bonding as a key crystal design element led us to address the challenges/opportunities embodied by crystal engineering with particular importance on how supramolecular concepts are crucial to understand supramolecular isomerism and superstructural diversity in the context of MOMs.

MOMs represent how crystal engineering has evolved as a paradigm for the design of new supramolecular structures, with predictable stoichiometry and modular architecture. In
this context, the work of Wells\textsuperscript{116} concerned with the overall structure determination of inorganic solids serves as a reference point, since he defined crystal structures in terms of their topology by reducing them to a series of ordered points (nodes) of a certain geometry (tetrahedral, trigonal planar, etc.) connected to a fixed number of other points.\textsuperscript{117} The resulting network structures, which can also be mathematically derived, can be either discrete (zero-dimensional) polyhedra or infinite (one, two, and three dimensional) periodic architectures. Richard Robson’s seminal contributions extended Wells work on inorganic network structures into the realm of MOMs.\textsuperscript{118-122} In this context, the resultant “node and spacer” approach has been particularly successful at the formation of predictable network architectures.

\textbf{Figure 1.7.} Schematic representation of some of the simple network architectures structurally characterized for MOMs: (a) 1D zigzag chain, (b) 1D ladder, (c) 2D square grid, (d) 2D honeycomb, (e) 3D hexagonal diamondoid, (f) 3D octahedral.

This approach, whereby a node is 3-connected (3-c) or greater and a linker is 2-connected (2-c), serves as a blueprint for the rational construction of MOMs with 0D (e.g.
nanoballs or, MOPs,\textsuperscript{123,124} 1D (e.g. chains, ladders), 2D (e.g. layered sheets), or 3D (e.g. MOMs)\textsuperscript{125} periodicity. Figure 1.7 illustrates some of the simple network architectures for MOMs assembled from commonly available metal moieties and linking them with linear “spacer” ligands. From a materials design standpoint, each of the networks illustrated in Figure 1.7 is constructed from at least two components, i.e. the node and the spacer. Therefore, such individual components can be pre-selected for chemically tailoring the resultant network solids. These network structures can therefore serve as blueprints for the construction of modular framework structures with a wide variety of rationally introduced chemical components. Explored in 1988 by Ermer, 1,3,5,7-adamantanetetraacetic acid is considered as being prototypical for self-assembled dia networks.\textsuperscript{126,127} Diamondoid architectures using a tetrahedral metal ion (Zn\textsuperscript{2+} or Cd\textsuperscript{2+}) as the node and cyanide ligands (CN\textsuperscript{−}) as the linker represent classical examples of dia topology coordination polymers. [Cu(2,5-dimethylpyrazine)\textsubscript{2}(PF\textsubscript{6})\textsubscript{2}] represents one of the first examples of a metal-organic diamondoid structure,\textsuperscript{128} and the related compound [Cu(bipy)\textsubscript{2}(PF\textsubscript{6})\textsubscript{2}] (bipy = 4,4′-dipyridyl) was reported shortly thereafter,\textsuperscript{129} both structures typifying the modular nature of crystal engineering derived topologies.

![Figure 1.8](image)

**Figure 1.8.** a) Interpenetrated square grid Zn(bipy)\textsubscript{2}SiF\textsubscript{6}.2H\textsubscript{2}O; b) Prototypal square grid [Cd(bipy)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}].
Around the same time, Robson exemplified the use of “node and linker” approach to obtain the prototypical square grid, \([\text{Zn(bipy)}_2(\text{H}_2\text{O})_2]^{2+}\) sheets exhibiting 2D-to-3D interpenetration with \(\text{SiF}_6^{2-}\) anions occupying 3D channels as shown in Figure 1.8a.\(^{130}\) By using \(\text{o-dibromobenzene}\) as solvent, Fujita was able to synthesize the first non-interpenetrated square grid, \([\text{Cd(bipy)}_2(\text{NO}_3)_2]\), in 1994 as depicted in Figure 1.8b.\(^{93}\) While the interactions between the linker and the aromatic guests clathrated between the square channels led to formation of a non-interpenetrated structure, the length of the organic linkers controlled the pore size (\(\sim 20 \text{ Å}\)). Other examples have subsequently been reported based on other transition metals, including \(\text{Co}^{2+}\), \(\text{Ni}^{2+}\), and \(\text{Zn}^{2+}\).\(^{131}\) Although these 4,4′-dipyridyl spacer ligands derived 2D coordination networks are isostructural within the coordination grid (diagonal dimension \(\sim 13 \times 13 \text{ Å}\)), the crystal structures can vary according to the manner in which the networks stack relative to each other (interlayer separations range from 4 to 8 Å, concomitant with varying degrees of clathration and interlayer interactions).

![Figure 1.9](image)

**Figure 1.9.** Representative MBBs used as nodes, a) \([\text{M(pyridyl)}_4(\text{L})_2]\) square/octahedron; b) \([\text{M}_2(\text{O}_2\text{CR})_4(\text{L})_2]\) square/octahedron; c) \([\text{Zn}_4(\mu_4-\text{O})(\text{O}_2\text{CR})_6]\) octahedron; d) \([\text{M}_3(\mu_3-\text{O})(\text{O}_2\text{CR})_6]\) trigonal prism.

Yaghi and co-workers reported the first permanently porous square grid, \([\text{Zn(bdc)}(\text{DMF})_2(\text{H}_2\text{O})]\) (bdc = 1,4-benzenedicarboxylate, DMF = dimethylformamide), also known as MOF-2.\(^{94}\) Contrary to the work of Robson and Fujita, they used square
paddlewheel MBBs and dicarboxylate linkers instead of dipyridyl linkers and isolated neutral square grids exhibiting porosity. Permanent porosity was measured using 77K N₂ and revealed a BET surface area of 310 m²/g.

Since the discovery of porosity in MOMs \(^{94,132}\) constructed from linear dipyridyl linkers and 4-c or 6-c MBBs, e.g. \([\text{M(pyridyl)}_4(L)_2]\), attempts have been made to obtain MOMs with ultra-high porosity. Use of dicarboxylate linkers and robust metal cluster MBBs, e.g. \([\text{M}_2(O_2CR)_4(L)_2]\) square paddlewheels/octahedra\(^{133}\) \([\text{Zn}_4(\mu_4-O)(O_2CR)_6]\) octahedra\(^{83}\) and \([\text{M}_3(\mu_3-O)(O_2CR)_6]\) trigonal prisms\(^{134}\) (Figure 1.9), afforded MOMs with high surface area and permanent porosity. MOF-5 (IRMOF-1 i.e. \([\text{Zn}_4O](\text{bdc})_3\); pcu topology)\(^{135}\) and HKUST-1 (\([\text{Cu}_3(\text{btc})_2(H_2O)_3]\); tbo topology) (btc = 1,3,5-benzenetricarboxylate) (HKUST = Hong Kong University of Science & Technology)\(^{97}\) exhibit high surface area of ca. 3,000 m²/g and 1,900 m²/g, respectively (Figure 1.10). Further, by systematic variation of linker length and fine-tuning the pore chemistry of MOMs, crystal engineering has led to MOM platforms with the potential to address applications such as CO₂ capture from flue-gas and DAC. High \(S_{\text{CN}}\) required to capture trace CO₂ may arise from two factors: favourable adsorption thermodynamics or fast kinetics. Thermodynamic \(S_{\text{CN}}\) is dictated by the energetics of interactions between the adsorbate surface and CO₂ and can be determined experimentally.

![Figure 1.10](image-url) Prototypical high surface area MOMs, a) HKUST-1; b) MOF-5.
by measuring $Q_{st}$. On the contrary, materials with pore size close to the kinetic diameter of CO$_2$ exhibit kinetic $S_{CN}$ because of differential diffusion rates and size exclusion (kinetic diameters for adsorbents: CO$_2$ = 3.3 Å; CH$_4$ = 3.76 Å; N$_2$ = 3.64 Å). In principle, CO$_2$ $Q_{st}$ is directly proportional to the amount of energy required to regenerate the adsorbent after each CO$_2$ sorption cycle. Current efforts are largely focused on enhancing the CO$_2$ binding affinity in MOMs as reflected by increased CO$_2$ $Q_{st}$ values. Reported strategies include amine grafting, incorporation of unsaturated metal centres, insertion of extra-framework cations/anions, framework interpenetration, construction of size/shape specific pores, polarized pore walls and introduction of inorganic pillars.$^{76,77}$ Amongst these, introduction of unsaturated metal centres (UMCs) and amine functionalised sites (AFS), either during MOM synthesis or via post-synthetic modification, are two approaches along with the relatively underexplored strategy of tuning pore size and pore chemistry among MOMs with SMCs.

### 1.4.2 Carbon Capture in MOMs with Unsaturated Metal Centres

UMCs often referred to as open metal sites, are one of the most commonly employed strategies for promoting selective gas sorption by physisorbent materials. After sorbent synthesis, following activation via vacuum and/or heating, UMCs in MOMs are generated by the removal of coordinated guest solvent molecule(s). Once the guest solvent molecules are removed, CO$_2$ molecules owing to high quadruple moment (43.0 $\times$ 10$^{-27}$ esu$^{-1}$cm$^{-1}$ i.e. 1.34 $\times$ 10$^{-39}$ Cm$^2$), have high affinity towards the UMCs, therefore, amplifying CO$_2$ capture ability. $S_{CN}$ as well as its surface binding energy is hugely impacted by the density of UMCs, as in situ neutron diffraction studies have firmly established that exposed metal ions function as the CO$_2$ binding sites.$^{136,137}$

Strong binding of CO$_2$ molecules to UMC makes a strong case for UMC-rich MOMs for carbon capture studies. In this context, M-MOF-74/CPO-27-M/M$_2$(dobdc) platform (where, dobdc = 2,5-dihydroxy 1,4-benzenedicarboxylate, and M = Ni$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mn$^{2+}$,
Co$^{2+}$, Cu$^{2+}$ and Mg$^{2+}$\textsuperscript{138,139} is widely studied as high performing CO$_2$-selective physisorbents with capture capacities up to 8.1 mmol/g under ambient conditions (298K and 1 bar). Amongst all the variants, Mg-MOF-74 (Figure 1.11), comprising of microporous cylindrical channels of ca. 11 Å replete with high density of UMCs, has been comprehensively studied for carbon capture owing to its benchmark CO$_2$ uptake at 0.15 bar (5.35 mmol/g) and moderate CO$_2$ $Q_{st}$ (47 kJ/mol). Thanks to the high density of UMCs and strong ionic character of the Mg-O bonds formed between the UMCs and CO$_2$, Mg-MOF-74 exhibited $S_{CN}$ of ca. 182\textsuperscript{140,141} under flue gas conditions, a record value for MOMs at that point of time and was comparable to benchmark inorganic physisorbents such as Zeolite 13X.

Despite the high adsorption capacity and selectivity for Mg-MOF-74 exhibited by pure gas isotherms, its separation performance in real applications is handicapped due to the presence of water. Exposure to moist gases or humid conditions leads to reduced CO$_2$ capture due to competitive water sorption and reduction in the number of active sites for CO$_2$ binding.\textsuperscript{142} This has been demonstrated through breakthrough experiments using simulated wet feed experiments (20:80 CO$_2$/N$_2$ at 70% RH). The CO$_2$ uptake performance for Mg-MOF-74, Ni-MOF-74 and Co-MOF-74 suffered steep decline during wet feed experiments and posed poor recyclability and regenerability just after one cycle. Further studies have revealed that exposure to moist conditions also leads to loss in structural integrity of the Mg-MOF-74 framework.\textsuperscript{143,144} Lack of stability in conjunction with reduced CO$_2$ uptake performance in the presence of humidity and $S_{CN} < 2000$ precludes the use of Mg-MOF-74 for DAC of CO$_2$.

In an attempt to identify a suitable physisorbent that efficiently captures trace amount of CO$_2$, many other UMC-based MOMs have been investigated. Some of the well-known MOMs with UMCs as the sole functionality investigated thus far include HKUST-1,\textsuperscript{97,145} mesoporous MIL compounds, (MIL = Materials Institut Lavoisier) such as MIL-100(Cr)
A number of (3,24)-c \textit{rht}-type (\textit{rht} = rhombicuboctahedra triangles) UMC MOMs, e.g. Cu-TPBTM \([\text{Cu}_{24}(\text{TPBTM})_8(\text{H}_2\text{O})_{24}]_n\) (TPBTM = N,N,N’-tris(isophthalyl)-1,3,5-benzenetricarboxamide), PCN-61 \([\text{Cu}(\text{H}_2\text{O})]_3(\text{btei})\cdot 5(\text{DMF})4(\text{H}_2\text{O})]_n\) (btei = 5,5’,5’’-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate), PCN = porous coordination network) and Cu-TDPAT \([\text{Cu}_3(\text{TDPAT})(\text{H}_2\text{O})_3]_n\) (TDPAT = 2, 4, 6-tris (3, 5-dicarboxyphenylamino)-1, 3, 5-triazine), also exhibit considerable CO\textsubscript{2} uptake capacity\textsuperscript{149-151} However, with moderate \(Q_{st}\) (40-50 kJ/mol) and low \(S_{CN}\) (< 50) these materials have not been able to deliver the desired performance with respect to CO\textsubscript{2} capture from mixtures comprising low concentrations of CO\textsubscript{2} (0.0004 bar for DAC conditions).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image11}
\caption{Crystal structure of a UMC-based MOM, Mg-MOF-74.}
\end{figure}

### 1.4.3 Carbon Capture in MOMs with Amine Functionalised Sites

The grafting of nitrogen-containing functional groups, particularly amines onto the Connolly surfaces of porous adsorbents has evolved as a model paradigm to enhance the CO\textsubscript{2} adsorption capacity and selectivity. This approach is similar to the post-synthetic
modification (PSM) of other classes of porous materials such as amine modified silicas and zeolites. However, the crystalline and modular nature of MOMs offers control at molecular level enabling modulation of the amine-driven CO$_2$-selective adsorption performance.$^{82,152,153}$ For MOMs, there are at least two amine incorporation methods that are practised. First involves covalent modification of the participating ligands with amine groups (primary, secondary and tertiary amino groups), prior to MOM synthesis, hence, termed as pre-synthesis functionalisation. Incorporation of pendant amino groups that project into the guest-accessible voids of MOMs can greatly enhance $S_{CN}$ over their parent structures. This is an appealing approach as aromatic amine based linker ligands are cheap and commercially available, for example, 2-amino 1,4-benzenedicarboxylate (NH$_2$-bdc), is a widely popular dicarboxylate linker ligand that has been demonstrated to generate a wide variety of amine-functionalised frameworks. A typical example lies with IRMOF-3 [Zn$_4$O(NH$_2$-bdc)$_3$], a prototypical variant of IRMOF-1,$^{83}$ i.e. MOF-5$^{135}$ platform. At 298 K and 1.1 bar, IRMOF-3 exhibits a CO$_2$ saturation uptake of 1.2 mmol/g, higher than its parent IRMOF-1 [Zn$_4$O(bdc)$_3$] (1.1 mmol/g), despite the reduction in BET surface area from 2833 m$^2$/g to 2160 m$^2$/g.

Other examples of MOMs with amine-rich ligands studied for CO$_2$ sorption include

MIL-101(Cr)-NH$_2$  [Cr$_3$(O)F(NH$_2$-bdc)$_3$(H$_2$O)$_2$]$_n$ (50kJ/mol),$^{154}$ CAU-1 [Al$_4$(OH)$_2$(OCH)$_3$i(NH$_2$-bdc)$_3$] (48kJ/mol),$^{155}$ bio-MOF-11 [Co$_2$(ad)$_2$(CO$_2$CH$_3$)$_3$] (ad = adenine) (45kJ/mol),$^{156}$ [Co$_2$(OH)$_2$(btca)$_2$] (btca = benzotriazole-5-carboxylic acid) (42.9kJ/mol),$^{157}$ [Zn$_2$(tcpt)OH] (tcpt = 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine) (40.9kJ/mol),$^{158}$ Zn$_2$(Atz)$_2$(ox) (Atz = 3-amino-1,2,4-triazole; ox = oxalate) (40.8kJ/mol),$^{159}$ NH$_2$-MIL-53(Al)$^{160}$ i.e. [Al(OH)(NH$_2$-bdc)] (38.4kJ/mol), rht-MOF-9 [Cu$_3$(TDCPAH)] (TDCPAH = 2,5,8-tris(3,5-dicarboxyphenylamino)-1,3,4,6,7,9,9b-heptaazaphenalene) (32kJ/mol),$^{161}$ Uio-66-NH$_2$[Zr$_6$O$_4$(OH)$_4$(NH$_2$-bdc)$_6$] (28kJ/mol),$^{162}$ MAF-66 [Zn(Atz)$_2$]
(26kJ/mol).\textsuperscript{163} The numbers in parentheses denote the CO$_2$ $Q_{st}$ at low coverage. Interestingly, 2-amino 1,4-benzenedicarboxylate (NH$_2$-bdc) was noted as the most commonly used ligand under this AFS approach, however exhibited only a low $S_{CN}$ and ensuing separation performances in the cases of UiO-66-NH$_2$, NH$_2$-MIL-53 (Al), CAU-1, MIL-101(Cr)-NH$_2$, Zn$_2$(NH$_2$-bdc)$_2$(TED),\textsuperscript{164} Ni$_2$(NH$_2$-bdc)$_2$(TED),\textsuperscript{165} and In(OH)(NH$_2$-bdc).\textsuperscript{166}

Another approach to this use of amine-functionalized organic ligands includes chemical modification of MOMs after the formation of crystalline network materials, i.e. post-synthetic modification (PSM) of MOMs. The PSM routes have emerged successful to furnish MOMs with high $Q_{st}$ for CO$_2$ (ca. 70-130 kJ/mol at low coverage) and high $S_{CN}$ parameters. Typically, the interactions between the localised amine dipoles and the quadrupoles of CO$_2$ would induce enough dispersion and electrostatic forces to enhance CO$_2$ adsorption and separation abilities of MOMs. The post-synthetic incorporation of amino groups on to UMC-rich MOMs can help the resultant NH$_2$-functionalised MOMs overcome the limitations of physisorbent materials whereby CO$_2$ sorption performance can be retained in the presence of moisture (vs. UMC-rich cases). However, abundance of amino groups projecting into the voids inherently changes the sorbent wall-CO$_2$ interactions as chemisorption comes into play, which results in elevated energy requirements for sorbent bed regeneration. For example, 60% UMC functionalisation with ethylenediamine coordinated to the UMCs in CPO-27-Mg (also known as Mg-MOF-74) led to isolation of CPO-27-Mg-e,\textsuperscript{167} a chemisorbent with high CO$_2$ $Q_{st}$ value of ~ 132 kJ/mol. While there is reduction in the saturation capacity at 298 K, as compared to that of the parent CPO-27-Mg, the amine-on-UMC introduction strategy appeared indicative of enhancing sorbate-CO$_2$ interactions reflected by a drastic increment (~ 2.8 times) in CO$_2$ $Q_{st}$.

X.-M. Chen and co-workers could react hydrazine with UMCs of Mg-MOF-74 to form [Mg$_2$(dobdc)(N$_2$H$_4$)$_{1.8}$],\textsuperscript{168} setting record CO$_2$ capture performance at DAC relevant
conditions (3.89 mmol/g) and post-combustion relevant conditions (5.18 mmol/g). These benchmark CO\textsubscript{2} uptakes could be attributed to the presence of “ultrahigh” concentration of hydrazine-derived free amino groups (6.01 mmol/g or 7.08 mmol/g) that enable reversible carboxylic acid formation on reacting with adsorbed CO\textsubscript{2}. Despite being a chemisorbent with high CO\textsubscript{2} $Q_{st}$ ($\sim$ 90 kJ/mol), the amine-tethered Mg-MOF-74 required a lower regeneration temperature under temperature-vacuum swing adsorption (TVSA) when compared to other alkylamine functionalised MOMs. To afford zero compromise in CO\textsubscript{2} sorption/trace capture performance and easier regeneration than MEA under TSA, development of such amine-appended MOM chemisorbents seemed a potential approach.

An expanded analogue of dobdc (dobpdc = 4,4′-dihydroxy-(1,10-biphenyl)-3,3′-dicarboxylic acid) was used to first report a microporous MOM, Mg\textsubscript{2}(dobpdc), with $\sim$ 18.4 Å wide pore window and then implant N,N′-dimethylethylenediamine (mmen) to afford mmen-Mg\textsubscript{2}(dobpdc).\textsuperscript{160} mmen-Mg\textsubscript{2}(dobpdc), despite offering a small BET surface area of 70 m\textsuperscript{2}/g could notch sharp 298 K capture performances; 2.05 mmol/g at 0.0004 bar, 3.13 mmol/g at 0.15 bar and 3.86 mmol/g at 1 bar, consistent with chemisorption phenomena associated with the initial CO\textsubscript{2} $Q_{st}$ of $\sim$ 71 kJ/mol. Until CO\textsubscript{2} loading $\sim$ 2.5 mmol/g, coordination event for all the accessible –NH\textsubscript{2} sites reach a saturation to trigger a rapid decline in CO\textsubscript{2} binding affinity (sudden drop in CO\textsubscript{2} $Q_{st}$ values to $\sim$ 23 kJ/mol). More PSM approaches exercised upon the same Mg\textsubscript{2}(dobpdc) led to the compounds = dmen-Mg\textsubscript{2}(dobpdc)\textsuperscript{170} and en-Mg\textsubscript{2}(dobpdc)\textsuperscript{171} (dmen = N,N′-dimethylethanediamine; en = ethylenediamine), both with strong capture properties, but somewhat handicapped by their regeneration energy penalty, synced with high CO\textsubscript{2} $Q_{st}$ values ($\sim$ 70 kJ/mol).

PSM using ethyl diamine (en), Long and co-workers isolated en-Cu-BTTri (where, the parent Cu-BTTri has the formula H\textsubscript{3}[(Cu\textsubscript{4}Cl)\textsubscript{3}(BTTri)\textsubscript{8}] (H\textsubscript{3}BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene)).\textsuperscript{172} en-Cu-BTTri features open Cu\textsuperscript{2+} coordination sites with a high CO\textsubscript{2}
$Q_{st}$ of $\sim 90$ kJ/mol. The parent CuBTTri has served as the prototype for PSM-derived AFS rich sorbents, designed and synthesised from UMC-rich parent MOMs. A high zero-coverage CO$_2$ $Q_{st}$ of $\sim 96$ kJ/mol for its exact analogue mmen-CuBTTri $^{173}$ (Figure 1.12) (mmen replacing en during the post-synthesis modification stage) plagues its application prospects, marring its high CO$_2$ capture properties of 2.38 mmol/g at 0.15 bar and moderate $S_{CN}$ ($\sim 327$).

**Figure 1.12.** An amine-functionalised MOM, mmen-CuBTTri. [Reproduced from reference 173].

UMC-replete mesopores of MIL-101(Cr) were post-synthetically modified using diethylenetriamine (DETA) to yield a low surface area material MIL-101-DETA.$^{174}$ This thermally stable compound ranks high amongst the chemisorbent MOMs with high CO$_2$ $Q_{st}$ (98 kJ/mol); thus regenerability being a concern. Mesoporous MIL-100(Cr) has also been subjected to PSM using alkyl amines (en-MIL-100(Cr)) thereby attaining high CO$_2$ $Q_{st}$ ($\sim 80$ kJ/mol) under low loading. These investigations exemplify that a correlation between material design principles and CO$_2$ sorption performance can be generalised. Though PSM approaches have led to sorbents with improved CO$_2$ capture performances, the energy penalty associated with the regeneration of these sorbents and high cost associated with the synthesis of the sorbents precludes their use for efficient CO$_2$ capture.
1.4.4 Carbon Capture in MOMs with Saturated Metal Centres

Traditionally, the use of UMCs and introduction of amine functionalities have been used to enhance $S_{CN}$. While these strategies enhance the CO$_2$ sorption performance and associated selectivities under ideal conditions, these selectivities take a downturn when exposed to industrially relevant conditions, especially moisture.$^{175,176}$ For some materials, the introduction of moisture to the gas stream was found detrimental to the sorption performance while for other materials the energy costs associated with activation, sorbent bed regeneration were found to be excessive for practical deployment.$^{175,176}$ As an energy-economic alternative to the traditional strategy, an approach whereby the optimisation of pore size and pore chemistry to enhance the CO$_2$-sorbent interactions has recently drawn significant attention. Using crystal engineering approaches, high performance MOM adsorbents can be synthesised through the judicious selection of metal nodes and organic linkers, and in some cases though the use of interpenetration.$^{177}$ Custom-design from first principles enables development of a number of high performance, task-specific physisorbent materials with benchmark $S_{CN}$ and separation performance. The crucial functionalities imparting high $S_{CN}$ and separation performance can be sub-divided into: A) organic ligand and/or pore size derived functionalization, and B) hybrid pillar introduction.

**Organic ligand and/or pore size derived functionalisation**

UTSA-16, i.e. [K(H$_2$O)$_2$Co$_3$(cit)(Hcit)] ($H_4$cit = citric acid),$^{140}$ exhibits a high volumetric CO$_2$ uptake, only second to the current benchmark Mg-MOF-74, recording 160 cc/cc CO$_2$ uptake at 296 K and 1 bar, however, outperforming Mg-MOF-74 (314.7 vs. 182) and all other UMC-rich sorbents in terms of $S_{CN}$. Ultramicropores ($3.3 \times 5.4 \text{ Å}^2$) that facilitate multiple interactions among the pore wall and adsorbed CO$_2$ molecules account for its benchmark selectivity.
In 2015, Vaidhyanathan and co-workers reported a new ultramicroporous MOM, Ni-4-PyC \[\text{Ni}_9(\mu-\text{H}_2\text{O})_4(\text{H}_2\text{O})_2(4-\text{pyc})_{18}\] \(_n\) (4-pyc = 4-pyridinecarboxylate) (Figure 1.13),\(^{178}\) which set a new benchmark for CO\(_2\)/H\(_2\) selectivity (285) and working capacities (3.95 mmol/g). Ni-4-PyC contains an ultramicroporous pore network (window size: 3.5 × 4.8 Å) and its sorption performance makes it suitable for H\(_2\) purification and pre-combustion trace CO\(_2\) capture processes. A higher density of CO\(_2\) binding sites in the Ni-4-Pyc framework paves the way to favourable CO\(_2\)-CO\(_2\) interactions and increased cooperative binding energies. An agw (agw = shp-derived, 3SP net) net compound NJU-Bai3 \([\text{Cu}_3\text{L}_2(\text{H}_2\text{O})_5]\] \(_n\) (L = 5-(4-carboxy-benzoylamino)-isophthalate, NJU-Bai3 = Nanjing University Bai group,\(^{179}\) synthesised from amide-functionalised tricarboxylate ligand 5-(4-carboxybenzoylamino)-isophthalate have also been investigated for CO\(_2\) capture. However, a moderate CO\(_2\) \(Q_{st}\) of ~36.5 kJ/mol and low \(S_{CN}\) < 60 reduces its potential for CO\(_2\) capture. Isoreticular (3,6)-c network compounds NJU-Bai7 and NJU-Bai8,\(^{180}\) synthesised from 5-(pyridin-3-yl)isophthalate and 5-(pyrimidin-5-yl) isophthalate, by virtue of polarised ligand environment with uncoordinated N-atoms, show improved \(S_{CN}\) (97 for NJU-Bai7 and 111.3 for NJU-Bai8) values as compared to NJU-Bai3, however, they still fall short of the desired \(S_{CN}\) value (> 2000) required for DAC by quite a margin.

Figure 1.13. Ni-4-Pyc, a SMC based MOM with a pore window of 3.5 × 4.8 Å.
Post-synthetic ligand exchange of terephthalate moiety in the prototypal UiO-66 platforms with a series of alkanedioic acids (HO\(_2\)C(CH\(_2\))\(_n\).2CO\(_2\)H; \(n = 4, 6, 8, 10\)) resulted in variable-length carboxyl pendants extending to the pores, yet recorded similar CO\(_2\) adsorption capacities for UiO-66-AD\(_n\) (\(n = 4, 8\)) to that of UiO-66. However, in the interesting case of UiO-66-AD\(_6\),\(^{181}\) uptake capacity was 34% higher at 298 K and 58% higher at 323 K, compared to those of UiO-66 (considerations under 1 bar). By increasing the interaction enthalpy between UiO-66-AD\(_6\) and sorbate CO\(_2\) molecules, and by mitigating the entropy loss upon CO\(_2\) adsorption through the formation of multiple carboxyl group and interacting CO\(_2\) molecules configuration, desirable CO\(_2\) \(Q_{st}\) of \(\sim 49.85\) kJ/mol, highest among UiO-66 series MOMs could be achieved. Mechanochemically synthesised, azine-functionalised Zn\(^{2+}\) MOM, TMU-5 [Zn(oba)(4-bpdh)\(_{0.5}\)]\(_n\) (oba = 4,4-oxybisbenzoate, 4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene)\(^{182}\) regardless of its low BET surface area of \(\sim 400\) m\(^2\)/g and low saturation capacity limitations, could lead to moderate CO\(_2\) \(Q_{st}\) values (\(\sim 44\) kJ/mol), owing to pronounced narrow-pore (5.6 × 3.8 Å\(^2\)) dipole-quadrupole interactions with CO\(_2\). Facile microwave-assisted synthesis was recently used to prepare a heterobimetallic (Na,Cd)-MOF i.e. [Cd\(_3\)Na\(_6\)(btc)\(_4\)(H\(_2\)O)\(_{12}\)]\(^{183}\) which notches high volumetric CO\(_2\) adsorption capacity (5.2 mmol/g) and moderate CO\(_2\) \(Q_{st}\) (42 kJ/mol), in spite of having a small micropore with a BET surface area \(\sim 526\) m\(^2\)/g. Easy regenerability, rapid 1 hour synthesis and performance cyclability for this compound makes it a promising adsorbent candidate for CO\(_2\) applications under appropriate conditions. Successive functionalization of a T-shaped ligand with amide and N-oxide groups led Xiong et al. to “open-donor” N-oxide sites which enhances the CO\(_2\) \(Q_{st}\) (53 kJ/mol, highest among SMC-MOMs without inorganics) at room temperature.\(^{184}\) Mechanistic insights on its CO\(_2\) adsorption and preferred binding sites have revealed that N-oxidisation of N-donor ligands can offer a new potential route to functionalise MOMs, suitable for CO\(_2\) capture with easy regeneration/cyclability traits. In
summary, the SMC based MOMs possessing SMCs and exclusively organic linkers often lacks strong host guest electrostatic interactions due to absence of strong binding sites. This leads to poor CO\textsubscript{2} capture performance, owing to low CO\textsubscript{2} $Q_{st}$ (20-40 kJ/mol) and low $S_{CN}$ (< 500) and minimises the potential of SMC based MOMs for selectivity-guided separation/purification applications such as DAC of CO\textsubscript{2}. 
Table 1.2. CO$_2$ sorption data for selected MOMs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat of Adsorption $Q_c$ (kJ/mol)</th>
<th>Surface Area, $S_{BET}$ (m$^2$/g)</th>
<th>CO$_2$/N$<em>2$ Selectivity ($S</em>{sc}$)</th>
<th>CO$_2$ Uptake At 0.15 bar (400 ppm) (mmol/g)</th>
<th>CO$_2$ Uptake At 1 bar (mmol/g)</th>
<th>Functionality$^{Ref}$</th>
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<tr>
<td>Zeolite 13X</td>
<td>49</td>
<td>780</td>
<td>440</td>
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<td>Inorganic$^{185}$</td>
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<td>3.0</td>
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<td>en-CuBTTri</td>
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<td>25</td>
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<td>dmen-Mg$_2$(dobpdc)</td>
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1.5 Pillared Square Grids for Carbon Capture

Pillared square grid materials were first reported by our group in 1995, where cationic square grids can be pillared by inorganic dianions (such as SiF\(_6^{2-}\)) to generate a pcu topology network, SIFSIX-1-Zn [Zn(bipy)\(_2\)SiF\(_6\)]\(_n\),\(^{95}\) with 8 × 8 Å\(^2\) square channels (Figure 1.14a). Within the framework, the trans fluorine of SiF\(_6^{2-}\) is axially coordinated to the Zn\(^{2+}\) metal ions, while the cis fluorines project towards the channels enhancing the micropore electrostatics. Use of NbOF\(_5^{2-}\) as the inorganic pillar, instead of SiF\(_6^{2-}\) was first done by Poeppelmeier in 1996. He reported NbOFFIVE-1-Cu [Cu(pyrazine)\(_2\)NbOF\(_5\)](pyrazine)(H\(_2\)O), a pillared square grid comprising pyrazine based cationic square grids that are cross-linked by NbOF\(_5^{2-}\) (Figure 1.14b).\(^{212}\) The NbOF\(_5^{2-}\) ions exhibit a distorted octahedral geometry, with the more electronegative oxygen and trans fluorines that link the sq1 net whereas the cis fluorines are pointed towards the net.

![Figure 1.14. The prototypical pillared square grids.](image)

Linking the neutral square grids with neutral dipyridyl linker was first illustrated by Kimoon Kim and colleagues, when a square grid of [Zn\(_2\)(BDC)\(_2\)] could be extended into a microporous 3D pcu structure i.e. DMOF-1 [Zn\(_2\)(bdc)\(_2\)(DABCO)]\(_n\) (DABCO = 1,4-diazabicyclo[2,2,2]octane) by using dabco, which occupies the axial positions.\(^{213}\) DMOF-1 served as the prototypical net for a huge number of such pcu MOMs in the years to follow,
However, lack of strong binding sites due to absence of inorganics makes them unfavourable for carbon capture.

Porosity in pillared square grids was first investigated by Kitagawa in 2000. He studied high pressure CH$_4$ in SIFSIX-1-Cu [Cu(bipy)$_2$(SiF$_6$)$_n$, an isostructural analogue to the parent SIFSIX-1-Zn.$^{214}$ The compound exhibited permanent porosity and had an uptake of 6.8 mmol/g of CH$_4$ at 40 atm. Hat two variables, organic linker and inorganic pillar, may be varied enables the possibility of fine-tuning the pore size as well as pore chemistry in pillared squared grids vs. IRMOFs or dia topology networks. However, no carbon capture studies were conducted up until 2012, when our group investigated carbon capture performance of these hybrid pillared materials.

Along with ultramicroporosity, introduction of anionic inorganic pillars such as SiF$_6^{2-}$, TiF$_6^{2-}$ or SnF$_6^{2-}$ used to support the cationic square grids to yield 3D pcu topology MOM can largely impact their CO$_2$ adsorption performance. With an aim to understand the effect of installing such inorganic linkers onto the material properties, our group studied CO$_2$ adsorption in SIFSIX-1-Cu (previously reported by Kitagawa and co-workers) (Figure 1.15a), a prototypal pcu net sustained by linear binodal pillar inorganics and SIFSIX-7-Cu [Cu(bpe)$_2$(SiF$_6$)$_n$ (bpe = 1,2-bis(4-pyridyl)ethene) (Figure 1.15b). Permanent porosity was determined using 77K N$_2$ with SIFSIX-1-Cu and SIFSIX-7-Cu, exhibiting BET surface areas of 1468 and 2718 m$^2$/g, respectively.$^{211}$ With an uptake of 5.7 mmol/g of CO$_2$ at 1 atm, SIFSIX-1-Cu outperformed Zeolite 13X and most of the UMC based MOMs. Notably, even though SIFSIX-7-Cu exhibited a larger surface area due to a longer organic linker, it had much lower adsorption capacity with an uptake of only 2.7 mmol/g of CO$_2$. It also had poorer performance in terms of CO$_2$ $Q_a$ and $S_{CN}$ with values of 21 kJ/mol and 8, respectively, when compared with SIFSIX-1-Cu (26.5 kJ/mol and 27). High CO$_2$ uptake and better CO$_2$ $Q_a$ for SIFSIX-1-Cu as compared to that of SIFSIX-7-Cu, emphasised the importance of narrow
pores that enable better overlap of the attractive potential fields from opposite pore walls, however, the role of inorganic pillars was not inferred in these studies.

Figure 1.15. Pillared square grids, a) SIFSIX-1-Cu b) SIFSIX-7-Cu.

To assess the role of electrostatics offered by inorganic pillars, two isostructural variants of SIFSIX-1-Cu, viz. TIFSIX-1-Cu [Cu(bipy)$_2$(TiF$_6$)]$_n$ and SNIFSIX-1-Cu [Cu(bipy)$_2$(SnF$_6$)]$_n$ were synthesized by systematically varying the inorganic pillar while retaining the organic ligand. CO$_2$ adsorption isotherms were measured for all three compounds. These studies reveal that TIFSIX-1-Cu (26.6 kJ/mol) had marginally better CO$_2$ $Q_{st}$ when compared to SIFSIX-1-Cu (26.5 kJ/mol) and SNIFSIX-1-Cu (26.4 kJ/mol) thanks to high polarisability of Ti$^{4+}$ ions. Due to this high polarisability, charge density on the fluorine atoms is enhanced and directly correlates to superior performance of TIFSIX-1-Cu. UTSA-48 [Cu(N-(pyridin-4-yl)isonicotinamide)$_2$(SiF$_6$)]$_n$, another pillar square grid was reported by Chen and co-workers in 2013. The length of organic linker was comparable to organic linker 7 in SIFSIX-7-Cu, however, UTSA-48 had much lower uptake of (1.2 mmol/g). This lower performance was attributed to the flexible amide moiety of the linker. Though the uptake was less than other hybrid pillared square grids, it exhibited a CO$_2$ $Q_{st}$ of 30 kJ/mol.
further emphasising the role of inorganic pillars in directing the CO₂ selectivity and related sorbent affinity.

1.5.1 Hybrid Ultramicroporous Materials

The term hybrid ultramicroporous materials (HUMs), coined by our group in 2015 to represent a subclass of coordination networks with a unique combination of strong electrostatics (inorganic dianions) and ultramicropores (< 0.7 nm).²¹⁵ The aforementioned compound, [Cu(pyrazine)₂NbOF₅(pyrazine)(H₂O)], comprising NbOF₅²⁻ as the inorganic pillar and pore size of ~ 3.7 Å is the first example of HUM with pcu topology reported in 1996.¹²⁶ However, the pyrazine guest molecules occupying the pores could not be removed and hence the framework was deemed non-porous. Further attempts to synthesise HUMs were made by Uemura and co-workers. Using the crystal engineering approach reported by our group in 1995, they prepared SIFSIX-3-Zn, [Zn(pyrazine)₂(SiF₆)₃]ₙ, a 3D pillared square grid comprising of Zn(pyrazine)²⁺ square grids and SiF₆²⁻ inorganic pillars. Use of pyrazine as the organic linker instead of 4,4′-bipyridyl resulted in reduction of pore size from 9.1 Å (SIFSIX-1-Zn) to 3.8 Å.

Use of angular inorganic pillars such as MoO₄²⁻, CrO₄²⁻ or WoO₄²⁻ resulted in mmo topology HUMs (MOFOUR-1-Ni/Co, CROFOUR-1-Ni/Co and WOFOUR-1-Ni) as shown in Figure 1.16 and can be denoted by [M′(ligand)₂(M''O₄)]ₙ (M′ = Ni²⁺, Co²⁺, M'' = Mo⁶⁺, Cr⁶⁺ and W⁶⁺ ) was reported by our group in 2012.¹⁹⁴,¹⁹⁵ The self-catenated square grids comprising octahedral metal ions and organic linker ligands are cross-linked by the tetrahedral linkers (M'O₄) with angular geometry to form HUMs with mmo topology such that helices with alternating 6-c metal ions propagate along c-axis. With only two oxygens coordinating to the metal ions, the remaining two oxygens project into the pores there by enhancing the electrostatics, i.e. pore chemistry.
Network interpenetration, a natural phenomenon defined by IUPAC as “two or more networks that are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken.” It has thus far been considered as undesirable as is evident from several studies focusing on the control of interpenetration in order to isolate the non-interpenetrated polymorph. However, our group demonstrated how HUMs can be created by use of longer organic linkers through pore size reduction by virtue of interpenetration. SIFSIX-2-Cu-i [Cu(dpa)\(_2\)(SiF\(_6\))]\(_n\) (dpa = 1,2-bis(4-pyridyl)acetylene) represents the parent interpenetrated HUM, Figure 1.17b. Further, the intertwining of networks in these interpenetrated HUMs led to more robust compounds exhibiting high physical stability (thermal as well as hydrolytic) as compared to their non-interpenetrated polymorphs (e.g. SIFSIX-2-Cu). Along with high physical stability, reduction in pore size due to interpenetration also led to improved sorption properties, which is discussed in the next section. With an aim to expand the scope of HUMs and network interpenetration, we also explored the potential of long inorganic pillars such as dichromate ion. Use of dichromate ions and various divalent metals resulted in a family interpenetrated HUMs represented by DICRO-3-M-i [M'(apy)\(_2\)(Cr\(_2\)O\(_7\))]\(_n\) (apy = 4,4'-azopyridine, M' = Zn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\)) that exhibit better sorption properties as compared to their non-interpenetrated polymorphs.

1.5.2 Carbon Capture with Hybrid Ultramicroporous Materials

Narrow pore channels combined with strong electrostatic contributions from an inorganic pillar paves the way for the generation of strong binding site(s), which can selectively adsorb small polarisable gases such as CO\(_2\) over its competing gases and water. The presence of these reversible strong binding sites in HUMs can help overcome the CO\(_2\) capture limitations faced by traditional physisorbents (low S\(_{CN}\)) due to strong interaction and demands lesser regeneration energy, as opposed to amine-based chemical adsorbents. First
report of CO$_2$ sorption in HUMs was by our group, where we investigated the potential of narrow pore mmo topology HUMs for CO$_2$ capture.$^{194,195}$ mmo topology HUMs, MOOFour-1-Ni, CROFOur-1-Ni and WOOFOur-1-Ni exhibited permanent porosity with surface areas of 505, 456, and 315 m$^2$/g, respectively. Carbon capture-related sorption properties were evaluated for all three HUMs via low pressure CO$_2$ sorption and sharp type-I isotherms were obtained for all the three with saturation uptake capacities of 2.45, 2.27, and 1.91 mmol/g respectively, suggesting strong interaction and high binding affinity between CO$_2$ and the framework. CO$_2$ $Q_{st}$ of 65.5, 56, and 50 kJ/mol at zero loading further confirmed the favourable interactions and was also eminent in the $S_{CN}$ at low pressure. At flue gas composition and full loading, $S_{CN}$ of 86, 195 and 179 displayed by the three HUMs superseded the values exhibited by most of the UMC-rich or amine-modified MOMs, highlighting the role of narrow pores and the strong electrostatics. Modelling studies provided more insights about the binding sites and could correlate sorption selectivity and choice of pillar. As per the studies, CO$_2$ molecules interact with the free oxygen present in the pore, and the strength of interactions was directly proportional to the polarisability of the pillar metal (e.g. Si for SiF$_6^{2-}$; Mo for MoO$_4^{2-}$), thus promoting strong CO$_2$ binding affinity within the different HUM narrow pores.

Motivated by the results of mmo topology HUMs, we explored the understudied hybrid class of pcu HUMs. SIFSIX-3-Zn shown in Figure 1.18a,$^{219}$ a previously reported HUM, along with two other sorbents obtained by using dpa as the organic linker was investigated for CO$_2$ sorption. As discussed before, use of dpa as the organic linker resulted in an interpenetrated HUM, SIFSIX-2-Cu-i, with a pore size of 5.15 Å (as discussed before) and also a non-interpenetrated pillared square grid, SIFSIX-2-Cu, with pore size $\sim$ 13.05 Å (Figure 1.17a and b).$^{141}$ Reduction in pore size due to interpenetration had a substantial impact on the sorption properties as confirmed by pure component CO$_2$ isotherms and
breakthrough studies. The doubly interpenetrated narrow pore SIFSIX-2-Cu-i exhibited superior uptake and selectivity towards CO$_2$ as compared to the non-interpenetrated variant (5.4 mmol/g and 140 vs 1.84 mmol/g and 13.7, at 298 K and 1 bar) and was comparable to the benchmark UMC and AFS based MOMs in terms of uptake and selectivity. Also, CO$_2$ $Q_{st}$ values indicates stronger binding in the interpenetrated variant (~32 kJ/mol) as compared to 22 kJ/mol in the non-interpenetrated polymorph and was evident during the breakthrough experiments. This study emphasised how a crystal engineering approach to yield narrow pore materials in conjunction with strong electrostatics offered by inorganic anions could be utilised to afford porous materials with exceptional $S_{CN}$, recyclability and moisture stability.

Figure 1.16. Parent mmo topology HUM, MOOFOUR-1-Ni.

Role of narrow pore in presence of inorganic pillar was further validated when SIFSIX-3-Zn comprising of the smallest pore dimension outperformed the other sorbents including SIFSIX-2-Cu-i in terms of CO$_2$ sorption properties. It exhibited a moderate CO$_2$ $Q_{st}$ of 45 kJ/mol comparable to most of the benchmark physisorbents including UMC based Mg-
MOF-74 and Zeolite 13X. SIFSIX-3-Zn also exhibited high $S_{CN} \sim 1,818$ a benchmark at that point of time, surpassing the previous benchmark Mg-MOF-74 and Zeolite 13X by an order of magnitude. Modelling studies revealed that the combination of tight fitting pores and strong electrostatics of inorganic pillars lead to the high $S_{CN}$ and affinity in SIFSIX-3-Zn. With moderate $Q_{st}$ and $S_{CN}$ comparable to the desired $S_{CN}$ ($> 2000$) required for efficient DAC of CO$_2$, SIFSIX-3-Zn appeared to be a promising candidate for DAC, however lack of stability towards moisture dented its potential for such applications.

![Figure 1.17](image)

**Figure 1.17.** a) Pillared square grids based on SiF$_6^{2-}$: a) Non interpenetrated SIFSIX-2-Cu; b) Interpenetrated HUM, SIFSIX-2-Cu-i.

With narrow pore materials being promising candidates for CO$_2$ capture, an attempt to further fine-tune the pore size in HUMs was made by Eddaoudi and co-workers. Exploiting the modular nature of hybrid **p**eu topology HUMs, they replaced the Zn$^{2+}$ metal ions with Cu$^{2+}$ ions to isolate SIFSIX-3-Cu[Cu(pyrazine)$_2$(SiF$_6$)]$_n$$^{196}$ (Figure 1.18b). The narrower pores in SIFSIX-3-Cu could be attributed to Jahn-Teller distortion of Cu$^{2+}$ ions, which uphold the pronounced CO$_2$ affinity. Strong binding of CO$_2$, evident from the high CO$_2$ $Q_{st}$ value of 54 kJ/mol and narrow pore promoted size exclusion of larger gases led to a benchmark $S_{CN}$ of 10,500. Further, the low pressure CO$_2$ uptakes exhibited by SIFSIX-3-Cu at 298 K, 1.2
47

mmol/g at 0.0004 bar and 2.4 mmol/g at 0.15 bar were best among all the physisorbents, and comparable only to chemisorbents.

Figure 1.18. SiF$_6^{2-}$ based HUMs depicting the role of metal ions: a) SIFSIX-3-Zn b) SIFSIX-3-Cu, c) SIFSIX-3-Ni. Use of Cu$^{2+}$ as the metal (b) resulted in shorter F-F distances (6.48 Å) and pore size (3.54 Å) due to Jahn-Teller distortion.

Though SIFSIX-3-Cu had excellent adsorption properties, it suffered the same fate as SIFSIX-3-Zn in terms of stability towards moisture. A crystal engineering approach offered a viable solution to overcome this shortcoming through systematic variation of the metal node led to more robust HUMs without any compromise in their sorption properties. SIFSIX-3-Ni [Ni(pyrazine)$_2$(SiF$_6$)]$_n$ (Figure 1.18c) and SIFISX-3-Co [Co(pyrazine)$_2$(SiF$_6$)]$_n$ obtained by use of Ni$^{2+}$ and Co$^{2+}$, respectively, exhibited improved sorption performances with high CO$_2$ $Q_{st}$ values of 50.8 and 49 kJ/mol, as compared to 45 kJ/mol for SIFSIX-3-Zn and was slightly lesser than SIFSIX-3-Cu, 54 kJ/mol. The CO$_2$ uptakes for all the HUMs were similar with saturation capacities recorded at 2.7, 2.6, 2.8 and 2.5 mmol/g for SIFSIX-3-Ni, SIFSIX-3-Co, SIFSIX-3-Zn and SIFSIX-3-Cu, respectively. However, the implications of higher $Q_{st}$ values could be clearly seen at low pressure. At 0.0004 bar, relevant for DAC applications, SIFSIX-3-Cu performed the best with an uptake of 1.2 mmol/g followed by SIFSIX-3-Ni, SIFSIX-3-Co and SIFSIX-3-Zn with uptakes of 0.35, 0.08, and 0.09 mmol/g respectively, thus highlighting the importance of narrow pore. However, with SIFSIX-3-Cu lacking the stability
towards moisture, SIFSIX-3-Ni becomes the most prominent candidate for CO₂ capture as gas streams consisting of CO₂ from static or mobile sources essentially comprise of moisture.

1.6 Conclusion and Project Aims

Conventional carbon capture strategies such as pre-combustion and post-combustion CO₂ capture from fixed point sources can only slow down the accumulation of CO₂ in the atmosphere but only the CNS such as trace capture of CO₂ from the air or DAC, can drastically reduce the global carbon footprint. In this regard a number of liquid and solid sorbents based on alkali metals, solid sorbents based on supported amines and amine modified MOMs exhibit good CO₂ uptake and high $S_{CN}$ due to the strong chemical reactivity between the sorbent and the sorbate. However most of these sorbents often require high regeneration energy. Along with high energy penalty, use of liquid alkali solutions also leads to large equipment size and high CO₂ abatement costs (US$600/tonne of CO₂) thus leading to low potential for this class of sorbents as described in Table 1.3. Bulk alkali carbonates suffers similar fate as alkali solutions owing to their slow chemical reactivity. Amine modified inorganic sorbents and MOMs often suffer from loss of tethered amines during the sorption-desorption cycles followed by subsequent loss in performance and efficiency. High cost involved in manufacturing these sorbents and large energy penalty associated with the regeneration of the material further limits their use for DAC of CO₂. Along with the above mentioned shortcomings, limited number of options available in terms of material choice, further reduces the scope of improvement for these classes of sorbents. As a result, these sorbents have low upside potential in the context of DAC of CO₂ which precludes their use for DAC applications.

Physisorbents can be an alternative to chemisorbents for DAC of CO₂ due to their high CO₂ uptake and moderate $Q_{st}$. However, these sorbents often lack high selectivity for CO₂ ($> 2000$) and stability towards humidity. Other than AFS MOMs that exhibits
chemisorption, no other class of MOMs have exhibited $S_{CN} > 500$. With the desired selectivity for DAC of CO$_2$ being $S_{CN} > 2000$, use of MOMs for DAC applications does not appear to be feasible. Contrary to MOMs, HUMs can provide a viable solution for DAC of CO$_2$ as they exhibit high CO$_2$ uptake, moderate $Q_{st}$ and high $S_{CN} (> 2000)$. Thanks to the presence of ultramicropores and strong electrostatics, these materials have exhibited high affinity for CO$_2$, even at low partial pressure and can target even the most difficult CO$_2$ capture process i.e. DAC. High modularity of HUMs provides avenues for improved design and synthesis of next generation sorbents with benchmark separation and capture performance for task-specific applications. This ability to fine tune HUMs provides an ample scope to develop them further, thus leading to high upside potential for HUMs with respect to DAC applications.

Table 1.3. Comparison of the strengths and weaknesses of selected DAC sorbents.

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<td>High</td>
<td>Very High</td>
<td>Very High</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Working Capacity</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Kinetics</td>
<td>Fast</td>
<td>Slow</td>
<td>Slow</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Fast</td>
</tr>
<tr>
<td>Upside Potential</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

The aim of this project is to investigate the use of pyrazine based isostructural HUMs for DAC of CO$_2$. The project involves use of crystal engineering approach to prepare and characterise a platform of pyrazine based HUMs by systematically varying the metal node or the inorganic pillar in order to develop advanced physisorbents with the following
characteristics: a) high thermal and hydrolytic stability, b) better DAC performance and c) cost-effective synthesis (high yield/low waste). The secondary objective is to gain insight into the mechanisms by which CO\textsubscript{2} sorption occurs and the factors which affect CO\textsubscript{2} adsorption. The factors responsible for the exceptional carbon capture performance of HUMs including high $S_{\text{CN}}$ and structure-property relationship amongst isostructural HUMs was also investigated. Stability of HUMs towards humidity and sorption performance in the presence of moisture was also investigated to have a better understanding about the potential of these sorbents for DAC applications. Various synthetic pathways was also investigated to find a facile synthetic route that can promote cost-economic bulk scale synthesis of HUMs.
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Scott, H. S. *et al.* Novel mode of 2-fold interpenetration observed in a primitive cubic network of formula [Ni{(1,2-bis(4-pyridyl)acetylene)₂(Cr₂O₇)}]ₙ. *Chemical Communications* **51**, 14832-14835 (2015).


Chapter Two: Direct Air Capture of CO₂ by Physisorbent Materials

2.1 Aim of the Chapter

Sequestration of CO₂, either from gas mixtures or directly from air (direct air capture, DAC), could mitigate carbon emissions. Here five materials are investigated for their ability to adsorb CO₂ directly from air and other gas mixtures. The sorbents studied are benchmark materials that encompass four types of porous material, one chemisorbent, TEPA-SBA-15 (amine-modified mesoporous silica) and four physisorbents: Zeolite 13X (inorganic); HKUST-1 and Mg-MOF-74/ Mg-dobdc (metal–organic frameworks, MOFs); SIFSIX-3- Ni, (hybrid ultramicroporous material). Temperature-programmed desorption (TPD) experiments afforded information about the contents of each sorbent under equilibrium conditions and their ease of recycling. Accelerated stability tests addressed projected shelf-life of the five sorbents. The four physisorbents were found to be capable of carbon capture from CO₂-rich gas mixtures, but competition and reaction with atmospheric moisture significantly reduced their DAC performance.

2.2 Note to Readers

This chapter has been previously published in Angewandte Chemie International Edition 2015, 54 (48), 14372-14377 and has been reproduced with permission of John Wiley and Sons. Amrit Kumar synthesized and characterized all compounds. David G. Madden carried out the breakthrough experiments and temperature programmed desorption studies. All the authors contributed to the writing of the manuscript.

2.3 Introduction

The development of a new generation of porous materials is key to enabling the “age of gas”, wherein new technologies develop around the use of gases.¹ Carbon dioxide (CO₂)
represents a topical challenge in this context: anthropogenic emissions of CO₂ are accepted as a significant risk to global climate; CO₂ is an undesirable component of commodities such as natural gas and biogas. The level of atmospheric CO₂ surpassed 400 ppm in 2013, which represents an increase of over 120 ppm since pre-industrial levels. Human activity is currently adding an additional 24 Gt of CO₂ per year to the atmosphere, of which, 14 Gt is from anthropogenic CO₂ point sources. While over half the CO₂ emissions are from large, industrial point sources, the remainder of these emissions are from small, mobile sources such as cars, trucks, and aircraft. It is becoming critical to develop economical pathways to reduce levels of CO₂ in the atmosphere and two approaches are being actively considered: 1) CO₂ removal from post- combustion industrial point sources (i.e. flue-gas capture) and 2) atmospheric CO₂ removal by direct air capture (DAC).

Post-combustion CO₂ capture would reduce emissions from large-scale sources of CO₂ such as coal-burning power stations; however, this technology may not be practical for application in mobile sources and fails to address the question of what to do with captured CO₂. Geological sequestration or use of the captured CO₂ as a commodity is feasible, but capture, purification, pressurization, and transportation must each be addressed in order to enable this carbon capture solution. DAC could mitigate CO₂ emissions from all sources and in turn enable onsite technologies that require CO₂ as a feedstock, thereby eliminating the need for storage and transport infrastructure. Examples of such technologies include “fuel from air” conversion of CO₂ into alcohols by algae and more efficient greenhouse growth of plants. Further, solving the challenge DAC would provide materials to facilitate other carbon capture needs such as pre-combustion removal of CO₂ from natural gas, biogas and other fuel gases.

However, implementation of DAC necessitates a low cost sorbent that combines optimum uptake, kinetics, energetics, physical/chemical stability and selectivity for CO₂ over
competing gases and vapours at atmospheric CO\textsubscript{2} concentrations. To date, DAC systems have typically employed solid organo-amine based chemisorbents, wherein amine functional groups are either physically or chemically anchored to the surface of cellulose\textsuperscript{5,6} porous silicas\textsuperscript{7-9} or porous polymer networks\textsuperscript{10,11} However, these sorbents require elevated temperatures (> 100 °C) for regeneration. DAC using physisorption is an attractive proposition, but has so far been handicapped by the lack of suitable physisorbents that are highly selective towards CO\textsubscript{2} and stable in the presence of competing gases and vapours. Nevertheless, physisorbents that can capture CO\textsubscript{2} with high selectivity are attractive since they would likely require much less energy for recycling. Porous metal–organic materials (MOMs)\textsuperscript{12} and the newly described subclass of coordination polymer called hybrid ultramicroporous materials (HUMs),\textsuperscript{13-18} show potential for use in sorbent-based applications such as gas purification,\textsuperscript{19,20} gas storage,\textsuperscript{21-24} and small-molecule separations.\textsuperscript{21,25-28} Further, their bench-mark selectivity towards CO\textsubscript{2} means they could serve as physisorbents for DAC. However, whereas the most selective MOMs and HUMs have received attention for the flue-gas capture of CO\textsubscript{2},\textsuperscript{20,23,29-32} to the best of our knowledge no work has yet been reported for these types of physisorbents in the context of DAC. Here, we use temperature-programmed desorption (TPD), thermogravimetric analysis (TGA), and mass spectrometry (MS) to evaluate five sorbents, SIFSIX-3-Ni,\textsuperscript{18} HKUST-1,\textsuperscript{33} Mg-MOF-74/Mg-dobdc,\textsuperscript{29} Zeolite 13X\textsuperscript{34-36} and TEPA-SBA-15,\textsuperscript{37} in the context of DAC and five other gas mixtures. We also address the stability of these sorbents to atmospheric water vapour via accelerated stability tests that simulate long-term storage or “shelf-life”.\textsuperscript{38}
Figure 2.1. The five sorbent materials investigated in this study. The colours of the atoms are as follows: orange, Mg; red, O; gray, C; salmon, Cu; blue, N; yellow, Si; pink, F; turquoise, Ni.

2.4 Results and Discussion

The five sorbents studied herein represent four classes of porous materials that have been widely investigated in the context of carbon capture (Figure 2.1). SIFSIX-3-Ni\(^{18}\) is a recently reported variant of a class of sorbents we call HUMs,\(^{13-16}\) because they combine ultramicropores (< 0.7 nm) in a material comprised of transition metals linked by two types of linker: organic ligands and inorganic anions.

The relatively high electrostatic contribution from the inorganic anions combined with tight binding sites affords strong interactions between adsorbent and adsorbate (large \(Q_{st}\)) and extra-high selectivity for polarizable gases (e.g. CO\(_2\)). HKUST-1\(^{33}\)(marketed as Basolite C300) and Mg-MOF-74\(^{29}\) are prototypical examples of physisorbent metal–organic materials, also known as MOFs\(^{39,40}\) or porous coordination polymers, PCPs.\(^{41-43}\) Zeolite 13X\(^{34-36}\) is a well-studied inorganic physisorbent that is already used in liquid bulk separations and fuel desulfurization.\(^{44,45}\) TEPA-SBA-15,\(^{37}\) an amine-modified mesoporous silicate, is a chemisorbent that belongs to the general class of sorbents known as amine-functionalized silica. These sorbents were synthesized following literature methods (see Appendix A), except for Zeolite 13X, which was used as received from commercial sources.
Each of the sorbents was characterized by powder X-ray diffraction (PXRD; see Appendix A, Figure A6–A8), thermogravimetric analysis (TGA; see Appendix A, Figure A9–A14), and infrared spectroscopy (FT-IR; see Appendix A, Figure A15–A19). Where required (e.g. HKUST-1, Mg-MOF-74, and SIFSIX-3-Ni), the sorbents were subjected to solvent exchange and activation using published procedures; details for the exchange process and activation protocols are given in the Appendix A. After activation, each sorbent was subjected to sorption experiments to verify that they met specifications according to the literature.

The DAC performance of each sorbent was evaluated using pristine, activated samples exposed to a specific gas mixture for a prescribed time period before being subjected to temperature-programmed desorption (TPD). In a typical TPD experiment, a sample was placed in a quartz reactor cell positioned within a tube furnace. This cell was heated to a temperature that guarantees the full evacuation of the host in the presence of He carrier gas while the exhaust gas was continuously monitored using a mass spectrometer (MS). These experiments provide the identity and relative quantity of gas(es) or vapour(s) desorbed by the sample as a function of temperature, or, if temperature is held constant, as a function of time. They also afford an understanding of the energy required for recycling the adsorbent material, although the TPD experiments we conducted do not provide information about the kinetics of CO₂ adsorption/desorption. Kinetics, along with recyclability and cost, are important aspects of DAC that will need to be carefully investigated in future experiments. In short, TPD experiments, address relative H₂O/ CO₂ uptake, and afford a qualitative indication of the ease with which the sorbent can be recycled.

In conjunction with the DAC experiments, the five sorbents were also subjected to TPD-TGA experiments in which each sorbent was placed in a TGA, heated to the temperature required for its activation and held for a prescribed period of time before being
cooled to ca. 30 °C. Upon cooling, the sample was then exposed to the conditions described below until the uptake remained constant. The mass gain for each sorbent was measured as a function of time. These conditions, including duration of exposure, were replicated for each sample using the TPD apparatus. The quantity and identity of adsorbed species in each sorbent was thereby determined (see Figure 2.2 for DAC plots; all TPD plots are in the Appendix A). Each sorbent was exposed to six gas mixtures, each designed to address a different aspect of the sorbent’s performance with respect to CO₂ sorption:

- DAC: Each sorbent was activated and then exposed to the laboratory atmosphere (avg. 23.4 °C; 49 % relative humidity, RH) for 12 h (see the Appendix A). This experiment tests the equilibrium contents of the sorbent following atmospheric exposure.
- Dry CO₂ (1 atm): To establish the CO₂ mass uptake for each sorbent, a dry 1 atm stream of CO₂ was passed over the sorbent.
- Moist CO₂ (1 atm): A 1 atm stream of CO₂ that had been bubbled through deionized water was flowed over the sorbent. The relative ability of each sorbent to capture CO₂ from a humid, high concentration CO₂ source was thereby determined.
- Dry CO₂ (0.15 atm): A 15% CO₂, 85% N₂ mix derived from pure gases mixed using a mass flow controller was used to simulate dry flue-gas conditions.
- Moist CO₂ (0.15 atm): The same mix as above, but bubbled through deionized water, was used to simulate realistic flue-gas conditions.
- Moist N₂ (1 atm): This gas mixture was produced by bubbling pure nitrogen gas through deionized water and estimates capacity of each sorbent for water in the absence of CO₂.

Data for TPD experiments are presented in Table 2.1. The chemisorbent TEPA-SBA-15 exhibits far superior DAC performance when compared to each of the physisorbents,
adsorbing the most CO\textsubscript{2} and the least H\textsubscript{2}O after 12 h of exposure. Of the physisorbents, SIFSIX-3-Ni performed best, followed by Mg-MOF-74, HKUST-1, and Zeolite 13X.

When exposed to simulated flue-gas (moist 0.15 atm CO\textsubscript{2}/0.85 atm N\textsubscript{2}), TEPA-SBA-15 and SIFSIX-3-Ni were again the top two performers, followed by Mg-MOF-74. Zeolite 13X performed somewhat better than HKUST-1, however, both sorbents performed significantly worse under these conditions than either TEPA-SBA-15 or SIFSIX-3-Ni. TPD experiments also provide an estimate of the relative ease of regeneration of the sorbent. The DAC plots in Figure 2.2 indicate that SIFSIX-3-Ni is the easiest sorbent to regenerate, needing the lowest temperature and the shortest time to remove adsorbed CO\textsubscript{2}. TEPA-SBA-15 required a slightly higher temperature to release CO\textsubscript{2} in about the same amount of time as SIFSIX-3-Ni. The significantly lower quantity of H\textsubscript{2}O adsorbed by TEPA-SBA-15 made for quicker regeneration than any of the other materials studied. However, chemisorbents can suffer from issues such as sorbent degradation over repeated cycling and amine deactivation in the presence of NO\textsubscript{X}, SO\textsubscript{X}, O\textsubscript{2} and CO\textsubscript{2}.\textsuperscript{46,47} HKUST-1 required a similar temperature to that of SIFSIX-3-Ni, but a much longer time was needed to remove adsorbed water. Mg-MOF-74 also requires a higher temperature and longer time than SIFSIX-3-Ni to remove CO\textsubscript{2} and H\textsubscript{2}O. In both HKUST-1 and Mg-MOF-74, H\textsubscript{2}O coordinates unsaturated metal sites, making removal of adsorbed water difficult.\textsuperscript{48,49} Zeolite 13X, which contains surface hydroxy groups and Na\textsuperscript{+} ions that can bind H\textsubscript{2}O molecules, required the highest temperature and longest regeneration time.

Performance in these TPD experiments correlates well with ideal selectivity\textsuperscript{50} for CO\textsubscript{2} over N\textsubscript{2} (S\textsubscript{CN}) and the isosteric heat of adsorption (Q\textsubscript{st}), both of which were determined from pure CO\textsubscript{2} adsorption isotherms. Amine-modified adsorbents exhibit Q\textsubscript{st} values of 50–100 kJ/mol and extra-high S\textsubscript{CN} as N\textsubscript{2} gas does not chemically react with the amine groups.\textsuperscript{51} SIFSIX-3-Ni (S\textsubscript{CN} ≈ 1874) exhibits much higher S\textsubscript{CN} than either HKUST-1 (S\textsubscript{CN} ≈ 101)\textsuperscript{52} or Mg-MOF-
74 ($S_{CN} \approx 148$). However, whereas ideal adsorbed solution theory (IAST)$^{50}$ can be used as an indicator of a material’s likely ability to selectively adsorb CO$_2$ over competing gases such as N$_2$, pure gas isotherms are not necessarily indicative concerning how a sorbent will behave when exposed to gas mixtures, especially those involving water vapour, hence the need to perform the TPD experiments detailed herein.

![Figure 2.2. TPD plots of direct air capture of CO$_2$ experiments for the five sorbents studied herein. The red curve is the temperature ramp profile used for desorption. The MS signals for CO$_2$ and H$_2$O are given by the black and blue curves, respectively.](image_url)

The TPD experiments revealed that the physisorbents adsorb large quantities of H$_2$O. This not only mitigates against CO$_2$ uptake, but recent studies suggest that MOMs can be susceptible to degradation when exposed to water or water vapour.$^{20,49,53,54}$ In this context, Walton and co-workers have presented guidelines to rank the water stability of MOMs.$^{55}$ However, to our knowledge there have been no reports concerning stability tests of the type regulated for the pharmaceutical industry where six months of storage under “accelerated” conditions are accepted as being representative of two years of long-term storage or shelf-life.$^{38,56,57}$ We exposed pristine samples of each of the five sorbents studied herein to 40 °C
and 75 % humidity and removed aliquots for analysis (PXRD, TGA, and gas sorption, see SI for full details) after 1, 7, and 14 days.

**Table 2.1.** TPD coupled with mass spectrometry.\(^a\)

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>DAC (1 atm; 49 % RH)(^b)</th>
<th>Moist CO(_2) (1 atm)(^c)</th>
<th>Moist CO(_2) (0.15 atm)(^c)</th>
<th>Moist N(_2) (1 atm)(^c)</th>
<th>Dry CO(_2) (1 atm)</th>
<th>Dry CO(_2) (0.15 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO(_2) H(_2)O CO(_2) H(_2)O CO(_2) H(_2)O CO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>&lt; 8 % &gt; 92 % &gt; 93 % &lt; 7 %</td>
<td>62 % 38 %</td>
<td>100 %</td>
<td>100 %</td>
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<td>100 %</td>
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<tr>
<td></td>
<td>(8.0) (93) (109.5) (7)</td>
<td>(76) (46)</td>
<td>(120)</td>
<td>(110)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1% 99 % &gt; 44 % &lt;56 %</td>
<td>8.5 % &gt;91 %</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
</tr>
<tr>
<td></td>
<td>(2.1) (178) (51.3) (65)</td>
<td>(12.8) (137)</td>
<td>(370)</td>
<td>(110)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-MOF-74</td>
<td>&lt; 4 % &gt; 96 % 39 % 61 %</td>
<td>51 % 49 %</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
</tr>
<tr>
<td></td>
<td>(6.3) (171) (100.5) (157)</td>
<td>(68) (65)</td>
<td>(360)</td>
<td>(250)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>1 % 99 % &gt; 45 % &lt;55 %</td>
<td>22 % 78 %</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
</tr>
<tr>
<td></td>
<td>(1.5) (146) (53.6) (66)</td>
<td>(26.3) (93)</td>
<td>(270)</td>
<td>(170)</td>
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</tr>
<tr>
<td>TEPA-SBA-15(^d)</td>
<td>93 % 7 % 98 % 2 %</td>
<td>92 % 8 %</td>
<td>100 %</td>
<td>100 %</td>
<td>100 %</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(158) (12) (148.8) (3)</td>
<td>(130.3) (11)</td>
<td>(120)</td>
<td>(160)</td>
<td>(152)</td>
<td></td>
</tr>
</tbody>
</table>

[a] Mass of analyte is given in parenthesis, expressed as mg g\(^{-1}\). [b] Relative humidity and temperature where measured using thermometer-hygrometer. [c] Water-saturated gas feeds were obtained by bubbling each pure gas through deionized water. [d] TEPA-SBA-15 is an amine-modified mesoporous chemisorbent material.

TEPA-SBA-15 and Zeolite 13X were both found to remain stable after 14 days of testing. The surface area of TEPA-SBA-15 was not measured as it is a chemisorbent and degassing under vacuum can degrade the amine grafts (see Appendix A, Figure A13). However, its capacity to adsorb CO\(_2\) at 293 K was unchanged after exposure to the humidity chamber for 1, 7, and 14 days (Figure 2.3). The surface area calculated for a pristine sample of Zeolite 13X, ca. 832 m\(^2\)/g, agrees well with previously reported values. After exposure to the humidity chamber for 1, 7, and 14 days, Zeolite 13X exhibited BET surface areas of ca. 816 m\(^2\)/g, 867 m\(^2\)/g, and 865 m\(^2\)/g, respectively. The amount of CO\(_2\) adsorbed (293 K, 1 atm) by Zeolite 13X was also unaffected by stability tests (ca. 6.07 mmol/g). SIFSIX-3-Ni also
maintained its adsorption performance after accelerated stability tests. Pristine SIFSIX-3-Ni exhibited a BET surface area of ca. 223 m$^2$/g, agreeing with values reported for its Zn and Cu variants.$^{15,16}$

Figure 2.3. Bar graphs depict BET surface area (top) and CO$_2$ uptake at 293 K and 1 atm (bottom) for each sorbent in pristine condition (red) and after 1 (blue), 7 (green), and 14 days (orange) exposure in a controlled humidity chamber (40 °C; 75 % RH).

After 1, 7, and 14 days, the BET surface areas for SIFSIX-3-Ni were measured to be ca. 222 m$^2$/g, 218 m$^2$/g, and 208 m$^2$/g, respectively (Figure 2.3). In terms of CO$_2$ uptake at 293 K and 1 atm, a pristine activated sample of SIFSIX-3-Ni adsorbs ca. 2.67 mmol/g. This value was little changed after accelerated stability tests.

Conversely, HKUST-1 and Mg-MOF-74 were degraded by exposure to humidity. The BET surface area measured for pristine activated HKUST-1, ca. 1900 m$^2$/g, matches the best values reported.$^{58}$ After exposure to the humidity chamber, the BET surface area of HKUST-1 decreased to 1370 m$^2$/g, 1270 m$^2$/g and 1240 m$^2$/g after 1, 7 and 14 days, respectively. The observed decrease in BET surface area for HKUST-1 is consistent with previous reports on its stability in the presence of water.$^{53}$ The amount of CO$_2$ HKUST-1 adsorbs at 293 K and 1
atm also diminished following exposure to humidity. The pristine activated sample can adsorb as much as 5.98 mmol/g, larger than SIFSIX-3-Ni and about the same as Zeolite-13X. However, after just 1 day the value dropped to 4.55 mmol/g (Figure 2.3). 7 days and 14 days uptakes of CO$_2$ dropped to 4.4 mmol/g and 3.97 mmol/g, respectively.

The sorption performance of Mg-MOF-74 after accelerated stability testing was the worst of the five sorbents studied. After just 1 day of exposure, the BET surface area decreased by 74 % (Figure 2.3), and after 7 or 14 days exposure only negligible N$_2$ uptake at 77 K was measured (BET surface area 6 m$^2$/g). These observations are consistent with earlier studies concerning the stability of Mg-MOF-74 to water.$^{48,49,53}$ CO$_2$ uptake was likewise diminished following exposure to humidity: pristine Mg-MOF-74 adsorbs 7.3 mmol/g CO$_2$ at 1 atm and 293 K. One day of exposure in the humidity chamber reduced uptake to ca. 5.66 mmol/g CO$_2$; 7 days to ca. 3.52 mmol/g (-52 %); 14 days to 2.36 mmol/g.

In addition to measuring adsorption performance, PXRD and TGA measurements were collected during the accelerated stability tests. TGA experiments for all sorbents showed little evidence of change in the thermal stability profile; there were only small changes in the thermal decomposition temperature and the weight loss (presumably water) for days 1, 7, and 14. PXRD patterns also remained largely unchanged after exposure to humidity. However, SIFSIX-3-Ni, exhibited a different PXRD pattern from the pristine activated sample, that is, it matches an as yet unidentified precursor to SIFSIX-3-Ni (see Appendix A, Figure A8 and A28). However, heating at 110 °C for 10 min resulted in a PXRD pattern that closely matches pristine activated SIFSIX-3-Ni. In each case (1, 7, and 14 days), the material obtained from the humidity chamber was activated and retained the surface area and CO$_2$ uptake of a pristine, activated sample of SIFSIX-3-Ni.

Interestingly, HKUST-1 and Mg-MOF-74 showed no discernible changes in their respective PXRD patterns after exposure to humidity yet, as discussed earlier, adsorption
performance diminished. Such an effect has been observed by several other research groups that have studied the effect of water and/or water vapour upon MOMs. One hypothesis offered is that the presence of water leads to partial pore blocking or pore collapse. If degradation of adsorption performance is associated with surface adulteration, then particle size should be addressed in future experimental protocols.

2.5 Conclusion

DAC remains a challenging but potentially fruitful approach to reduce the impact of anthropogenic emissions of CO₂. In this contribution, we address how water vapour impacts two important practical considerations with respect to DAC, in particular, and carbon capture, in general: competition between water vapour and CO₂ in gas mixtures including air and simulated flue gas; shelf-life of sorbents following exposure to atmospheric stability. With respect to the former, all four physisorbents studied exhibit strong $S_{CN}$ but their performance with respect to CO₂ uptake was diminished in the presence of water vapour. The chemisorbent was unaffected by water vapour, but its energetics are not as favourable for recycling as SIFSIX-3-Ni. With respect to stability, the use of a relatively simple and standard stability test suggests that even short-term exposure to humidity can result in significant degradation of performance. In conclusion, there are two take-home messages: a standard stability test, perhaps of the type described herein, should be adopted and applied to candidate sorbents; physisorbents can compete with chemisorbents with respect to $S_{CN}$ but DAC performance is mitigated because of competition with water vapour. The strong performance of SIFSIX-3-Ni highlights how controlling pore size and pore chemistry to improve DAC performance and stability in the presence of water vapour must be further addressed if physisorbents are to compete with chemisorbents.
2.6 References


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Scott, H. S. et al. Novel mode of 2-fold interpenetration observed in a primitive cubic network of formula [Ni(1,2-bis(4-pyridyl)acetylene)\textsubscript{2}(Cr\textsubscript{2}O\textsubscript{7})\textsubscript{n}]. *Chemical Communications*\textbf{51}, 14832-14835 (2015).


Chapter Three: Hybrid Ultramicroporous Materials with Enhanced Stability and Trace Carbon Capture Performance

3.1 Aim of the Chapter

Fine-tuning of HUMs through pillar substitution can significantly enhance trace CO$_2$ sorption performance and stability. The resulting materials, exemplified by the new material TIFSIX-3-Ni, [Ni(pyrazine)$_2$(TiF$_6$)$_n$], are shown through temperature programmed desorption experiments to remove trace quantities of CO$_2$ from moist gas mixtures.

3.2 Note to Readers

This chapter has been previously published in Chemical Communications 2017, 53 (44), 5946-5949 and has been reproduced with permission of Royal Society of Chemistry. Amrit Kumar synthesized and characterized all compounds. David G. Madden carried out the breakthrough experiments and temperature programmed desorption studies. Carol Hua studied the low pressure gas adsorption isotherms. All the authors contributed to the writing of the manuscript.

3.3 Introduction

There is a crucial need in society from both environmental and industrial perspectives for effective capture and sequestration of CO$_2$. Currently, strategies to mitigate atmospheric CO$_2$ levels include the post-combustion capture of CO$_2$ (e.g. flue gas capture) and the trace removal of CO$_2$ directly from the air by Direct Air Capture (DAC). The trace removal of CO$_2$ from industrially important gases such as natural gas is already conducted at an industrial scale but as an energy intensive process that can require multiple steps.
Recently, the development of advanced physisorbents suggests implementation in both trace and bulk carbon capture processes, which have traditionally been dominated by chemisorbents. The lower energy cost involved with regenerating physisorbents makes them an attractive alternative to chemisorbents for carbon capture applications. Metal-Organic Materials (MOMs),\(^6\) including Porous Coordination Polymers (PCPs),\(^7,8\) and Metal-Organic Frameworks (MOFs),\(^9-13\) are modular physisorbent materials that offer potential game-changing improvements to a myriad of applications including trace removal of impurities. In 1995, SIFSIX-1-Zn, \([\text{Zn}(4,4'-\text{bipyridine})_2(\text{SiF}_6)]_n\), became the prototypal “pillared square grid” platform (Figure 3.1).\(^{14}\) SIFSIX-1-Zn is based upon 2D sql nets pillared by \(\text{SiF}_6^{2-}\) anions (‘SIFSIX’) and thereby exists as a 3D network with primitive cubic (pcu) topology. Substituting the organic linker means that the pore size of such materials can be adjusted from mesoporous (> 2nm) to ultramicroporous (< 0.7 nm). Recently, our group has defined a subclass of MOM, Hybrid Ultramicroporous Materials (HUMs),\(^{15}\) that combines two key features that enhance their selectivity for small polarizable gases: the incorporation of strong electrostatics in the form of inorganic anions with electronegative atoms and the presence of ultramicropores that provide a tailored fit for important sorbates such as \(\text{CO}_2.\)\(^{15,16}\) This precise control of both pore size and chemistry has afforded new benchmark isosteric heats of adsorption \((Q_a)\) that enable exceptional performance for a wide variety of small molecule gas separations.\(^{16-23}\) The modular nature of SIFSIX-3-M’ (SIFSIX = \(\text{SiF}_6^{2-}\); \(3 = \text{pyrazine}, \text{M’} = \text{Ni, Co, Zn, Cu}\)) enables the platform of HUMs to be fine-tuned to optimize their performance for specific applications. \(\text{M’}\) substitution results in changes to the pore size, \(\text{CO}_2\) uptake and \(Q_a\) and can also enhance moisture stability.\(^{24,25}\) This is exemplified by comparing SIFSIX-3-Ni, which is stable up to 80\% RH and in the presence of \(\text{H}_2\text{S},\) with SIFSIX-3-Zn, which undergoes a phase change upon exposure to 50\% RH.\(^{18,25}\)
Figure 3.1. Pillared square grid networks exhibit primitive cubic (pcu) topology from self-assembled metal nodes (red), organic linker ligands (purple) and inorganic pillars (green).

In two of our earliest studies, the effect of changing the pillar from SiF$_6^{2-}$ to TiF$_6^{2-}$ resulted in enhanced sorbent-CO$_2$ interactions and higher selectivity towards CO$_2$. Given the exceptional CO$_2$ uptake and stability exhibited by SIFSIX-3-Ni when compared to other members of the SIFSIX-3-M’ family, we decided to further explore the use of TiF$_6^{2-}$ pillars in order to improve affinity towards CO$_2$ at trace levels, whilst also addressing thermal and hydrolytic stability. Herein we report the synthesis, structure and gas sorption properties of a new HUM variant of the MFSIX-3-M’ family, TIFSIX-3-Ni where TIFSIX = TiF$_6^{2-}$; 3=pyrazine. The performance of TIFSIX-3-Ni towards carbon capture in both trace and bulk quantities is assessed by comparison to current benchmark materials and the thermal and water stability of the material determined.

3.4 Results and Discussion

Microcrystalline TIFSIX-3-Ni was synthesised by slurring nickel hexafluorotitanate and pyrazine in deionized water and heating the isolated solid at 160 °C for 16 h in vacuo. Unit cell parameters from peak fitting are $a = b = 6.99784(14)$ Å and $c = 7.79358(18)$ Å in
P4/mmm, isostructural to SIFSIX-3-Ni (see Appendix B for more details). The slightly shorter lengths of the $a$ and $b$ axes in the unit cell parameters of TIFSIX-3-Ni compared with SIFSIX-3-Ni combined with the increased pillar M-F bond distances (1.67 Å vs. 1.81 Å for SiF$_6^{2-}$ and TiF$_6^{2-}$, respectively) would be expected to create a tighter binding site for CO$_2$.

It is apparent from the powder X-ray diffraction, PXRD, (Figure 3.2) patterns that the pillar in effect creates two types of HUMs in this platform. Whereas SIFSIX-3-Ni, Co, and Zn exhibit matching PXRD patterns, TIFSIX-3-Ni, NbOFFIVE-1-Ni, and SIFSIX-3-Cu exhibit different PXRD patterns. We attribute these differences to the longer $c$-axis for TiF$_6^{2-}$ and NbOF$_5^{2-}$, or Jahn-Teller effects at the Cu$^{II}$ node. These structural changes manifest themselves in corresponding shifts in the $00l$ and $h0l$ PXRD peaks. The isostructural nature of SIFSIX-3-Ni, TIFSIX-3-Ni and NbOFFIVE-1-Ni enables us to investigate the effects of the electrostatics of the different pillars on the gas sorption performance with respect to trace carbon capture.

The CO$_2$ uptake and $Q_{st}$ for TIFSIX-3-Ni and other physisorbent materials that are recognised to exhibit strong CO$_2$ capture performance (NbOFFIVE-1-Ni, Uio-66-NH$_2$, HKUST-1, Mg-MOF-74 and Zeolite 13X) were evaluated at the very low pressures of 0 to 3000 ppm (Figure 3.3a). SIFSIX-3-Cu was excluded from testing due to the inherent instability of the adsorbent. At 400 ppm, which is a pressure relevant to CO$_2$ concentrations in the atmosphere, TIFSIX-3-Ni was found to perform very favourably when compared with the current benchmark, NbOFFIVE-1-Ni, with uptakes of 1.2 and 1.3 mmol/g respectively. Remarkably, when these adsorption capacities are evaluated as a percentage of the CO$_2$ loading at 1.0 bar, TIFSIX-3-Ni and NbOFFIVE-1-Ni are already 46% and 54% loaded, respectively, at 400 ppm. The outstanding performance of these HUMs was exemplified by comparing this uptake with that of SIFSIX-3-Ni (0.4 mmol/g, 14%). Overall these three
isostructural variants exhibit remarkable CO$_2$ uptake at 400 ppm, however, the tuning of the pillar leads to significant differences in CO$_2$ uptake at low partial pressures.

![Figure 3.2](image.png)

**Figure 3.2.** Calculated PXRD patterns for benchmark HUMs and experimentally measured PXRD pattern of TIFSIX-3-Ni.

Zeolite 13X (0.44 mmol/g) was the third best performing material in terms of uptake at 400 ppm, but was only 7% loaded at 400 ppm due to its high CO$_2$ uptake at 1 bar. Two prototypical MOFs, Mg-MOF-74 (0.14 mmol/g, 2%), which contains open metal sites, and Uio-66-NH$_2$ (0.18 mmol/g, 8%), which contains pendant amine groups both exhibited significantly lower CO$_2$ uptake and percentage loading at 400 ppm than the HUMs measured in this study. HKUST-1 displayed less than 0.13 mmol/g adsorption at 3000 ppm and negligible uptake at 400 ppm.

The $Q_{st}$ values for HKUST-1, Mg-MOF-74, NbOFFIVE-1-Ni, SIFSIX-3-Ni, TIFSIX-3-Ni, Uio-66-NH$_2$ and Zeolite 13X (Figure 3.3b) were calculated using the adsorption data collected in the low-pressure region between 0 to 3000 ppm (See Appendix B, Figure B14-B19). The HUMs TIFSIX-3-Ni (50 kJ/mol), NbOFFIVE-1-Ni (54 kJ/mol) and SIFSIX-
3-Ni (45 kJ/mol) exhibited the highest $Q_{st}$ values at zero loading. Although TIFSIX-3-Ni and NbOFFIVE-1-Ni have similar $Q_{st}$ values, we note that the $Q_{st}$ value for TIFSIX-3-Ni increases between loadings of 0.1 and 0.6 mmol/g of CO$_2$ whilst the $Q_{st}$ for NbOFFIVE-1-Ni decreases in value over the same range. It is possible that such different $Q_{st}$ profiles could impact adsorption kinetics but that will be the subject of future studies. The $Q_{st}$ values we determined at zero loading for Mg-MOF-74 (42 kJ/mol), UiO-66-NH$_2$ (38 kJ/mol), HKUST-1(23 kJ/mol) and Zeolite 13X (39 kJ/mol) are comparable to those reported in the literature.

We note that these values are much lower than those of the HUMs studied herein. This observation further emphasizes the importance of being able to tailor a binding cavity to a particular sorbate.$^{32}$ We anticipated that the high $Q_{st}$ values measured from pure gas isotherms might translate into outstanding performance for trace CO$_2$ capture.

The DAC performance of each of the above materials was evaluated using Temperature Programmed Desorption (TPD).$^{16,22}$ For the DAC experiments, a pristine sample was fully activated and then exposed to ambient air (25 °C, 49% RH) for 12 h. The sample was then placed in a quartz reactor and heated to 90 °C under a flow of He. The composition of the evolved gas was continuously monitored using mass spectrometry (MS), enabling identification and quantification of each component present during the desorption process. Data for the TPD experiments are presented in Table 3.1. TIFSIX3-Ni (17.9 mg/g) and NbOFFIVE-1-Ni (18.5 mg/g) exhibited the highest CO$_2$ uptakes of the physisorbents analysed equating to 9.09 and 9.42 L CO$_2$/kg material respectively. The remainder of the desorbed species during these experiments was found to be adsorbed atmospheric moisture. TIFSIX-3-Ni exhibited a CO$_2$/H$_2$O selectivity ($S_{CW}$) of 12.8, which is more than double that of SIFSIX-3-Ni. The percentage CO$_2$ uptake (17.1%) coupled with the CO$_2$/H$_2$O selectivity for TIFSIX-3-Ni represent new benchmarks in terms of CO$_2$ sorption performance of physisorbents for DAC.
Figure 3.3. (a) CO$_2$ adsorption isotherms in the range 0 to 3000 ppm at 298 K, and (b) CO$_2$ isosteric heats of adsorption ($Q_{st}$) at low loading for HKUST-1, Mg-MOF-74, SIFSIX-3-Ni, TIFSIX-3-Ni, Zeolite 13X, NbOFFIVE-1-Ni, and UiO-66-NH$_2$.

The superior DAC performance of TIFSIX-3-Ni and NbOFFIVE-1-Ni when compared to SIFSIX-3-Ni further highlights how subtle changes in pore chemistry and pore size can have a dramatic effect on the sorption performance of a series of isostructural materials. We attribute this to the increase in $Q_{st}$ of 5 kJ/mol from SIFSIX-3-Ni to TIFSIX-3-Ni that in turn more than doubles CO$_2$ uptake. The increased affinity towards CO$_2$ is also
reflected in the moist flue gas (0.15 atm CO\textsubscript{2}, 75% relative humidity) experiments as TIFSIX-3-Ni and NbOFFIVE-1-Ni exhibit the highest CO\textsubscript{2}/H\textsubscript{2}O selectivities (0.87 and 0.91, respectively) and volumetric uptakes (77.15 and 78.84 L CO\textsubscript{2}/L, respectively) of the physisorbents analysed herein. In terms of the traditional benchmark adsorbents, UiO-66-NH\textsubscript{2} was the best performing material during DAC experiments in terms of volumetric CO\textsubscript{2} uptake. Ligand decoration with polar species such as amino groups can significantly enhance the CO\textsubscript{2} binding ability and selectivity of MOFs.

Table 3.1. TPD coupled with mass spectrometry.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>DAC (1 atm; 49% RH)</th>
<th>Moist CO\textsubscript{2} (0.15 atm; 75% RH)</th>
<th>Dry CO\textsubscript{2} (0.15 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO\textsubscript{2} (mg/g)</td>
<td>H\textsubscript{2}O L/Kg (L/L)</td>
<td>S\textsubscript{cw}</td>
</tr>
<tr>
<td>TIFSIX-3-Ni</td>
<td>17.1% (17.9)</td>
<td>9.09 (14.97)</td>
<td>12.80</td>
</tr>
<tr>
<td>NbOFFIVE-1-Ni</td>
<td>16.5% (18.5)</td>
<td>9.42 (16.57)</td>
<td>12.35</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>&lt; 8% (8.0)</td>
<td>4.07 (6.55)</td>
<td>5.43</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1% (2.1)</td>
<td>1.07 (0.95)</td>
<td>0.63</td>
</tr>
<tr>
<td>Mg-MOF-74</td>
<td>&lt; 4% (6.3)</td>
<td>3.21 (2.94)</td>
<td>2.60</td>
</tr>
<tr>
<td>UiO-66-NH\textsubscript{2}</td>
<td>&lt; 2% (11.2)</td>
<td>5.70 (7.38)</td>
<td>1.28</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>1% (1.5)</td>
<td>0.76 (0.99)</td>
<td>0.63</td>
</tr>
</tbody>
</table>

a Previously reported adsorbents, see ref. 16 and 23. b Water saturated gas feeds were obtained by bubbling each pure gas through deionized water.

The thermal stability of TIFSIX-3-Ni was determined by thermogravimetric analysis (TGA) and variable-temperature powder X-ray diffraction (VT-PXRD) (See Appendix B, Figure B7 and B26). TIFSIX-3-Ni was observed to be stable up to 280 °C (compared to 180 °C for NbOFFIVE-1-Ni).
°C and 360 °C for SIFSIX-3-Ni and NbOFFIVE-1-Ni, respectively). The long-term moisture stability of TIFSIX-3-Ni was determined by subjecting it to accelerated stability protocols as used in the pharmaceutical industry (40 °C and 75% RH, see SI) over 1, 7 and 14 days. After 14 days, the BET surface areas for SIFSIX-3-Ni, TIFSIX-3Ni and NbOFFIVE-1-Ni were found to be reduced by 7%, 5% and 7%, respectively (Figure 3.4). Despite these losses in surface area, there was only a negligible loss in terms of CO$_2$ sorption performance after 14 days of accelerated stability testing demonstrating the robust nature of the HUM materials.

![Figure 3.4](image)

**Figure 3.4.** Percentage sample surface area for SIFSIX-3-Ni, TIFSIX-3-Ni and NbOFFIVE-1-Ni in pristine condition (red) and after 1 (blue), 7 (green), and 14 days (orange) exposure in a controlled humidity chamber (40 °C; 75% RH).

The improved thermal stability of TIFSIX-3-Ni compared to SIFSIX-3-Ni further emphasises how the tuning of the pillaring functionality can significantly influence both the physical properties and sorption performance of isostructural materials.

### 3.5 Conclusion

In summary, we have synthesized and characterized a new HUM variant of the MFSIX-3-M' platform, TIFSIX-3-Ni. TIFSIX-3-Ni performs favourably for CO$_2$ adsorption
when compared to the current benchmark material NbOFFIVE-1-Ni, as highlighted through the results of the single-component gas isotherms, and low-pressure $Q_{st}$. TIFSIX-3-Ni was found to exhibit benchmark performance in terms of percentage CO$_2$ uptake (17.1%) and CO$_2$/H$_2$O selectivity (12.8) for DAC in TPD studies. We attribute the enhanced interactions between CO$_2$ and TIFSIX-3-Ni and NbOFFIVE-1-Ni to stronger electrostatics imparted by TiF$_6^{2-}$ and NbOF$_5^{2-}$ anions that in turn lead to an increased affinity towards polarizable gases such as CO$_2$, when compared with SiF$_6^{2-}$. The thermal and moisture stability of TIFSIX-3-Ni are significantly improved over SIFSIX-3-Ni. We also note the straightforward synthesis of TIFSIX-3-Ni which avoids the use of HF required for the synthesis of NbOFFIVE-1-Ni. The findings herein afford a greater understanding of the structure-property relationships in HUMs and could enable crystal engineering approaches to the design of even better performing materials for trace CO$_2$ capture.
3.6 References


Scott, H. S. *et al.* Novel mode of 2-fold interpenetration observed in a primitive cubic network of formula [Ni(1,2-bis(4-pyridyl)acetylene)₂(Cr₂O₇)]ₙ. *Chemical Communications* **51**, 14832-14835 (2015).


Chapter Four: Mechanochemical Synthesis and Gas Sorption Performance of a Family of Isostructural Hybrid Ultramicroporous Materials

4.1 Aim of the Chapter

In view of the fossil-fuel free transition to green energy resources, it is essential to develop new technologies and materials for effective and energy-efficient carbon dioxide (CO₂) capture at a wide range of concentrations, i.e. trace (< 2%) and bulk (> 2%). Physisorption-based separation technologies using porous adsorbents have long been touted for their potential to significantly reduce the energy requirements for industrial gas separations. It is in this context that a class of porous materials which exhibits benchmark performance with respect to CO₂ sorption, hybrid ultramicroporous materials (HUMs), has recently emerged. HUMs have thus far demonstrated benchmark performance with respect to the following separations: CO₂/flue gas, CO₂/air; CO₂/C₂H₂; and C₂H₂/CO₂. However, their potential has been hampered due to issues with accessibility from solution crystallization and scalability of production. Herein, we demonstrate facile synthesis of HUMs via mechanochemistry using commercially available ball-mills. Gram scale quantities of ten new and existing HUMs are afforded using a dry grinding process.

4.2 Introduction

The development and scale-up of porous physisorbent materials in the “age of gas”, is key to enabling new technologies around the use of gases.¹ Current separation and purification technologies such as distillation are energy intensive and consume large amounts of global energy annually.² Development of new separation processes that offer much reduced energy footprints is therefore an urgent technological need. In this context,
Physisorption-based technologies have shown potential to reduce the energy requirements for industrial processes. Metal-Organic Materials (MOMs), also known as metal-organic frameworks (MOFs) or porous coordination polymers (PCPs), have gained attention in this context thanks to their modular structures and the resulting diversity of composition. Indeed, there are now tens of thousands of MOMs. Trace carbon capture, which is relevant to a number of industrial processes, has yet to be achieved by MOMs because of relatively poor selectivity towards CO₂ vs. C₂H₂, N₂ and CH₄. It is in this context that a class of porous materials which exhibits benchmark CO₂ selectivity and working capacity, hybrid ultramicroporous materials (HUMs), have emerged. HUMs have thus far demonstrated excellent performance with respect to the following separations: CO₂/flue gas, CO₂/air; Xe/Kr; C₂H₂/C₂H₄; CO₂/C₂H₂; and C₂H₂/CO₂. However, synthesis of this type of materials has long relied on traditional solution-based methods, i.e. layering or solvothermal, which is time consuming and requires excessive amounts of solvent. The lack of a suitable method for production scale up has thus far been a barrier to HUMs in maximising their potential for numerous applications.

A mechanochemical reaction is induced by direct absorption of mechanical energy and in principle offers advantages over solution synthesis such as high yield with little waste. Further, mechanochemical reactions can be conducted at scale using continuous processes such as twin-screw extrusion (TSE). Mechanochemical synthesis of a limited number of MOMs has been demonstrated using commercially available ball-mills. James and co-workers employed a neat grinding method for the synthesis of Cu(ina)₂ and HKUST-1. Grinding has also been employed in the synthesis of ZIF-8, MIL-78, MIL-101(Cr), DABCO pillared MOFs, IRMOFs, UiO-66/UiO-66-NH₂, and MOF-74. TSE has also been employed for the Kg mechanochemical synthesis of MOMs. However, facile
synthesis of HUMs in multi gram scale without any solvent involved by mechanochemical method has yet to be realized.

In this contribution, we investigate the first use of mechanochemical methods to synthesize a family of HUMs. The prototypical “pillared square grid” platform, [Zn(4, 4’-bpy)2(SiF₆)]ₙ, SIFSIX-1-Zn,³⁶ was first reported in 1995. This was comprised of 2D sql nets pillared by SiF₆²⁻ anions (‘SIFSIX’) so as to form 3D nets with primitive cubic (pcu) topology. By varying the organic linker, the pore size of these materials can be adjusted from mesoporous (> 2 nm) to ultramicroporous (< 0.7 nm).¹² In recent studies, variations in the inorganic pillar and metal nodes have been found to influence the gas sorption performance of isostructural materials.¹³,³⁷,³⁸ Herein, ten isostructural HUMs were synthesised via a mechanochemical synthesis method (Figure 4.1), six of which have been previously reported, [M(pyrazine)₂(SiF₆)]ₙ (M = Zn, Ni, Co, Fe), SIFSIX-3-Zn/Ni/Co/Fe,¹³,³⁹ [Ni(pyrazine)₂(TiF₆)]ₙ, TIFSIX-3-Ni³⁸ and [Ni(pyrazine)₂(NbOF₅)]ₙ, NbOFFIVE-1-Ni,⁴⁰ an analogue of [Cu(pyrazine)₂(NbOF₅)]ₙ which was first reported by Poeppelmeier and co-workers in 1996.⁴¹ We have also synthesised four new HUM variants based on the TiF₆²⁻ and NbOF₅²⁻ inorganic pillars ([M(pyrazine)₂(TiF₆)]ₙ (M = Zn, Co), TIFSIX-3-Zn/Co and [M(pyrazine)₂(NbOF₅)]ₙ (M = Zn, Co), NbOFFIVE-1-Zn/Co) which were not readily synthesised by traditional solution based synthesis methods. The materials synthesized in this study were characterized using the following experiments: powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), single-component gas adsorption isotherms, particle size distribution experiments, thermogravimetric analysis (TGA) and accelerated stability testing.
4.3 Results and Discussion

Microcrystalline HUMs were synthesised via a mechanochemical synthesis process (See Electronic Supporting Information (ESI†) for full details). The crystallinity and purity of the mechanochemically synthesized HUMs was confirmed by PXRD. The PXRD patterns obtained were found to be in agreement with the simulated patterns (Figure 4.2B-4.2D and Appendix C, Figure C1-C16). Optimisation of the ball milling process was performed using PXRD. In the case of SIFSIX-3-Ni (Figure 4.2A), PXRD was performed on the physical mix of the NiSiF$_6$·6H$_2$O salt and pyrazine, and subsequently on aliquots of ball milled material extracted at time intervals of 1, 5, 10, 15, 30, 60, 90, 120 and 150 minutes. The characteristic peak for pyrazine at 18.1 2θ degrees and NiSiF$_6$·6H$_2$O at 19.3 2θ degrees started to diminish after 1 min of grinding. After 120 min of ball-milling, these peaks were found to be absent thus signalling completion of the reaction. The powdered sample obtained was found to be the desired sql precursor. This was then heated at 100 °C to obtain the pcu topology HUM, SIFSIX-3-Ni. Interestingly, while SiF$_6^{2-}$ and TiF$_6^{2-}$ variants required heating to form the
desired **pcu** networks, NbOF$_5^{2-}$ based variants were found to have **pcu** topology in the as-synthesised form.

**Figure 4.2.** Powder X-ray diffraction and microscopy of the HUMs studied. A, PXRD of SIFSIX-3-Ni formation during ball milling process, including physical mix of starting ingredients, formation of precursor and fully activated HUM. B-D, PXRD of ball milled SiF$_6^{2-}$, TiF$_6^{2-}$ and NbOF$_5^{2-}$ pillared HUMs, respectively. E, SEM images depicting the morphology of the HUMs; (I) SIFSIX-3-Ni, (II) NbOFFIVE-1-Ni, (III) TIFSIX-3-Ni, (IV) TIFSIX-3-Co.

SEM studies were used to analyse the morphology of the materials synthesised *via* ball milling. All crystalline samples were found to comprise of block shaped crystals with cubic morphology (Figure 4.2E). Particle size distribution studies were carried out for the ball milled powder samples using a Morphologi G3 instrument. Narrow particle size distributions were observed for all HUMs with mean size varying between 1.63 and 7.07 µm (Figure 4.3A-4.3B, and Appendix C, Figure C108-C127 and Table C1). The unit cell parameters were obtained for the four new HUMs by peak fitting (Appendix C, Figure C128-C131) and
have been tabulated in Table C2-C5. TiF$_6^{2-}$ and NbOF$_5^{2-}$ variants possess slightly longer $c$-axes when compared to SiF$_6^{2-}$ based HUMs. The longer $c$-axis can be attributed to the presence of the NbOF$_5^{2-}$ and TiF$_6^{2-}$ inorganic pillars. The bulkier inorganic pillar also gives way to shorter F···F distances within in the unit cells of TiF$_6^{2-}$ and NbOF$_5^{2-}$ materials which have previously been shown to significantly affect the gas sorption performance of the resulting materials.$^{37,38}$

![Figure 4.3](image.png)

**Figure 4.3.** Particle size distribution and gas sorption. A, Particles around the mean length of SIFSIX-3-Ni. B, Particle size distribution for the bulk powder of HUMs. C, Comparison of CO$_2$ uptake at 0-1 bar and 0.0004 bar for all HUMs. D, CO$_2$ uptake at 0-0.01 bar partial pressure regions. E, CO$_2$ isosteric heats of adsorption ($Q_d$). F, CO$_2$/N$_2$ IAST selectivity (0.04:99.96) for all HUMs. Note: SiF$_6^{2-}$, TiF$_6^{2-}$ and NbOF$_5^{2-}$ pillars represented by red, blue and green, respectively. Metal nodes are represented by the following symbols; Zn (▲), Co (O), Ni (●) and Fe (■).

The porosity of all the HUMs was confirmed via gas sorption experiments (Full details provided in Appendix C). Gas sorption isotherms were collected under several
conditions (273, 298 K CO₂; 298 K N₂; 298 K CH₄) to examine various properties such as saturation uptake capacity, isosteric heat of adsorption (Qₑ) and Ideal Adsorbed Solution Theory (IAST) selectivity. The CO₂ gas sorption isotherms obtained for mechanochemically synthesized HUMs exhibited similar curve profiles and saturation uptake when compared with HUMs obtained via traditional synthesis approaches (Appendix C, Figure C34, C36, and C38). The effect of inorganic pillar and metal node substitution on the gas sorption properties of isostructural HUMs is apparent when the CO₂ sorption isotherms are examined in the ultra-low (0-0.01 bar) partial pressure region (Figure 4.3C-4.3D). TiF₆²⁻ and NbOF₅²⁻ variants were found to outperform all SiF₆²⁻ variants. NbOFFIVE-1 Ni and TIFSIX-3-Ni were found to exhibit CO₂ uptake capacities of 1.2 and 1.1 mmol/g, respectively, at ca. 400 ppm which translates to 48 and 43 percent of their saturation capacities. The next best performing HUM was TIFSIX-3-Co followed by NbOFFIVE-1-Co, NbOFFIVE-1-Zn and TIFSIX-3-Zn with uptake capacities of 0.80, 0.625, 0.55 and 0.53 mmol/g at ca. 400 ppm, respectively. SIFSIX-3-Ni was found to be the best performing compound of the SiF₆²⁻ variants, followed by SIFSIX-3-Co. SIFSIX-3-Zn and SIFSIX-3-Fe were found to have low uptake under similar conditions. All materials were found to exhibit low N₂ and CH₄ uptake at 298 K (Figure 4.3D-4.3F and Appendix C, Figure C27-C42). Improved CO₂ sorption by TiF₆²⁻ and NbOF₅²⁻ variants at low pressure compared to SiF₆²⁻ variants was reflected in the isosteric heats of adsorption (Qₑ). NbOFFIVE-1-Ni and TIFSIX-3-Ni exhibited Qₑ values in excess of 55 kJ/mol; this was closely followed by the remaining TiF₆²⁻ and NbOF₅²⁻ variants (See Table 4.1; Figure 4.3E). SIFSIX-3-Ni had the highest Qₑ (50.8 kJ/mol) among the SiF₆²⁻ variants. SIFSIX-3-Zn, SIFSIX-3-Co, SIFSIX-3-Fe were found to exhibit Qₑ values of 45, 49 and 42 kJ/mol, respectively. Interestingly, subtle differences in terms of pore size and pore chemistry in a series of isostructural compounds gave way to significant variations in the gas sorption performance.
Table 4.1. Physicochemical properties, gas sorption and IAST selectivity data.

<table>
<thead>
<tr>
<th>HUMs</th>
<th>Surface Area (m²/g)¹</th>
<th>$Q_a$ (kJ/mol)</th>
<th>Total Uptake @ 298K (mmol/g)</th>
<th>CO₂ Uptake @ 298K (mmol/g)</th>
<th>IAST Selectivity CO₂/N₂</th>
<th>IAST Selectivity CO₂/CH₄</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
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<td>CH₄</td>
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<tr>
<td>SIFSIX-3-Zn¹²</td>
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<td>0.11</td>
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<td>0.18</td>
<td>0.38</td>
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<td>2.57</td>
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<tr>
<td>TIFSIX-3-Ni¹⁸</td>
<td>209</td>
<td>55.3</td>
<td>2.49</td>
<td>0.17</td>
<td>0.09</td>
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<tr>
<td>NbOFFIVE-1-Ni</td>
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<td>55.4</td>
<td>2.44</td>
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<tr>
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<td>222</td>
<td>49</td>
<td>2.62</td>
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<tr>
<td>TIFSIX-3-Co</td>
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<tr>
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<td>0.30</td>
<td>0.95</td>
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</tbody>
</table>

¹ Surface area calculated from CO₂ 298K

In order to further investigate the effect of subtle variations in isostructural materials, IAST selectivities were calculated for CO₂/N₂ ($S_{CO}$) and CO₂/CH₄ ($S_{CM}$) binary gas mixtures. IAST selectivity values for CO₂/N₂ ratios of 0.04:99.96 (equivalent composition for Direct Air Capture (DAC); (Figure 4.3F) and 15:85 (equivalent composition of Industrial Flue Gas) were calculated, while CO₂/CH₄ ratios of 50:50 (equivalent composition for Natural Gas Sweetening) were also calculated. NbOFFIVE-1 Ni and TIFSIX-3-Ni outperformed all other HUMs with selectivity of 24000 and 19200 for a 0.04:99.96 CO₂/N₂ gas mixtures. SIFSIX-3-Ni was found to have the highest selectivity ($S_{CN}$-5100) among the SiF₆²⁻ variants. A similar trend in selectivity values was observed at trace levels and flue gas composition, however, the magnitude decreased. NbOFFIVE-1-Ni performed the best at all compositions with
selectivity of 5000 and 700 at DAC and flue gas compositions respectively (See Table 1 for more details). With respect to $S_{CM}$, TIFSIX-3-Ni performed the best with selectivity of 371 for an equimolar mixture of CO$_2$ and CH$_4$. NbOFFIVE-1-Ni was the next best performing material with $S_{CM}$ of 290. The remaining TiF$_6^{2-}$ and NbOF$_5^{2-}$ variants exhibited $S_{CM}$ of ~ 100 for an equimolar mixture of CO$_2$ and CH$_4$, thus highlighting the potential of these materials for natural gas purification.

Thermal stability of each HUM variant was determined using TGA and variable-temperature powder X-ray diffraction (VT-PXRD) (Appendix C, Figure C17-C26, C88-C97). NbOFFIVE-1-Ni, was found to be the most stable variant thermally, retaining structural integrity to ca. 350 °C. Conversely, SIFSIX-3-Zn was found to be the least stable material. On comparing the thermograms, a trend was observed wherein NbOF$_5^{2-}$ variants were found to be more stable compared to SiF$_6^{2-}$ and TiF$_6^{2-}$ variants. Stability of the sorbents towards humidity is also an important factor for addressing the shelf life of synthesised materials. In order to address this, accelerated stability tests were performed as per pharmaceutical industry guidelines. HUMs were exposed to 40 °C and 75% relative humidity for periods of 1, 7 and 14 days (Appendix C, Figure C68-C87). Ni-based HUMs performed best with < 10% loss of surface area after 14 days compared to the pristine sample. NbOFFIVE-1-Ni remained unaltered, whereas SIFSIX-3-Ni and TIFSIX-3-Ni converted to sql precursor on exposure to humidity, pcu variants could be recycled upon exposure to heat. When exposed to humidity, Co, Zn and Fe variants revert to the sql precursor, however, regeneration upon heating was found to be limited. SIFSIX-3-Co and SIFSIX-3-Fe retained more than 90% of their surface area after 1 day of exposure; this gradually degraded during stability testing until minimal surface area was recorded after 14 days exposure.

Compared to the previous solvent based synthesis strategies (i.e. solvothermal, slurrying or layering), mechanochemical synthesis gave way to gram scale synthesis of high
purity HUMs in one-step. SEM studies validated the morphology of synthesised materials, while PXRD and gas sorption experiments were used to verify purity of the bulk phase. Zn variants of HUMs were found to produce smaller particle size regardless of the inorganic pillar, meanwhile, Ni variants tended to form larger particles. Interestingly, the mechanochemical synthesis process yields materials with a narrow particle size distribution (*ca.* 1 to 10 µm). This narrow particle size distribution would be desirable for subsequent formulation and shaping processes, enabling denser compaction of powders and minimising dead volume within the shaped body.

The use of a mechanochemical synthesis process was found to significantly reduce the reaction time (60-150 mins vs. multiple days) and starting reactants (no solvent used) required during synthesis. In a typical slurry process, 20 equivalents of pyrazine can be required to obtain TIFSIX-3-Ni, however only 2.1 equivalents were needed during the mechanochemical synthesis process. The mechanochemical synthesis process also reduced the need for hazardous substances such as HF to be present during the synthesis of NbOF$_5^{2-}$ pillared variants, these variants are typically synthesised using a solvothermal process using significant quantities of HF. The mechanochemical synthesis of HUMs also led to the synthesis of four previously unreported HUM variants (TIFSIX-3-Zn, TIFSIX-3-Co, NbOFFIVE-1-Zn and NbOFFIVE-1-Co). Interestingly, synthesis of these materials had previously been difficult to realise using traditional solution based strategies. Additionally, before this study only a single HUM variant for each of the TiF$_6^{2-}$ and NbOF$_5^{2-}$ pillars using pyrazine as a linker ligand, TIFSIX-3-Ni and NbOFFIVE-1-Ni, respectively.

Study of these isostructural analogues led to better understanding of structure property relationship and how subtle differences in terms of pore size and pore chemistry in a series of isostructural compounds gave way to significant variations in the gas sorption performance. Variations in the inorganic pillar can result in shorter F···F distances and enhanced
electrostatics offered by the NbOF$_5^{2-}$ and TiF$_6^{2-}$ pillars which in turn increase the HUM-CO$_2$ interactions and thus increase the CO$_2$ $Q_{st}$ observed. With respect to the metal node, Ni variants performed the best irrespective of the inorganic pillar; this can be credited to the stronger Ni-N bonds, which leads to contraction of the pore diameter thus creating a tighter CO$_2$ binding site. The enhanced electrostatics offered by the NbOF$_5^{2-}$ and TiF$_6^{2-}$ pillars gives way to improved gas sorption performance and selectivity in HUMs, regardless of the metal node, compared to SiF$_6^{2-}$ variants. High $S_{CN}$ and $S_{CM}$ observed for TIFSIX-3-Ni and NbOFFIVE-1-Ni illustrates the potential of these materials for multiple gas separation and purification processes.

Finally, study of these isostructural analogues led to better understanding of how subtle differences in a series of isostructural compounds can affect their thermal and hydrolytic stability. NbOF$_5^{2-}$ variants were found to exhibit high thermal stability of up to 350 °C for NbOFFIVE-1-Ni. Ni containing variants were found to be the most thermally stable regardless of inorganic pillar. The overall order of thermal stability upon metal node substitution followed the trend; Ni > Co ~ Fe > Zn. The Zn variants were found to exhibit poor stability in the presence of humidity with over 50% loss in surface area after 1 day exposure to moisture. The overall order of hydrolytic stability upon metal node substitution followed the trend; Ni > Co ~ Fe > Zn. This can be attributed to varying strengths of M-N and M-F/O interactions with Ni-N bond being the strongest and the least H$_2$O ligand exchange rate for Ni$^{2+}$. The pcu formation in the as-synthesised form of the NbOF$_5^{2-}$ variants as compared to the sqi precursor observed in SiF$_6^{2-}$ and TiF$_6^{2-}$ materials can be attributed to the out-of-centre distortion in the NbOF$_5^{2-}$ pillar. The distortion leads to strong nucleophilic centres at the negatively charged oxide and trans fluoride of NbOF$_5^{2-}$ leading to a stronger M-O and M-F bond in NbOF$_5^{2-}$ based materials as compared to M-F bonds in case of SiF$_6^{2-}$ and TiF$_6^{2-}$ materials.
4.4 Conclusions

In conclusion, HUM physisorbents have been synthesised in gram scale using a mechanochemical synthesis approach. Facile synthesis was achieved in the absence of organic solvents and corrosive reactants such as HF. The use of mechanochemical synthesis techniques enabled the synthesis of four previously unreported HUM variants and thus enabled the systematic study of the structure property relationships in a series of isostructural compounds. Gas sorption and stability studies illustrated the significant affect that subtle variations in metal node and inorganic pillar can have on the resulting properties in HUMs. Pillar substitution gave way to enhanced electrostatics offered by the NbOF$_5^{2-}$ and TIF$_6^{2-}$ pillars compared to SiF$_6^{2-}$ variants which in turn leads to improved gas sorption performance in terms of $Q_{st}$ and selectivity. Metal node substitution can lead to enhanced thermal and hydrolytic stability. Overall, this work illustrates how HUMs are amenable to mechanochemical synthesis and that subtle changes in pore structure and pore chemistry can enable large improvements in CO$_2$ capture performance.
4.5 References


Halasyamani, P., Heier, K. R., Willis, M. J., Stern, C. L. & Poeppelmeier, K. R. Syntheses and Structures of Two New Cu/Nb/pyrazine Complexes: Three dimensional CuNb(pyrazine)2OF5·pyrazine(H2O) and two dimensional...


Chapter Five: Flue-Gas and Direct Air Capture of CO₂ by Porous Metal–Organic Materials

5.1 Aim of the Chapter

Sequestration of CO₂, either from gas mixtures or directly from air (Direct Air Capture, DAC), is a technological goal important to large-scale industrial processes such as gas purification and the mitigation of carbon emissions. Previously, we investigated five porous materials, three porous metal-organic materials (MOMs), a benchmark inorganic material, Zeolite 13X, and a chemisorbent, TEPA-SBA-15, for their ability to adsorb CO₂ directly from air and from simulated flue gas. In this contribution, a further ten physisorbent materials that exhibit strong interactions with CO₂ have been evaluated by temperature-programmed desorption for their potential utility in carbon capture applications: four hybrid ultramicroporous materials (HUMs), SIFSIX-3-Cu, DICRO-3-Ni-i, SIFSIX-2-Cu-i and MOOFOUR-1-Ni; five microporous MOMs, DMOF-1, ZIF-8, MIL-101, UiO-66 and UiO-66-NH₂; an ultramicroporous MOM, Ni-4-PyC. The performance of these MOMs was found to be negatively impacted by moisture. Overall, we demonstrate that the incorporation of strong electrostatics from inorganic moieties combined with ultramicropores offers improved CO₂ capture performance from even moist gas mixtures but not enough to compete with chemisorbents.

5.2 Note to Readers

This chapter has been previously published in Philosophical Transactions of the Royal Society A 2017, 375 (2084), 20160025 and has been reproduced with permission of Royal Society. Amrit Kumar, David G. Madden and Hayley S. Scott synthesized and characterized all compounds. David G. Madden carried out the breakthrough experiments and
temperature programmed desorption studies. All the authors contributed to the writing of the manuscript.

5.3 Introduction

Anthropogenic emissions of carbon dioxide (CO$_2$) are accepted as a significant risk to global climate. Atmospheric CO$_2$ concentration has surpassed 400 ppm on several occasions since 2013, which represents an increase of over 100 ppm since pre-industrial revolution levels. At the 2015 United Nations Climate Change Conference, the 196 parties in attendance signed an agreement calling for zero net anthropogenic greenhouse gas emissions to be reached during the second half of the 21st century. There are two pathways currently being considered for the reduction of CO$_2$ emissions: 1) CO$_2$ removal from CO$_2$ rich post-combustion industrial point sources (i.e. flue-gas capture); 2) the removal of CO$_2$ from the atmosphere via direct air capture (DAC). Whereas addressing the increase in global CO$_2$ concentrations presents a scientific and technological challenge of the highest order, it also presents an opportunity since DAC becomes more viable at higher CO$_2$ levels and CO$_2$ is a useful commodity. Carbon Capture and Storage (CCS) technologies focus on capturing and storing CO$_2$. Carbon Capture and Utilisation (CCU) looks to exploit the large volumes of CO$_2$ produced by industrial practices for use in other applications. For example CO$_2$ is currently used as a feed gas in the chemical industry for the production of various alcohols, dimethyl ether, biodiesel and polymers. These large-scale processes are suited to the high volumes of CO$_2$ associated with post-combustion CO$_2$ capture. However, other niche applications such as the use of CO$_2$ gas in greenhouses to encourage photosynthesis or in algae-farms to promote biofuels production may be more applicable to smaller scale CO$_2$ capture via DAC technologies. DAC may also be feasible for mitigating emissions from mobile sources and if recycling costs are minimal, might represent an approach to the introduction of new carbon negative technologies. The catch is that DAC is handicapped by
the relative availability of CO$_2$ in the atmosphere (0.0004 atm versus 0.15 atm in post-combustion capture) and, in the case of physisorption, by competition with other gases and vapours such as N$_2$ and H$_2$O.$^{10}$ DAC is therefore much more challenging to physisorbents than post-combustion CO$_2$ capture, but it may be practical if an adsorbent offers optimum uptake, appropriate CO$_2$ selectivity over N$_2$ and H$_2$O and facile recyclability.$^{11,12}$

At present, DAC systems typically employ solid supported amine-based adsorbents, wherein amine functional groups are tethered to the surface of cellulose,$^{13,14}$ porous polymer networks,$^{15,16}$ and porous silica materials.$^{10,17-20}$ Chemisorption of CO$_2$ is feasible but in order for chemisorbents to be recycled one must reverse the chemical reaction that captures CO$_2$. Therefore, although chemisorbents achieve moderate CO$_2$ adsorption capacities (0.5-3.6 mmol/g) for DAC, they also typically require elevated temperatures for sorbent regeneration (> 100 °C). It has also been found that gas constituents such as NO$_x$, SO$_x$ and CO$_2$ itself can negatively impact amine-modified solids by poisoning the chemisorbent and deactivating the amine adsorption sites.$^{21-23}$ Further, amine-modified materials are sometimes subject to thermal and oxidative degradation.$^{24,25}$ DAC using physisorbent materials has been much less studied, presumably due to the lack of suitable candidate materials. In principle, advanced sorbents that capture CO$_2$ through highly selective physisorption offer great promise because they require much less energy for recycling. Unfortunately, existing classes of physisorbent materials do not meet the requirements for DAC, mainly high CO$_2$ selectivity over N$_2$ ($S_{CN}$) and H$_2$O ($S_{CW}$), which are major constituents of air.

Recently, we reported a systematic study of DAC performance for a number of benchmark physisorbents;$^{10}$ prototypal Metal-Organic Materials (MOMs) HKUST-1 and Mg-MOF-74, a zeolite, Zeolite 13X, and a Hybrid Ultramicroporous Material (HUM),$^{26}$ SIFSIX-3-Ni. A highly adsorbent amine-modified chemisorbent material, TEPA-SBA-15, was included in the study for comparison. All four physisorbent materials were observed to
exhibit a dramatic decrease in performance with respect to CO$_2$ uptake in the presence of water vapour. **SIFSIX-3-Ni** exhibited the highest CO$_2$ uptake from DAC of the physisorbent materials at 4.07 L CO$_2$/kg adsorbent. While the chemisorbent **TEPA-SBA-15** was unaffected by water vapor, its energetics and recyclability were not as favorable as those of **SIFSIX-3-Ni**. In this contribution we examine the performance of ten additional benchmark physisorbent materials for capturing CO$_2$ from flue-gas and DAC using a combination of temperature-programmed desorption (TPD), thermogravimetric analysis (TGA) and mass spectrometry (MS). **SIFSIX-3-Cu**, **DICRO-3-Ni-i**, **MOOFOUR-1-Ni**, **SIFSIX-2-Cu-i**, **Ni-4-PyC**, **ZIF-8**, **DMOF-1**, **UiO-66**, **UiO-66-NH$_2$** and **MIL-101** were evaluated for their performance with respect to DAC and five other CO$_2$-rich gas mixtures. The ten physisorbents studied herein represent two classes of MOMs that have been widely studied for carbon capture (Figure 5.1).

The rich structural and functional diversity of MOMs means that they can be tuned for specific purifications and separations of gas mixtures. **SIFSIX-3-Cu**, **SIFSIX-2-Cu-i**, **DICRO-3-Ni-i**, and **MOOFOUR-1-Ni** are HUMs, which exhibit ultramicropores (< 0.7 nm) and are comprised of metal cation nodes linked by two types of linkers: neutral organic ligands and anionic inorganic pillars. The use of an appropriately charged inorganic pillar means that the resulting network is uncharged and creates a relatively high electrostatic contribution that, when combined with tight binding sites, enables strong interactions between adsorbent and adsorbate (large $Q_{st}$) and ultra-high selectivity for polarizable gases such as CO$_2$ vs. less polarizable gases such as N$_2$. **ZIF-8**, **DMOF-1**, **UiO-66**, **UiO-66-NH$_2$** and **MIL-101**, are prototypal examples of physisorbent MOMs, also known as Metal-Organic Frameworks, MOFs, or Porous Coordination Polymers, PCPs. **Ni-4-PyC** is a recently reported example of an ultramicroporous MOM and, being built from a single small ligand; **Ni-4-PyC** exhibits similar pore dimensions to HUMs (0.35 and 0.48 nm). However, there is a
reduced electrostatic contribution due to the lack of an inorganic pillar. These sorbents were synthesized following literature methods (refer to Appendix D). Each of the sorbents was characterized via powder X-ray diffraction (PXRD; Appendix D, D3-D12) to verify phase purity. Sorbents were then subjected to solvent exchange and activation using published procedures; details for the exchange process and activation protocols are given in the Appendix D. After activation, each sorbent was subjected to sorption experiments to verify a match with their reported apparent surface area, uptake capacity and isosteric enthalpy of adsorption for CO$_2$ (Isotherms; Appendix D, D13-D22).

**Figure 5.1.** Ten physisorption materials were evaluated in this study. Elements C, O, N, Si, F, Cu, Cr, Ni, Mo, Zn and Zr are represented by grey, red, blue, yellow, pink, salmon, dark red, sky blue, orange, brown and purple, respectively; H atoms have been omitted for clarity. The dark green net represents the second interpenetrated network in SIFSIX-2-Cu-i and DICRO-3-Ni-i.

The CO$_2$ adsorption performance of each physisorbent was evaluated using pristine, activated samples exposed to a specific gas mixture for a prescribed time period before being subjected to temperature-programmed desorption (TPD). In a typical TPD experiment, a
sample was placed in a quartz reactor cell positioned within a tube furnace. This cell was heated to a temperature that promotes expulsion of guest molecules from the host in the presence of He carrier gas. The exhaust gas was continuously monitored using a mass spectrometer (MS). These experiments provide the identity and relative quantity of gases and vapors desorbed by the sample as a function of temperature, or, if temperature is held constant, as a function of time. They also afford an understanding of the energy required for recycling the adsorbent. In short, TPD experiments address relative CO₂/H₂O uptake and afford at least a qualitative indication of the ease with which the sorbent can be recycled. In conjunction with the DAC experiments where the material was exposed to laboratory atmosphere, the ten physisorbents were also subjected to TPD-TGA experiments in which each material was exposed to five additional gas mixtures following a protocol previously established. Each of the five gas mixtures was selected to address a different aspect of the sorbent’s performance with respect to CO₂ sorption. Data from the DAC and TPD-TGA experiments on the ten adsorbents, as well as the five previously studied materials, are presented in Table 5.1 (for full dataset of results see Appendix D).

5.4 Results and Discussion

In terms of DAC from laboratory atmosphere, SIFSIX-3-Cu exhibits the highest gravimetric uptake of CO₂ (7.18 L CO₂/kg) of the ten physisorbents examined during this study, outperforming SIFSIX-3-Ni, the top physisorbent from our previous study. SIFSIX-3-Cu was previously found to exhibit a high $Q_{st}$ (56 kJ/mol) and high CO₂ uptake at low partial pressure (1.24 mmol/g) during single-component CO₂ adsorption experiments. SIFSIX-3-Cu exhibits a higher $Q_{st}$ and gravimetric uptake at 400 ppm than SIFSIX-3-Ni (50.8 kJ/mol, 1.10 mmol/g respectively), which explains why the DAC uptake of CO₂ for SIFSIX-3-Cu (7.18 L CO₂/kg) is larger than that of SIFSIX-3-Ni (4.07 L CO₂/kg). The ultramicroporous pore channel and high electrostatic contribution of the inorganic SiF₆²⁻ pillar is key to the DAC
performance of the SIFSIX-3-M compounds.\textsuperscript{11,12} While, pristine SIFSIX-3-Cu performs best in terms of DAC performance, the material was found to be inherently unstable. When SIFSIX-3-Cu is exposed to elevated temperature and humidity (40 °C, 75% RH) there is a notable change in terms of PXRD (Appendix D, D100) and surface area (Appendix D, D101).

UiO-66-NH\textsubscript{2} was observed to exhibit the next highest gravimetric uptake of CO\textsubscript{2} (5.7 L CO\textsubscript{2}/kg) of the ten physisorbents examined during this study. The “decoration” of the terephthalic acid linker with an amine group to form UiO-66-NH\textsubscript{2} has a significant effect on the CO\textsubscript{2} uptake by this adsorbent compared with the parent material, UiO-66 (DAC < 1.0 L CO\textsubscript{2}/kg), under all adsorption conditions. The reason UiO-66-NH\textsubscript{2} outperforms UiO-66 is again correlated with isosteric enthalpy of adsorption ($Q_{st}$). UiO-66 and UiO-66-NH\textsubscript{2} exhibit $Q_{st}$ values of 25.5 kJ/mol and 35.1 kJ/mol, respectively.\textsuperscript{42,43} High $Q_{st}$ values are reflective of stronger adsorbate/adsorbent interactions, but they also require higher regeneration energies during the desorption process to liberate the adsorbed CO\textsubscript{2}.\textsuperscript{44} The improvement in CO\textsubscript{2} adsorption and increase in enthalpy of adsorption of UiO-66-NH\textsubscript{2} over UiO-66 is attributed to the addition of the highly polar amine group; this in turn increases the affinity of UiO-66-NH\textsubscript{2} towards polarizable gases such as CO\textsubscript{2}.\textsuperscript{43,45} The addition of highly polar ligands also leads to a considerable enhancement of CO\textsubscript{2}/N\textsubscript{2} selectivity ($S_{CN}$).\textsuperscript{46,47} The affinity of UiO-66-NH\textsubscript{2} towards CO\textsubscript{2} has previously been observed to increase with an increase in the amine density.\textsuperscript{48} This phenomenon also has been observed in other amine functionalized MOMs.\textsuperscript{49-53} The increase in the amount of CO\textsubscript{2} adsorbed may also be as a result of a quasi-chemisorption interaction between CO\textsubscript{2} and the functional amino group in UiO-66-NH\textsubscript{2}, whereby CO\textsubscript{2} interacts with the amine to form anhydrous carbamates in the absence of H\textsubscript{2}O or bicarbonate species under moist conditions as observed in other amine functionalized porous materials.\textsuperscript{54} This increased affinity towards CO\textsubscript{2} also improves $S_{CW}$ compared with
that of the parent \textbf{UiO-66} material and is supported by TPD experiments, which estimate the relative ease of regeneration of the sorbent. The DAC plot in Figure 5.2 reveals that \textbf{UiO-66-NH}_2 requires notably more energy and time to liberate CO\textsubscript{2} compared with \textbf{UiO-66} and the other physisorbents studied herein.

\textbf{Figure 5.2.} Temperature-Programmed Desorption (TPD) plots for DAC for the ten sorbents studied. The red curve depicts the temperature profile used for desorption. The MS signal for CO\textsubscript{2} and H\textsubscript{2}O are given by the black and blue curves, respectively.

Comparing \textbf{SIFSIX-3-Cu} and \textbf{Ni-4-PyC} provides insight into the relative impact of two key aspects of HUMs: the presence of ultramicropores and the strong electrostatics by use of inorganic pillars. The use of ultramicropores alone has been shown to significantly enhance the selective adsorption of H\textsubscript{2} over CO\textsubscript{2}\textsuperscript{55} or CO\textsubscript{2} over other gases\textsuperscript{18,56,57} \textit{via} size selective exclusion. However, size exclusion requires very precise and uniform pore size, which is difficult to design and has only been observed in a few instances. While both adsorbents exhibit similar pore dimensions (3.5 and 4.8 Å for \textbf{Ni-4-PyC} and 3.5 Å for \textbf{SIFSIX-3-Cu}), \textbf{Ni-4-PyC} lacks inorganic pillars (SiF\textsubscript{6}\textsuperscript{2-} anions), which results in a reduced
electrostatic contribution and $Q_{st}$ values (34 vs. 56 kJ/mol). This, in turn, results in lower CO$_2$ uptake at very low partial pressures such as those in the atmosphere. Ni-4-PyC exhibits lower CO$_2$ uptake (1.68 L CO$_2$/kg) from laboratory atmosphere compared with SIFSIX-3-Cu (7.18 L CO$_2$/kg), which further suggests that electrostatics plays an important role in the performance of physisorbt materials in terms of $S_{CN}$ and $S_{CW}$ and that pore-size alone does not determine the adsorption performance of ultramicroporous materials.

SIFSIX-2-Cu-i and MOOFOUR-1-Ni performed only marginally better than the non-HUM physisorbents. While MOOFOUR-1-Ni (1.27 L CO$_2$/kg) has a very high $Q_{st}$ (56 kJ/mol), its larger pores (ca. 7 Å) are borderline supermicroporous. Comparing SIFSIX-2-Cu-i (< 1.0 L CO$_2$/kg) with SIFSIX-3-Cu, we see the former has a somewhat larger pore-size (ca. 5 Å), but also a lower density of inorganic pillars than the latter due to the interpenetrated nature of this compound. These two factors combine to create a lower $Q_{st}$ (31.9 kJ/mol) for SIFSIX-2-Cu-i and presumably account for the decreased DAC performance. Of the non-HUM physisorbents in this study, UiO-66-NH$_2$ aside, ZIF-8 performed the best, adsorbing 1.2 L CO$_2$/kg from the laboratory atmosphere. DMOF-1, MIL-101, and UiO-66 all adsorbed less than 1.0 L CO$_2$/kg under these conditions.

When the materials were exposed to simulated flue-gas (moist 0.15 atm CO$_2$/0.85 atm N$_2$), SIFSIX-3-Cu was again the top performer of the ten adsorbents studied herein in terms of gravimetric CO$_2$ uptake, adsorbing 51.42 L CO$_2$/kg. This is comparable to SIFSIX-3-Ni and Mg-MOF-74, which were previously found to adsorb 38.69 L CO$_2$/kg and 34.62 L CO$_2$/kg, respectively. UiO-66-NH$_2$ (26.12 L CO$_2$/kg), MOOFOUR-1-Ni (19.85 L CO$_2$/kg) and Ni-4-PyC (12.57 L CO$_2$/kg) were the next best materials under simulated flue-gas conditions.
Table 5.1. Comparison of the strengths and weaknesses of selected DAC sorbents.

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<th>Sorbent</th>
<th>DAC (1 atm; 49% RH)</th>
<th>Moist CO₂ (0.15 atm; 75% RH)</th>
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<td></td>
<td>CO₂</td>
<td>H₂O</td>
<td>CO₂ L/kg(L/L)</td>
</tr>
<tr>
<td>SIFSIX-3-Ni[a]</td>
<td>&lt;8%</td>
<td>&gt;92%</td>
<td>4.07 (6.55)</td>
</tr>
<tr>
<td>HKUST-1[a]</td>
<td>1%</td>
<td>99%</td>
<td>1.07 (0.95)</td>
</tr>
<tr>
<td>Mg-MOF-74[a]</td>
<td>&lt;4%</td>
<td>&gt;96%</td>
<td>3.21 (2.94)</td>
</tr>
<tr>
<td>Zeolite 13X[a]</td>
<td>1%</td>
<td>99%</td>
<td>0.76 (0.99)</td>
</tr>
<tr>
<td>TEPA-SBA-15[b]</td>
<td>93%</td>
<td>7%</td>
<td>80.44 (N/A)</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>13.8%</td>
<td>&gt;86%</td>
<td>7.18 (11.55)</td>
</tr>
<tr>
<td>DICO-3-Ni-i</td>
<td>&gt;2%</td>
<td>&lt;97%</td>
<td>0.97 (1.40)</td>
</tr>
<tr>
<td>SIFSIX-2-Cu-i</td>
<td>1%</td>
<td>99%</td>
<td>&lt;1.00 (1.247)</td>
</tr>
<tr>
<td>MOOFOUR-1-Ni</td>
<td>&gt;5%</td>
<td>&lt;95%</td>
<td>1.27 (1.60)</td>
</tr>
<tr>
<td>Ni-4-PyC</td>
<td>2%</td>
<td>98%</td>
<td>1.68 (1.74)</td>
</tr>
<tr>
<td>DMOF-1</td>
<td>&gt;2%</td>
<td>&lt;98%</td>
<td>1.00 (0.83)</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>23%</td>
<td>77%</td>
<td>1.20 (1.10)</td>
</tr>
<tr>
<td>MIL-101</td>
<td>&lt;1%</td>
<td>&gt;99%</td>
<td>&lt;1.00 (0.62)</td>
</tr>
<tr>
<td>UiO-66</td>
<td>&lt;1%</td>
<td>&gt;99%</td>
<td>0.36 (1.45)</td>
</tr>
<tr>
<td>UiO-66-NH₂</td>
<td>&lt;2%</td>
<td>&gt;98%</td>
<td>5.70 (7.38)</td>
</tr>
</tbody>
</table>

[a] Previously reported adsorbents [10]. [b] Water saturated gas feeds were obtained by bubbling each pure gas through deionized water. [c] Density for TEPA-SBA-15 is indeterminate. Mass of analyte in mg/g.
The addition of moisture to the gas stream significantly impacts CO$_2$ uptake by the physisorbent materials studied herein. The gravimetric CO$_2$ uptake from moist simulated flue-gas was reduced by up to 62% when compared to dry flue-gas results obtained for the ten physisorbents examined in this study. The presence of water vapor in CO$_2$ containing gas streams can have a detrimental effect on physisorbent materials both in terms of CO$_2$ adsorption performance$^{10,58}$ and overall stability of the adsorbent.$^{59-62}$ The selectivity of sorbent materials for CO$_2$ over H$_2$O ($S_{CW}$) is an important aspect in determining the suitability of sorbent materials for CO$_2$ capture via post-combustion and DAC methods. From the current study, ZIF-8 performed best in terms of $S_{CW}$ for both DAC ($S_{CW} \sim 18.7$) and moist simulated flue-gas ($S_{CW} \sim 0.5$). ZIF frameworks are inherently hydrophobic as long as the imidazolate linkers do not contain hydrophilic functional groups.$^{63-65}$ Despite the high $S_{CW}$ for ZIF-8, it exhibits low overall gravimetric CO$_2$ uptake for both DAC (1.2 L CO$_2$/kg) and simulated flue-gas (1.27 L CO$_2$/kg). SIFSIX-3-Cu was the next best physisorbent in terms of CO$_2$/H$_2$O selectivity (DAC $S_{CW} \sim 10.03$), which is almost double that of our previous benchmark physisorbent, SIFSIX-3-Ni (DAC $S_{CW} \sim 5.43$).

The regeneration performance of the ten materials studied in this contribution was also examined using TPD experiments (Figure 5.2). The results of these experiments correlates well with the isosteric enthalpy of adsorption ($Q_{st}$) determined from pure CO$_2$ adsorption isotherms. However, while pure gas isotherms can be used as an indicator of a material’s likely ability to selectively adsorb CO$_2$ over competing gases such as N$_2$, TPD studies are necessary to examine the adsorption performance of MOMs when exposed to specific adsorption conditions such as atmosphere and simulated flue-gas conditions. The results of TPD experiments illustrate that water competition is a significant issue when carrying out adsorption studies under humid conditions on physisorbent materials. Consequently, chemisorbents are still the current benchmark materials for CO$_2$ capture via
DAC, with CO$_2$ uptakes of up to 80.44 L CO$_2$/kg reported in previous studies.$^{10,13,17}$ TEPA-SBA-15 exhibits the highest $S_{CW}$ under all adsorption conditions. However, as mentioned previously, chemisorbent materials can suffer from a high energy penalty in terms of sorbent regeneration.

### 5.5 Conclusion

Capture of CO$_2$ either from flue-gas or directly from air presents a challenge but also an opportunity to play a significant role in tackling greenhouse gases such as CO$_2$ over the coming century. In this contribution, we examine the use of benchmark Metal-Organic Materials for their potential use in CO$_2$ adsorption processes under humid conditions, particularly, direct air capture and moist simulated flue-gas. Competition with water vapor was found to significantly reduce the CO$_2$ adsorption performance of the physisorbent materials compared with anhydrous conditions. However, there was quite a wide range in performance, with both pore size and pore-chemistry affecting the performance of physisorbents studied herein. Humid conditions exacerbated the situation and even wider ranges of uptakes and selectivity were observed. The functionalization of organic ligands with hydrophobic decoration, such as methyl groups in the case of ZIF-8, may be an approach that could be used to improve $S_{CW}$ of physisorbents. However, our results indicate that increased electrostatics generated by inorganic pillars in HUMs or grafted amines are most effective at improving $Q_{st}$ and overall CO$_2$ adsorption performance. In conclusion, competition with water vapor is a significant challenge for implementation of physisorbent materials in CO$_2$ capture, either from DAC or from flue-gas. Control of pore-size and pore-chemistry through crystal engineering may be a successful strategy to improve CO$_2$ capture performance even in the presence of water vapor and must be further addressed if physisorbents are to compete with chemisorbents in terms of uptake. However, the best physisorbents studied herein were found to be much easier to recycle than the benchmark
chemisorbent TEPA-15-SBA, suggesting that faster and less energy intensive recycling of physisorbents could compensate for the lower uptake values.
5.6 References


Scott, H. S. *et al.* Novel mode of 2-fold interpenetration observed in a primitive cubic network of formula \(\text{[Ni}(1,2\text{-bis}(4\text{-pyridyl})\text{acetylene})_2(Cr}_2\text{O}_7)\text{]}_n\). *Chemical Communications* **51**, 14832-14835 (2015).


Chapter Six: Conclusions

6.1 Conclusions

Modularity and amenability to crystal engineering makes HUMs the only class of potential sorbents that can offer viable solution for DAC of CO₂ owing to high degree of control over pore-size (i.e. ultramicroporous) and pore-chemistry (i.e. inorganic pore walls), contributing towards strong separation performances (S_{CN} and S_{CW}). As reported in chapters two, three and five, pyrazine based HUMs exhibited S_{CN} > 10000 (Table 6.2) as compared to the prerequisite of > 2000 [in air, CO₂ (400 ppm, 0.04%) over N₂ (ca. 80%), CO₂:N₂= 1:2000] required for efficient DAC of CO₂. No other class of physisorbent has reached a value of S_{CN} > 500 (Table 1.2). Thanks to high S_{CN} (~ 23772) for a 0.04:99.96 binary mixture of CO₂:N₂, NbOFFIVE-1-Ni, a pyrazine based HUM, exhibited the highest gravimetric uptake of CO₂ (9.42 L CO₂/kg, corresponding to 16.5% of the total uptake) amongst all the physisorbents under DAC conditions. NbOFFIVE-1-Ni, was closely followed by its hexafluorotitanate variant, TIFSIX-3-Ni, having gravimetric CO₂ uptake of 9.09 L CO₂/kg (17.1% of the total uptake and S_{CN} ~ 19282 for 0.04:99.96 binary mixture of CO₂:N₂ ).¹ DAC performance of NbOFFIVE-1-Ni and TIFSIX-3-Ni was found to be second only to a chemisorbent, TEPA-SBA-15, with a gravimetric uptake of 80.44 L CO₂/kg. However, unfavourable energetics of recycling for TEPA-SBA-15 as compared to NbOFFIVE-1-Ni and TIFSIX-3-Ni led to low upside potential for TEPA-SBA-15 in terms of DAC utility.¹³⁻³

Physisorbents with S_{CN} < 500, did not exhibit desired DAC performance (high CO₂ uptake from air and low regeneration energy), Table 6.1, thus highlighting the significance of high S_{CN}. Amongst these, UiO-66-NH₂ exhibited moderate gravimetric uptake (5.70 L CO₂/kg) and could be attributed to the strong interactions between the –NH₂ group and CO₂ molecules. However, these interactions also result in high regeneration energy making UiO-
66-NH$_2$ unsuitable for DAC application. Further, comparison of DAC performance of an ultramicroporous material, Ni-4-Pyc, with pyrazine based HUMs, provide insights regarding the impact of strong electrostatics offered by inorganic anions and its role in the capture of small polarizable gas. Ni-4-Pyc has comparable pore size (3.5 Å and 4.8 Å, as compared to 3.5-3.8 Å for the HUMs). However, the low DAC performance (gravimetric CO$_2$ uptake of 1.68 L CO$_2$/kg) could be attributed to the lack of inorganic pillar and hence the reduced electrostatics. Further, our studies demonstrate that the presence of ultramicropores and inorganic anions alone may not be sufficient as is evident in case of SIFSIX-2-Cu-i and DICRO-3-Ni-i. The disposition of inorganic anions that creates strong binding sites is equally important for optimal DAC performance and is the primary factor for the reduced DAC performance of interpenetrated HUMs. The unique combination of the two aforementioned factors leads to creation of strong binding sites with perfect fitting pores for CO$_2$. Pyrazine based HUM fulfil both these factors and hence pave way for design of next generation advanced sorbents for DAC application.

As discussed in chapters two, three and four, apart from high $S_{CN}$ (> 2000), high $S_{CW}$ (> 100) is equally important for DAC of CO$_2$. The abundance of water in the atmosphere and its small kinetic diameter (2.69 Å) precludes DAC of CO$_2$. As shown in Table 6.1, CO$_2$ adsorption capacity for sorbents was found to decline upon exposure to DAC conditions or wet gas mixture as compared to dry gas mixture. With high $S_{CW}$ (~830), TEPA-SBA-15 was the only sorbent to perform efficiently under all conditions. However, TEPA-SBA-15 being a chemisorbent, requires high regeneration energy thus limiting its potential for energy economic DAC applications. Thanks to inherent hydrophobicity, ZIF-8 ($S_{CW}$ ~ 18.67) exhibited the highest $S_{CW}$ amongst physisorbents, but poor gravimetric uptake (1.2 L of CO$_2$ per kg of sorbent) resulted in overall inadequate DAC performance. Amongst the HUMs, TIFSIX-3-Ni and NbOFFIVE-1-Ni exhibited $S_{CW}$ of 12.80 and 12.35 respectively and were
in fact the only physisorbents other than ZIF-8 to exhibit $S_{CW} > 10$ for DAC conditions. Though $S_{CW} > 100$ is yet to be achieved in case of physisorbents, functionalization of organic ligands with hydrophobic decoration, such as methyl groups in the case of ZIF-8 or increased electrostatics generated by introduction of inorganic pillars in case of HUMs may be an approach that could be used to synthesize sorbents with high $S_{CW}$ in the future.

The presence of water vapour not only deteriorated the adsorption capacity but in some cases, was also found to affect the structural stability, i.e. assist in structural collapse/framework breakdown. To gain insights, accelerated stability protocol implemented by the pharma industry was deployed.\textsuperscript{4,6} Accordingly, six months of storage under accelerated stability conditions (40 °C and 75% RH) corresponds to two years of shelf life. For our study, fourteen days under accelerated stability conditions followed by preliminary characterisation (comparison of $S_{BET}$ and PXRD) was conducted for all the sorbents. As described in chapters two, three and four, no change in phase or performance was observed for TEPA-SBA-15 and NbOFFIVE-1-Ni. TIFSIX-3-Ni and SIFSIX-3-Ni underwent phase change from 3D HUMs (\textbf{pcu} topology) to 2D square grids (\textbf{sql} topology).\textsuperscript{7} However, the sorbents could be regenerated by heating under vacuum with minimal loss in sorption performance ($< 5\%$). Other pyrazine based HUMs and some of the benchmark MOFs, Mg-MOF-74 and HKUST-1, lost their structural integrity and could not be regenerated. This is in agreement with the reports hitherto published in the literature.\textsuperscript{8,9} Interestingly, even though the pyrazine based HUMs are isostructural with minute variations, their stability towards humidity vastly differs, which highlights the role of crystal engineering towards design and synthesis of sorbents with improved performance and stability.
Table 6.1. DAC performance of representative sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>DAC (1 atm; 49% RH) CO₂ L/kg (L/L) S₁₀₀</th>
<th>moist CO₂ (0.15 atm; 75% RH) CO₂ L/kg (L/L) S₁₀₀</th>
<th>dry CO₂ (0.15 atm) CO₂ L/kg (L/L) S₁₀₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ H₂O</td>
<td>CO₂ H₂O</td>
<td></td>
</tr>
<tr>
<td>TIFSIX-3-Ni⁺</td>
<td>17.1% (17.9) &gt;82% (86) 9.09 (14.97)</td>
<td>12.80 (83%)</td>
<td>46.84 (77.15) 0.87</td>
</tr>
<tr>
<td>NbOFFIVE-1-Ni⁺</td>
<td>16.5% (18.5) &gt;83% (93) 9.42 (16.57)</td>
<td>12.35 (85%)</td>
<td>44.80 (77.84) 0.91</td>
</tr>
<tr>
<td>SIFSIX-3-Ni⁺</td>
<td>&lt;8% (8.0) &gt;92% (93) 4.07 (6.55)</td>
<td>5.43 (62%)</td>
<td>38.69 (62.29) 0.27</td>
</tr>
<tr>
<td>HKUST-1ᵇ</td>
<td>1% (2.1) 99% (178) 1.07 (0.95)</td>
<td>0.63 (8.5%)</td>
<td>&gt;91% (12.8) 6.52 (5.78)</td>
</tr>
<tr>
<td>Mg-MOF-74ᵇ</td>
<td>&lt;4% (6.3) &gt;96% (171) 3.21 (2.94)</td>
<td>2.60 (51%)</td>
<td>49% (65) 34.62 (31.71)</td>
</tr>
<tr>
<td>Zeolite 13Xᵇ</td>
<td>1% (1.5) 99% (146) 0.76 (0.99)</td>
<td>0.63 (22%)</td>
<td>78% (93) 13.39 (17.54)</td>
</tr>
<tr>
<td>TEPA-SBA-15ᵇ</td>
<td>93% (158) 7% (12) 80.44 n.a.</td>
<td>830 (92%)</td>
<td>8% (11) 66.33 n.a.</td>
</tr>
<tr>
<td>SIFSIX-3-Cu⁺</td>
<td>13.8% (14.1) &gt;86% (88) 7.18 (11.55)</td>
<td>10.03 (65%)</td>
<td>35% (54) 51.42 (82.68)</td>
</tr>
<tr>
<td>Dicro-3-Ni⁻ᵇ</td>
<td>&gt;2% (1.9) &lt;97% (80) 0.97 (1.40)</td>
<td>1.47 (53%)</td>
<td>&lt;47% (17.2) 9.77 (14.08)</td>
</tr>
<tr>
<td>SIFSIX-2-Cu⁻ᵇ</td>
<td>1% (1.6) 99% (155) 1.00 (1.247)</td>
<td>0.63 (59.5%)</td>
<td>40.5% (12.3) 9.21 (11.48)</td>
</tr>
<tr>
<td>MOOFour-1-Ni⁻</td>
<td>&gt;5% (2.5) &lt;95% (49) 1.27 (1.60)</td>
<td>3.29 (60%)</td>
<td>40% (26) 19.85 (25.01)</td>
</tr>
<tr>
<td>Ni-4-PyCᶜ</td>
<td>2% (3.3) 98% (154) 1.68 (1.74)</td>
<td>1.28 (61%)</td>
<td>39% (20.1) 7.94 (8.20)</td>
</tr>
<tr>
<td>DMOF-1ᶜ</td>
<td>≥2% (1.3) &lt;98% (56) 100 (0.83)</td>
<td>1.28 (56%)</td>
<td>44% (7.7) 4.94 (4.08)</td>
</tr>
<tr>
<td>ZIF-8ᶜ</td>
<td>23% (2.3) 77% (7.6) 1.20 (1.10)</td>
<td>18.67 (75%)</td>
<td>25% (16.8) 1.27 (3.53)</td>
</tr>
<tr>
<td>MIL-101ᶜ</td>
<td>&lt;1% (1.0) &gt;99% (95) 0.62 (0.84)</td>
<td>&lt;0.63 (40%)</td>
<td>60% (16.8) 5.70 (3.53)</td>
</tr>
<tr>
<td>UiO-66ᶜ</td>
<td>&lt;1% (0.7) &gt;99% (195) 0.36 (1.45)</td>
<td>&lt;0.63 (29.6%)</td>
<td>70.4% (19.6) 4.28 (5.30)</td>
</tr>
<tr>
<td>UiO-66-NH₂ᶜ</td>
<td>&lt;2% (1.2) &gt;98% (237) 5.70 (7.38)</td>
<td>1.28 (46.7%)</td>
<td>53.3% (58.5) 26.12 (33.83)</td>
</tr>
</tbody>
</table>

ᵃ Studied in chapter two. ᵇ Studied in chapter three. ᵇ Studied in chapter five.
In an attempt to rationalise the structure–property relationship in terms of DAC performance, a family of isostructural pyrazine based HUMs was generated by systematic variation of metal ions or inorganic pillars. As discussed in chapters three and four, amongst the pyrazine based HUMs, NbOFFIVE-1-Ni and TIFSIX-3-Ni had the best CO$_2$ sorption performance at DAC conditions with uptakes of 1.2 and 1.15 mmol/g, respectively, at 400 ppm partial pressure. Overall, TiF$_6^{2-}$ and NbOF$_5^{2-}$ variants exhibited better sorption performance as compared to SiF$_6^{2-}$ variants, thanks to the shorter F···F distances in case of TiF$_6^{2-}$ and NbOF$_5^{2-}$ and enhanced electrostatics originating from the higher polarizability of Ti$^{4+}$ and Nb$^{5+}$. SIFSIX-3-Cu was an exception amongst the SiF$_6^{2-}$ variants with a sorption performance identical to NbOFFIVE-1-Ni and TIFSIX-3-Ni (CO$_2$ uptake of 1.2 mmol/g at 400 ppm partial pressure). Improved CO$_2$ sorption performance of SIFSIX-3-Cu could be ascribed to the Jahn-teller effects at the Cu$^{2+}$ node resulting in narrower pores and tighter binding sites for CO$_2$. With respect to the metal node, apart from Cu$^{2+}$, Ni$^{2+}$ variants performed the best irrespective of the inorganic pillar; credit to the stronger Ni-N bonds, which leads to contraction of the pore window, thus creating a tighter CO$_2$ binding site.$^{10}$

Study of this family of HUMs also led to better understanding of structure-property relationship in terms of stability (thermal and humidity) of the framework. Overall, the NbOF$_5^{2-}$ and TiF$_6^{2-}$ variants exhibited greater thermal stability (~ 300 °C) as compared to SiF$_6^{2-}$(100-200 °C). With regards to the metal nodes, use of Ni$^{2+}$ led to a more thermally robust sorbent. A similar trend was observed related to the aspect of stability towards humidity. NbOF$_5^{2-}$ variants were more robust as compared to TiF$_6^{2-}$ and SiF$_6^{2-}$ owing to out-of-centre distortion observed in the former. The distortion leads to strong nucleophilic centres at the negatively charged oxide and trans fluoride of NbOF$_5^{2-}$, leading to stronger M-O and M-F bonds in NbOF$_5^{2-}$ based materials as compared to M-F bonds in case of SiF$_6^{2-}$ and TiF$_6^{2-}$ materials. Amongst the metal nodes, Ni$^{2+}$ exhibited the best hydrolytic stability thanks to
stronger Ni-N bond and least H$_2$O ligand exchange rate when compared with other metal ions (Zn$^{2+}$, Cu$^{2+}$, Co$^{2+}$).\textsuperscript{10-13}

Table 6.2. Sorption performance and stability (thermal and humidity stability) of HUMs.

<table>
<thead>
<tr>
<th>HUMs</th>
<th>Surface Area (m$^2$/g)</th>
<th>$Q_{st}$ (kJ/mol)</th>
<th>Total Uptake @ 298K (mmol/g)</th>
<th>CO$_2$ Uptake @ 298K (mmol/g)</th>
<th>IAST Selectivity CO$_2$/N$_2$</th>
<th>Thermal Stability (°C)</th>
<th>Stability towards humidity (Regener ability)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Zn</td>
<td>217</td>
<td>44.1</td>
<td>2.56</td>
<td>0.26</td>
<td>0.11</td>
<td>1.45</td>
<td>912</td>
</tr>
<tr>
<td>TIFSIX-3-Zn</td>
<td>206</td>
<td>51.6</td>
<td>2.44</td>
<td>0.20</td>
<td>0.53</td>
<td>2.18</td>
<td>6975</td>
</tr>
<tr>
<td>NbOFFIVE-1-Zn</td>
<td>202</td>
<td>53.1</td>
<td>2.40</td>
<td>0.18</td>
<td>0.54</td>
<td>1.99</td>
<td>8529</td>
</tr>
<tr>
<td>SIFSIX-3-Cu</td>
<td>210</td>
<td>54</td>
<td>2.40</td>
<td>0.26</td>
<td>1.20</td>
<td>2.14</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>SIFSIX-3-Ni</td>
<td>215</td>
<td>50.8</td>
<td>2.57</td>
<td>0.16</td>
<td>0.35</td>
<td>1.75</td>
<td>5155</td>
</tr>
<tr>
<td>TIFSIX-3-Ni</td>
<td>209</td>
<td>55.3</td>
<td>2.49</td>
<td>0.17</td>
<td>1.15</td>
<td>2.15</td>
<td>19282</td>
</tr>
<tr>
<td>NbOFFIVE-1-Ni</td>
<td>205</td>
<td>55.4</td>
<td>2.44</td>
<td>0.14</td>
<td>1.20</td>
<td>2.20</td>
<td>23772</td>
</tr>
<tr>
<td>SIFSIX-3-Co</td>
<td>222</td>
<td>49</td>
<td>2.62</td>
<td>0.18</td>
<td>0.17</td>
<td>1.70</td>
<td>2111</td>
</tr>
<tr>
<td>TIFSIX-3-Co</td>
<td>211</td>
<td>54.6</td>
<td>2.50</td>
<td>0.17</td>
<td>0.80</td>
<td>2.23</td>
<td>13901</td>
</tr>
<tr>
<td>NbOFFIVE-1-Co</td>
<td>215</td>
<td>52.9</td>
<td>2.56</td>
<td>0.18</td>
<td>0.62</td>
<td>2.05</td>
<td>9065</td>
</tr>
<tr>
<td>SIFSIX-3-Fe</td>
<td>217</td>
<td>42.4</td>
<td>2.54</td>
<td>0.3</td>
<td>0.10</td>
<td>1.05</td>
<td>529</td>
</tr>
</tbody>
</table>

Large scale synthesis of robust HUMs with benchmark DAC performance would ensure advancement of HUMs to higher TRLs as mentioned in Table 6.3 and can facilitate its commercialisation in the future.\textsuperscript{14} In an attempt to address this issue, we developed a facile synthetic pathway for rapid syntheses of HUMs. As illustrated in chapter four, use of dry solid grinding rather than traditional synthesis methods, such as layering, solvothermal or slurry, resulted in development of a versatile method for scale-up of HUMs. This method enabled the synthesis of ten pyrazine based HUMs, six previously reported and four new
(TIFSIX-3-Co/Zn and NbOFFIVE-1-Ni/Zn), that could not be prepared by traditional methods. Synthesis of more HUMs facilitated better understanding of structure-function relationships. Mechanochemical synthesis reduced the reaction time from days to a few hours and eliminated use of toxic organic solvents paving way for clean and green chemistry. Moreover, the use of hazardous HF during the reaction was eliminated leading to milder reaction conditions, which has enabled use of other fragile ligands. High product yields with no by-products precluded the need for washing/solvent exchange and the product could be used as is thus leading to reduced manufacturing cost.

Table 6.3. Technology Readiness Levels as defined in the European Commission (EC).

<table>
<thead>
<tr>
<th>Technology Readiness Level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRL 1.</td>
<td>basic principles observed</td>
</tr>
<tr>
<td>TRL 2.</td>
<td>technology concept formulated</td>
</tr>
<tr>
<td>TRL 3.</td>
<td>experimental proof of concept</td>
</tr>
<tr>
<td>TRL 4.</td>
<td>technology validated in lab</td>
</tr>
<tr>
<td>TRL 5.</td>
<td>technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)</td>
</tr>
<tr>
<td>TRL 6.</td>
<td>technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)</td>
</tr>
<tr>
<td>TRL 7.</td>
<td>system prototype demonstration in operational environment</td>
</tr>
<tr>
<td>TRL 8.</td>
<td>system complete and qualified</td>
</tr>
<tr>
<td>TRL 9.</td>
<td>actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)</td>
</tr>
</tbody>
</table>

That commercial viability of physisorbents for DAC of CO₂ largely depends on the cost of the CO₂ capture process, we also assess the economic benefits associated with the use of HUMs for DAC of CO₂. DAC of CO₂ can incur costs from a number of factors such as (i) capital investment, (ii) cost of capture (energy for operating the process), (iii) cost of CO₂ release and regeneration of the sorbent, and (iv) maintenance of equipment.¹⁵ Taking all the above factors into consideration, the cost for DAC of CO₂ is estimated to be around of $30–100/t of CO₂.¹⁵ In this context, sorbents exhibiting $S_{CN} > 2000$ could significantly
reduce this cost and make DAC a viable solution. Direct correlation between $S_{CN}$ and cost of DAC of CO$_2$ is yet to be established, however, related studies regarding direct correlation between $S_{CN}$ and cost of capture of CO$_2$ from flue gas have been reported by Wiley and co-workers (Figure 6.1).$^{16,17}$ These investigations show that sorbents with $S_{CN} > 500$ (Figure 6.1) for binary mixture (10:90; CO$_2$:N$_2$) relevant to flue gas capture of CO$_2$, can reduce the cost to $< 20$ US$/t$ CO$_2$, which is an improvement of $\sim 100\%$ when compared with the traditional physisorbents exhibiting $S_{CN}$ around 50-100. In this regard, using pyrazine based HUMs (NbOFFIVE-1-Ni and TIFSIX-3-Ni) that exhibit $S_{CN} > 10000$, will render DAC of CO$_2$ and flue gas capture of CO$_2$ further cost-effective.

**Figure 6.1.** Relationship between the cost of CO$_2$ capture, CO$_2$ selectivity, and working capacity for solid physisorbents.$^{16,17}$

To conclude a family of pyrazine based HUMs, isostructural to the parent HUM, SIFSIX-3-Zn, have been developed by use of crystal engineering and evaluated for their DAC performance. Fine tuning of SIFSIX-3-Zn by systematic variation of the metal ion or the inorganic pillar have led to sorbents with enhanced sorption properties as exemplified by the two best performing HUMs, NbOFFIVE-1-Ni and TIFSIX-3-Ni. They exhibit sorption
properties (CO$_2$ uptake at 400 ppm, $S_{CN}$) which are higher by an order of magnitude when compared to that of SIFSIX-3-Zn. NbOFFIVE-1-Ni and TIFSIX-3-Ni have exhibited benchmark DAC performance at the lab scale, thanks to their high $S_{CN}$ ($\sim$ 20000) and moderate CO$_2$ $Q_{st}$ ($\sim$ 54 kJ/mol). Improved thermal stability (100 °C for SIFSIX-3-Zn to 350 °C for NbOFFIVE-1-Ni) and stability towards humidity (low hydrolytic stability for SIFSIX-3-Zn to high hydrolytic stability for the Ni$^{2+}$ based HUMs) without any compromise in the sorption properties further emphasizes the importance of crystal engineering approach followed in this work. Study of a family of isostructural HUMs also led to better understanding of structure property relationship. This work also addresses the bulk scale synthesis of HUMs, a prerequisite for their advancement to higher TRLs ($>$ 5). Facile mechanochemical synthetic pathway has been developed to yield HUMs in large scale. Use of dry solid grinding approach and high atom efficiency minimises the hazardous waste and promotes green chemistry. This mechanochemical approach can be translated to a continuous manufacturing process by use of twin-screw extruder and can facilitate the industrial scale synthesis of HUMs. Consequently, easy to synthesize HUMs with benchmark DAC performance will pave the way to affordable, effective, and energy-efficient DAC of CO$_2$ and will render the DAC technology competitive and self-sustainable.
6.2 References


Chapter Seven: Future Directions

7.1 Future Directions

New HUMs surpassing the performance of previously reported benchmark HUMs on an ongoing basis emphasises that development of HUMs is truly in its infancy and there is wide scope of progress and opportunities for efficient physisorptive CO\textsubscript{2} capture. Exquisite control over pore size and pore chemistry in HUMs thanks to their high modularity and amenability towards crystal engineering, has enabled fine-tuning of physisorbents for task-specific applications based on the nature and source of CO\textsubscript{2} to be captured. Such precise tuning of HUMs has resulted in considerable improvements in the sorption performance subsequently leading to reduced cost and energy requirements for the capture process. Use of HUMs has not only facilitated the capture process but has also eased the regeneration process. Regeneration of sorbents is the main contributor to the overall energy requirement for CO\textsubscript{2} capture. However, using HUMs, exhibiting high S\textsubscript{CN} and extremely low regeneration temperature of \(<\) 55 °C compared to 75-150 °C for conventional CO\textsubscript{2} capture systems, the energy demand of capture can be reduced by \(~\)50\%. Low cost CO\textsubscript{2} capture enabled by HUMs also implies low cost CO\textsubscript{2} feedstock for a number of industries involved in the production of essential chemicals such as NH\textsubscript{3}, urea\textsuperscript{1} and fuels.\textsuperscript{2}

DAC of CO\textsubscript{2} by HUMs can also facilitate development of new onsite technologies that use CO\textsubscript{2} as feedstock thus eliminating the need for storage and transportation, which further reduces in the overall cost of CO\textsubscript{2} processing. One such sector that will benefit from these efficient capture processes is the agriculture sector. An atmosphere with CO\textsubscript{2} concentration in the range of 1400-1500 ppm favours cultivation of crops such as corn, apple and melons by increasing the yield and reducing the amount of irrigation required with this
increased rate of photosynthesis.\textsuperscript{3} Currently, CO\textsubscript{2} supplied using CO\textsubscript{2} generator helps maintain such high levels in greenhouses, however, it is deemed energy intensive due to the energy required to run the generator. Physisorbents, such as HUMs with high DAC adsorption capacity (1.3 mmol/g) and easy regeneration conditions, offer a promising alternate particularly because they enable onsite use of recovered CO\textsubscript{2} with minimum energy penalty. CO\textsubscript{2} is also used as a feedstock in other areas, such as food, beverages, refrigerants and fire extinguishing gases, offers a huge opportunity for reuse of captured CO\textsubscript{2}. However, as per the recent data, only 2\% of the total emissions is being used for chemical utilisation due to high processing cost.\textsuperscript{4,5} In this regard use of HUMs could offer a potential viable solution and help to increase chemical utilization of emitted CO\textsubscript{2}.

As the use of HUMs have recently been illustrated at the lab scale, it is unlikely that the optimal HUM have been discovered and tested. Also, scale-up and stability of most of the existing HUMs need to be addressed so as to promote them to higher TRLs. With a wide range of organic linkers and inorganic pillars to choose from, the modular nature of HUMs offers a unique opportunity to develop and investigate a wide range of new task-specific HUM physisorbents. The author considers these sorbents attractive candidates for further investigations because:

- Over the last five years, there has been a significant upsurge in the field of HUMs’ systematic development. They have exhibited exceptional DAC performance as compared to benchmark physisorbents, however efficient capture of CO\textsubscript{2} in the presence of H\textsubscript{2}O, with HUMs exhibiting \(S_{\text{CW}} > 50\) for DAC and \(S_{\text{CW}} > 1\) for wet flue gas are yet to be reported. With \(S_{\text{CW}} > 100\) for DAC and \(S_{\text{CW}} > 50\) for wet flue gas being the desired selectivity parameters for practical realization of carbon capture, a lot of effort needs to be put in to develop a new generation of advanced HUM physisorbents to achieve the same. Also, moisture-induced phase change in the HUMs
needs to be addressed. This can be accomplished either by rendering the framework more hydrophobic or by coating the HUMs with hydrophobic polymer, thus preventing any contact between the HUMs and water molecules. This will also help to achieve a high $S_{CW}$, as entry of water into the framework could be avoided thus minimising the competition for CO$_2$.

- Gas separation or storage would require formulation and fabrication of HUM powders into compressed composites, as loose powders would not be preferred due to difficulties in transport and handling. Future work would involve merging of powder processing technologies with compaction and consolidation methods for efficient conversion of crystalline powders into more viable forms, without any loss of sorption performance.

- Integration of MOMs into electronic devices is one of the potential application sector and is under recent performance scrutiny. Integration of thin film forms of HUMs into electronic devices for serving the purpose of gas sensing is one of the many deliverables. Keeping the goal of producing a new CO$_2$ sensor, HUMs seem worthwhile candidates, thanks to their benchmark CO$_2$ selectivity performances over competing gases and humidity. For this, we aim to explore ergonomic methods and strategies of fabricating task-specific thin-film composites from HUMs that can either be grown directly onto a component of an electronic device, or pre-fabricated and then integrated with the device components.

- Membrane based separation can become an ideal solution in the cases of engaging size and/or shape-selective molecular sieves to separate right-sized gas/vapour mixtures. Inefficiently packed adsorbent beds can permit the passage of a gas even though it would have otherwise been left out by the size-limiting pores of the sieving adsorbent. The high flux and mechanical flexibility advantage of membranes, when
combined with the high selectivity of HUM physisorbents for small polarizable gas molecules can lead to ideal molecular sieve based gas separating HUM-membrane composites for energy-efficient purification challenges over prolonged cycles.

- Promotion of HUMs to TRLs > 5 requires bulk scale production of HUMs in an efficient manner. We have illustrated that by the use of mechanochemistry, HUMs could be synthesized in gram-scale, adopting facile and rapid production routes. However, an even more feasible, bulk scale (kilogram to tonne), continuous manufacturing process such as using twin-screw extruder needs to be developed that can facilitate large scale production of HUMS and their targeted implementation in the environment related sectors, for better energy management.

This thesis work has not involved commercialisation, since the focus has remained at the frontier of HUMs design/synthesis and obtaining more insights into the structure-function relationships. That we could address HUMs scale-up and bench testing as an integral part of the material design processes has enabled us to reach TRL4 and seemingly offers incentives to take development of HUMs to higher TR levels. HUM based CO₂ capture performance currently sits at TRL5; when exposed to relevant gas mixtures mimicking DAC conditions and they could register several new benchmark performance records across a wide range of CO₂ capture processes such as selective physisorption of CO₂ over N₂, CH₄ and H₂O. Further, HUMs are facile to prepare from cheap, readily available starting materials. HUMs are now ready for scale-up from lab scale to the industrial scale needed for commercial use. The proposed final products would be highly amenable to integration into existing and next generation carbon capture technologies.
7.2 References


Solvents and reagents were purchased from chemical suppliers and used without further purification. Zeolite 13X was purchased from Sigma Aldrich (Lot #MKBR8919V) in powder form. Methanol (ACS Reagent Grade > 99%), Ethanol (ACS Reagent Grade 96%) and N,N’-Dimethylformamide (HPLC Grade, > 99.7%) were purchased from Sigma Aldrich.

### A.1 Synthesis of Sorbents

**Preparation of \{[\text{Cu}(\text{C}_9\text{H}_3\text{O}_6)2(\text{H}_2\text{O})_3]\}_n** (HKUST-1; Cu-BTC). HKUST-1, also known as Cu-BTC (copper 1,3,5-benzenetricarboxylic acid), was synthesized following a procedure modified slightly from one published previously.\(^1\) In a typical reaction, 1.00 g (4.76 mmol) of 1,3,5-benzenetricarboxylic acid (H\(_3\)BTC) and 2.00 g (6.87 mmol) of Cu(NO\(_3\))\(_2\)·3H\(_2\)O were mixed and suspended in 20 mL N,N’-Dimethylformamide followed by stirring and sonication for 10 minutes. Ethanol (20 mL) was added to this suspension followed by additional stirring and sonication (5 minutes). Finally, deionised water (20 mL) was added to the suspension and the mixture was stirred and sonicated for 30 minutes to allow for complete dissolution of all components. The mixture was heated at 85 °C for 24 hours, whereupon blue crystals were obtained, separated via filtration, washed and immersed in methanol. The methanol solvent was exchanged twice a day for three days before the HKUST-1 sample was used for sorption experiments. Activation of HKUST-1 was achieved by degassing the methanol-exchanged sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 hours (sample heated from room temperature to 180 °C with a ramp rate of 10 °C).
Preparation of Mg\(_2\)(dobdc) (Mg-MOF-74, CPO-27-Mg; dobdc\(^{4-} = 2,5\)-dioxido-1,4-benzenedicarboxylate). The compound Mg-MOF-74 was synthesized and activated using a modified synthesis from previous reports.\(^2\) \(\text{H}_4\text{dobdc} \) (1.11 g, 5.6 mmol) and \(\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (4.75 g, 18.6 mmol) were dissolved in a 15:1:1 (v/v/v) mixture of DMF:ethanol:H\(_2\)O (500 mL) and sparged using N\(_2\) for 1 h. The resulting solution was distributed into thirty-five 20 mL vials, which were sealed with Teflon-lined caps and heated to 120 °C for 8 h. Following the reaction, the resulting yellow material was washed repeatedly with DMF. The DMF was decanted and replaced with fresh DMF repeatedly for a week, refreshing the DMF twice daily. Then, the DMF was decanted and replaced by methanol (MeOH). The MeOH was decanted, and replaced with fresh MeOH twice daily for a further three days. The resulting dark yellow powder was collected by filtration and then activated under vacuum at 180 °C for 24-48 h.

Preparation of \([\text{Ni(pyr)}_2\text{(SiF}_6\text{)}]\)_\(n\) (SIFSIX-3-Ni). An as yet uncharacterised polycrystalline precursor of SIFSIX-3-Ni was synthesized by slurrying 870 mg (3 mmol) of \(\text{Ni(NO}_3\text{)}_2\), 534 mg (3 mmol) of (NH\(_4\))\(_2\)SiF\(_6\) and 480 mg (6 mmol) of pyrazine in 4 mL of water for 2 days. The resulting suspension was filtered under vacuum and dried in air. This precursor was soaked in methanol for 1 day and then washed twice with two portions (ca. 10 mL) of methanol on a Buchner filter. After drying in air, the solid was heated at 140 °C for 1 day to obtain SIFSIX-3-Ni. Activation of SIFSIX-3-Ni was achieved by degassing the methanol-exchanged sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 hours (sample heated from RT to 140 °C with a ramp rate of 10 °C).

Preparation of TEPA-SBA-15 (TEPA = tetraethylenepentamine; SBA-15 = Santa Barbara Amorphous-15). SBA-15 was prepared by a modified method previously reported.\(^3\) In a typical synthesis, 12 g of pluronic P-123 was added to 90 g (90 mL) of heated distilled water. To this, 360 g (305.08 mL) of HCl (2M) was added. This was stirred using a magnetic
stirrer for 2 h to facilitate dissolution of the surfactant at a temperature of 40 °C. After 2 h, 24 g (25.72 mL) of tetraethylorthosilicate (TEOS) was added. This was left for 24 h. The white suspension was then placed into an autoclave in the oven at 80 °C for 3 days. The resulting mixture was filtered using a Buchner funnel and rinsed with distilled water. It was left to dry overnight in the fume-hood, leaving a white powder. This powder was then calcined in air at 550 °C for eight hours. Characterisation of the calcined unmodified SBA-15 solid was carried out using N\textsubscript{2} adsorption isotherms, low-angle PXRD and TEM microscopy. The so-obtained SBA-15 was then used for preparation of the amine modified adsorbent. Typically, 2.3 g (12.2 mmol) TEPA was dissolved in 25 mL of anhydrous toluene under constant stirring. After 30 minutes, 1 g of SBA-15 was added to the beaker and was left stirring for two hours. The contents of the beaker were then added to a round-bottomed flask and attached to a rotary evaporator. The remaining white powder was then activated under a flow of helium at 100 °C for 3 h. Adsorbent characterisation was conducted using TGA and CO\textsubscript{2} adsorption isotherms.

Preparation of Zeolite 13X (Na-X, FAU; Na\textsubscript{50}Al\textsubscript{50}Si\textsubscript{59}O\textsubscript{218}). Zeolite 13X was purchased as a pure powder from Sigma-Aldrich. The zeolite was activated by heating at 250 °C under vacuum for 24 h as per previous reports.\textsuperscript{2}

A.2 Experimental Section

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction experiments were carried out using a PANalytical Empyrean™ diffractometer equipped with a PIXcel\textsuperscript{3D} detector operating in scanning line detector mode with an active length of 4 utilizing 255 channels. The diffractometer is outfitted with an Empyrean Cu LFF (long fine-focus) HR (9430 033 7310x) tube operated at 40 kV and 40 mA and Cu K-alpha radiation (λα = 1.540598 Å) was used for diffraction experiments. Experiments were conducted in continuous scanning mode with the goniometer in the theta-theta orientation. Incident beam
optics included the Fixed Divergences slit with anti-scatter slit PreFIX module, with a 1/8°
divergence slit and a 1/4° anti-scatter slit, as well as a 10 mm fixed incident beam mask and a
Soller slit (0.04 rad). Divergent beam optics included a P7.5 anti-scatter slit, a Soller slit (0.04 rad), and a Ni β filter. The samples were typically dry and ground into a fine powder, applied
to a low background sample holder and mounted to a bracket flat sample stage. In a typical
experiment, data was collected via a continuous scan in the range of 5°-45° (2θ) with a step-
size of 0.02626° and a scan time of 29 seconds per step. Raw data was then evaluated using
the X’Pert HighScore Plus™ software V 4.1 (PANalytical, The Netherlands). Plots of
stacked PXRD spectra for each adsorbent displaying patterns for calculated, as synthesized,
solvent exchanged, and after sorption analysis are provided below (Figure A6-A8). Additional plots of stacked PXRD spectra displaying patterns for calculated, pristine sample,
and post-humidity chamber exposure (after 1 day, 7 days, and 14 days) are provided for each
sorbent. (Figure A24, A26, A28, A30)

**Thermogravimetric Analysis (TGA).** Thermogravimetric analysis was carried out
under nitrogen using TGA instrument TA Q50 V20.13 Build 39. Experiments were carried
out using platinum pans and with a flow rate of 60 mL/min for the nitrogen gas. The data was
collected in the High Resolution Dynamic mode with a sensitivity of 1.0, a resolution of 4.0,
and a temperature ramp of 20 °C/min up to 500 °C. The data was analyzed using the T.A.
Universal Analysis suite for Windows XP/ Vista Version 4.5A. Plots of stacked thermograms
for each microporous sorbent are provided below (Figure A9 – A14).

**Infrared (IR) Spectra.** Infrared spectra were obtained on a PerkinElmer Spectrum
100 FT-IR Spectrometer with a resolution setting of 2 and 16 scans per sample. Data was
plotted as percent transmittance with a spacing of 1.929 cm⁻¹ and analyzed using the
Spectrum V 6.3 software package. Plots of stacked infrared spectra are provided for each
microporous sorbent (Figure A15 – A19).
TGA-Temperature-Programmed Desorption (TPD) Studies. TGA-TPD studies were carried out on a gas mixing rig coupled independently with a TGA instrument TA Q50 V20.13 Build 39 and mass spectrometer (MS) Agilent 5975 MSD, see Figure A2. In a typical TGA uptake test the given sample was activated by heating to a desired temperature under a 60 ml/min flow of nitrogen gas. This was then cooled to 30 °C before the chosen gas mixture was introduced to the sample. A mass flow controller was used to control the gas ratios for each test while moisture was introduced by passing the pre-mixed gas through a gas bubbler containing water. The weight increase for each solid was monitored until the weight began to plateau. The exposure time and gas flow conditions were then noted and subsequently applied to samples during TPD studies to analyse the composition of the adsorbed species during the desorption cycle.

TPD tests were carried out using a custom-made fixed-bed flow system. The system consists of a gas delivery system, a reactor housed in a furnace and a mass spectrometer detection system. There are two aims to this testing; to determine the CO\textsubscript{2} adsorbed by the sorbents; to examine the temperatures at which the CO\textsubscript{2} desorption occurs. Both of these parameters will be investigated using CO\textsubscript{2} TPD profiles. In a typical CO\textsubscript{2} TPD cycle, the sorbent is placed in a quartz tubular reactor. The sample is fixed in the reactor using quartz wool. Helium is then passed through the reactor at room temperature until a constant signal is observed using an Agilent 5975 MSD mass spectrometer (MS). The temperature is then increased at a rate of 10 °C/min to an appropriate temperature to remove impurities in the sample. The sample is then cooled to 30 °C. A gas mixture is then introduced to the sorbent for the required length of time. When the required adsorption parameters have been achieved, the gas flow is switched to nitrogen gas until the carbon dioxide concentrations are returned to background levels. The carrier gas is then switched to helium and heated to the required temperature at a rate of 10 °C/min in a flow of helium. The gas composition leaving the
reactor is continuously monitored by MS for the identity and quantity of each component of the desorbed gas. Helium is used as a carrier gas as this is not detected by the MS, ensuring that all desorbed species from the adsorbents are detected.

During a direct air capture (DAC) test, a sample is activated under vacuum as per the conditions previously outlined. This sample is then exposed to the laboratory environment for 24 h. The sample is then analyzed using TPD studies to analyze the composition of the exhaust gas from the sorbent.

For calibration, a gas syringe (Valco precision sampling syringe, 2 mL, from Aldrich) was used to introduce pure CO₂, taken directly from a gas cylinder, into the system. Known volumes of CO₂ gas, between 0.2 mL and 5 mL, were injected at a location before the reactor which contained several grams of adsorbent material. The gas flows were continuously monitored using the Agilent 5975 MS. The MS allowed the operator to monitor specific ions continuously throughout the run cycle as well as retrieve complete mass spectra of ions over 12 h for any given time during a test. The material adsorbed all the injected CO₂. Helium gas was allowed to flow through the sample for a further 10 minutes to ensure all the injected CO₂ was adsorbed. If no CO₂ was detected by the MS, the sample was then heated to 200°C at 10°C/min while continuously monitoring the level of the desorbed CO₂. The area of the subsequent CO₂ desorption peak was used as a measure of the known volume of injected CO₂. This was repeated several times with different volumes of CO₂ gas. The peak areas associated with the different volumes of injected CO₂ were then used to determine the mass of CO₂ adsorbed in milligrams using the ideal gas law. The culmination of these injections was used to generate a calibration graph seen in Figure A3. This graph was used to calculate the amount of CO₂ desorbed during a typical TPD run. The H₂O uptake was determined from the overall weight loss/gain observed during gravimetric analysis.
**Gas Sorption Measurements.** Ultra-high-purity grade N$_2$ and CO$_2$ were used for adsorption experiments. Low-pressure N$_2$ adsorption measurements (up to 1 bar) were performed on Micromeritics TriStar II PLUS and Micromeritics 3 Flex surface area and pore size analyzer. About 200 mg of activated samples were used for the measurements. BET surface areas for HKUST-1, Zeolite 13X and Mg-MOF-74 were determined from the N$_2$ adsorption isotherms collected at 77 K by applying the Brunauer-Emmett-Teller (BET) model. For SIFSIX-3-Ni, the CO$_2$ adsorption isotherm collected at 293 K was used for the calculation of the BET surface area.

**Accelerated Stability Testing** Within the pharmaceutical industry, there exist well-established criteria for the determination of a compound’s stability to long-term and accelerated storage conditions. The protocols are designed to represent possible storage conditions from different regions around the globe. In order to minimize the required testing, the International Conference of Harmonization (ICH) was formed and consensus was achieved for a unified testing condition. Subsequent to this meeting, a set of long-term, intermediate and accelerated storage conditions valid for the USA, EU and Japan were established. The accelerated stability conditions are accepted throughout the different regions to mimic an acceleration of the storage at ambient conditions. The accelerated stability conditions have been proven, through a modified Arrhenius equation, to be a valid model such that six months of accelerated stability testing is similar to two years of long-term storage conditions.

In the accelerated stability experiment, a pristine sample of each adsorbent was prepared and placed into an environment where temperature and relative humidity were controlled. A saturated aqueous solution of sodium chloride was prepared and placed in the base of a glass desiccator. Each adsorbent sample was placed in a separate, open glass vial and stored within the desiccator. The desiccator was kept in an oven held at 40 °C, at which
temperature the saturated aq. NaCl solution produces a relative humidity of 75% within the enclosed chamber. The time frame used for our studies was 1 day, 7 days and 14 days. Once the sample was subjected to the desired amount of time, it was taken out of the desiccator and characterization studies were carried out to detect the change if any in the sample. Characterization studies included PXRD, TGA and surface area measurements. For the surface area measurements, the sample was activated under the same conditions as the ones used for the parent compound. (Figure A24-A32)
Scheme of Experimental Protocol for Direct-Air Capture (DAC) & Accelerated Aging.

Figure A1. Flowchart of accelerated aging and moisture stability testing.
A.3 Scheme of Thermogravimetric - Temperature-Programmed Desorption

Figure A2. Schematic of gas mixing system, TGA uptake analysis and TPD analysis units.

Figure A3. CO₂ calibration graph.
A.4 Characterization of SBA-15 Support

Figure A4. (A) N\textsubscript{2} adsorption/desorption isotherms for calcined SBA-15 silica. BET surface area = 835 m\textsuperscript{2}/g. (B) Pore size distribution (PSD) curves for calcined SBA-15 silica. Surface area and pore size distributions were obtained using the Barrett-Joyner-Halenda (BJH) method.

Figure A5. TEM images of mesostructured SBA-15 silica obtained via calcination in air at 550 °C
A.5 Powder X-Ray Diffraction of Sorbents

Figure A6. PXRD of pristine HKUST-1.

Figure A7. PXRD of pristine Mg-MOF-74.
Figure A8. PXRD of pristine SIFSIX-3-Ni.
A.6 Thermogravimetric Analysis of Sorbents

Figure A9. TGA of HKUST-1 after accelerated stability testing.

Figure A10. TGA of Mg-MOF-74 after accelerated stability testing.
Figure A11. TGA of SIFSIX-3-Ni after accelerated stability testing.

Figure A12. TGA of TEPA-SBA-15 after accelerated stability testing.
Figure A13. TGA of TEPA-SBA-15 samples that had been heated at 100 °C while under a flow of helium (red) versus when under dynamic vacuum (red).

Figure A14. TGA of Zeolite-13X after accelerated stability testing.
A.7 Fourier-Transform Infrared Spectroscopy Spectrogram for Sorbents

Figure A15. FTIR spectrum of HKUST-1.

Figure A16. FTIR spectrum of Mg-MOF-74.
Figure A17. FTIR spectrum of SIFSIX-3-Ni.

Figure A18. FTIR spectrum of TEPA-SBA-15.
Figure A19. FTIR spectrum of Zeolite 13X.
A.8 Sorption Isotherms of Sorbents

Figure A20. CO$_2$ and N$_2$ sorption isotherms on pristine HKUST-1.

Figure A21. CO$_2$ and N$_2$ sorption isotherms on pristine Mg-MOF-74.
Figure A22. CO$_2$ and N$_2$ sorption isotherms on pristine SIFSIX-3-Ni.

Figure A23. CO$_2$ and N$_2$ sorption isotherms on pristine Zeolite-13X.
A.9 Accelerated Stability Test of Sorbents

Figure A24. PXRD of HKUST-1 after accelerated stability testing.

Figure A25. CO$_2$ sorption isotherms at 293 K for HKUST-1 after accelerated stability testing.
Figure A26. PXRD of Mg-MOF-74 after accelerated stability testing.

Figure A27. CO$_2$ sorption isotherms at 293 K for Mg-MOF-74 after accelerated stability testing.
Figure A28. PXRD of SIFSIX-3-Ni after accelerated stability testing.

Figure A29. CO$_2$ sorption isotherms at 293 K for SIFSIX-3-Ni after accelerated stability testing.
Figure A30. PXRD of Zeolite 13X after accelerated stability testing.

Figure A31. CO$_2$ sorption isotherms at 293 K for Zeolite 13X after accelerated stability testing.
Figure A32. Gravimetric CO$_2$ uptake for TEPA-SBA-15 after accelerated stability testing.
A.10 Scheme of Thermogravimetric-Temperature-Programmed Desorption Analysis of Sorbents

Figure A33. Lab temperature and relative humidity during DAC experiment.
TGA-TPD Results

Table A1 reveals that, when exposed to the laboratory atmosphere for 12 h, TEPA-SBA-15 adsorbs ca. 158 mg/g of CO$_2$, by far the most of any of the five sorbents tested. Conversely, TEPA-SBA-15 adsorbed only ca. 12 mg/g of H$_2$O, the lowest value of the five sorbents studied herein. The 92%/8% CO$_2$/H$_2$O ratio represents the strongest performance by far of any of the sorbents with respect to DAC. However, TEPA-SBA-15 also exhibits the highest temperature for initial CO$_2$ desorption, as would be expected for recovery of a chemisorbent. The physisorbents exhibit initial CO$_2$ desorption at 40-50 °C. CO$_2$ adsorbed from dry CO$_2$ (1 atm) and dry CO$_2$ (0.15 atm) are roughly the same (160 vs. 152 mg/g), indicating full uptake. The moist CO$_2$ experiments show only marginal uptakes of H$_2$O.

Table A1. Temperature-Programmed Desorption (TPD) coupled with mass-spectrometry.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>DAC (1 atm; 49% RH)$^a$</th>
<th>Moist CO$_2$ (1 atm)$^c$</th>
<th>Moist CO$_2$ (0.15 atm)$^c$</th>
<th>Moist N$_2$ (1 atm)$^c$</th>
<th>Dry CO$_2$ (1 atm)</th>
<th>Dry CO$_2$ (0.15 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-3-Ni</td>
<td>&lt;8%</td>
<td>&gt;92%</td>
<td>&gt;93%</td>
<td>&lt;7%</td>
<td>62%</td>
<td>38%</td>
</tr>
<tr>
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<td>&lt;56%</td>
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$^a$ Relative humidity and temperature where measured using a temperature and humidity sensitive thermometer. $^b$ Mass of analyte (mg/g). $^c$ Water saturated gas feeds were obtained by bubbling each pure gas through deionized water. $^d$ TEPA-SBA-15 is an amine modified mesoporous chemisorbent material.

The second best sorbent for DAC in terms of selectivity was found to be SIFSIX-3-Ni, which adsorbed ca. 8 mg/g CO$_2$ and ca. 93 mg/g H$_2$O. However, a composition of 8% CO$_2$ to 92% H$_2$O still represents for selectivity towards CO$_2$ vs. the atmosphere, where
CO₂ concentration is ca. 0.04%. The amount of CO₂ adsorbed by SIFSIX-3-Ni under dry CO₂ (1 atm) and dry flue-gas (0.15 atm) atmospheres was ca. 110 mg/g CO₂. In the moist, high-concentration CO₂ atmosphere, SIFSIX-3-Ni (110 mg/g CO₂; > 93%) performs almost as well as TEPA-SBA-15 (149 mg/g CO₂; > 98%).

HKUST-1 and Mg-MOF-74 were the weakest DAC performers of the sorbents studied herein with uptakes of < 4% of CO₂ vs. > 96% H₂O (Table A1). Dry CO₂ (1 atm) experiments showed roughly equal uptake by HKUST-1 and SIFSIX-3-Ni (ca. 110 mg/g) whereas Mg-MOF-74 adsorbed ca. 250 mg/g under the same conditions. However, in the DAC experiment, Mg-MOF-74 adsorbed less mass than SIFSIX-3-Ni (6.3 mg/g vs. ca. 8 mg/g) and HKUST-1 adsorbed even less CO₂ (ca. 2 mg/g). In the experiment simulating moist flue-gas, Mg-MOF-74 and HKUST-1 adsorbed ca. 51/49% and 8.5/91% CO₂ to H₂O, respectively, which means that they are less selective than SIFSIX-3-Ni (Table A1).

Zeolite 13X adsorbed ca. 1.5 mg/g CO₂ to ca. 146 mg/g H₂O in the DAC study. Performance under moist, highly concentrated CO₂ was > 45% CO₂ to < 55% H₂O), while moist flue-gas resulted in ca. 22% CO₂ to 78% H₂O.
TGA-TPD analysis for HKUST-1.

Figure A34. TPD profiles and composition for HKUST-1 DAC test.

Figure A35. Moist N\textsubscript{2} uptake test using TGA for HKUST-1.
Figure A36. Moist 1.0 atm CO\textsubscript{2} uptake test using TGA for HKUST-1.

Figure A37. TPD profiles and composition for HKUST-1 moist 1.0 atm CO\textsubscript{2} test.
Figure A38. Dry 1.0 atm CO\textsubscript{2} uptake test using TGA for HKUST-1.

Figure A39. Moist 0.15 atm CO\textsubscript{2} uptake test using TGA for HKUST-1.
Figure A40. TPD profiles and composition for HKUST-1 moist 0.15 atm CO$_2$ test.

Figure A41. Dry 0.15 atm CO$_2$ uptake test using TGA for HKUST-1.
TGA-TPD analysis for Mg-MOF-74.

Figure A42. TPD profiles and composition for Mg-MOF-74 DAC test.

Figure A43. Moist N₂ uptake test using TGA for Mg-MOF-74.
Figure A44. Moist 1.0 atm CO$_2$ uptake test using TGA for Mg-MOF-74.

Figure A45. TPD profiles and composition for Mg-MOF-74 moist 1.0 atm CO$_2$ test.
Figure A46. Dry 1.0 atm CO\textsubscript{2} uptake test using TGA for Mg-MOF-74.

Figure A47. Moist 0.15 atm CO\textsubscript{2} uptake test using TGA for Mg-MOF-74.
Figure A48. TPD profiles and composition for Mg-MOF-74 moist 0.15 atm CO$_2$ test.

Figure A49. Dry 0.15 atm CO$_2$ uptake test using TGA for Mg-MOF-74.
TGA-TPD analysis for SIFSIX-3-Ni.

Figure A50. TPD profiles and composition for SIFSIX-3-Ni DAC test.

Figure A51. Moist N\textsubscript{2} uptake test using TGA for SIFSIX-3-Ni.
Figure A52. Moist 1.0 atm CO$_2$ uptake test using TGA for SIFSIX-3-Ni.

Figure A53. TPD profiles and composition for SIFSIX-3-Ni moist 1.0 atm CO$_2$ test.
Figure A54. Dry 1.0 atm CO\textsubscript{2} uptake test using TGA for SIFSIX-3-Ni.

Figure A55. Moist 0.15 atm CO\textsubscript{2} uptake test using TGA for SIFSIX-3-Ni.
Figure A56. TPD profiles and composition for SIFSIX-3-Ni moist 0.15 atm CO\textsubscript{2} test.

Figure A57. Dry 0.15 atm CO\textsubscript{2} uptake test using TGA for SIFSIX-3-Ni.
TGA-TPD analysis for TEPA-SBA-15

Figure A58. TPD profiles and composition for TEPA-SBA-15DAC test.

Figure A59. Moist N$_2$ uptake test using TGA for TEPA-SBA-15.
Figure A60. Moist 1.0 atm $\text{CO}_2$ uptake test using TGA for TEPA-SBA-15.

Figure A61. TPD profiles and composition for TEPA-SBA-15 moist 1.0 atm $\text{CO}_2$ test.
Figure A62. Dry 1.0 atm CO$_2$ uptake test using TGA for TEPA-SBA-15.

Figure A63. Moist 0.15 atm CO$_2$ uptake test using TGA for TEPA-SBA-15.
Figure A64. TPD profiles and composition for TEPA-SBA-15moist 0.15 atm CO₂ test.

Figure A65. Dry 0.15 atm CO₂ uptake test using TGA for TEPA-SBA-15.
TGA-TPD analysis for Zeolite 13X.

Figure A66. TPD profiles and composition for Zeolite 13X DAC test.

Figure A67. Moist N₂ uptake test using TGA for Zeolite 13X.
Figure A68. Moist 1.0 atm CO$_2$ uptake test using TGA for Zeolite 13X.

Figure A69. TPD profiles and composition for Zeolite 13X moist 1.0 atm CO$_2$ test.
Figure A70. Dry 1.0 atm CO$_2$ uptake test using TGA for Zeolite 13X.

Figure A71. Moist 0.15 atm CO$_2$ uptake test using TGA for Zeolite 13X.
Figure A72. TPD profiles and composition for Zeolite 13X moist 0.15 atm CO₂ test.

Figure A73. Dry 0.15 atm CO₂ uptake test using TGA for Zeolite 13X.
A.11 Variable Temperature Powder X-Ray Diffraction of SIFSIX-3-Ni

Figure A74. VT-PXRD of SIFSIX-3-Ni. This series of diffractograms shows the temperature-induced transformation (front to rear) of the precursor (red: 25 °C) into SIFSIX-3-Ni (orange: 110 °C).
A.12 References


Appendix B: Supplementary Data for Chapter Three

Zeolite 13X was obtained from Sigma-Aldrich. SIFSIX-3-Ni,\(^{1}\)Mg-MOF-74,\(^{2}\)UiO-66-NH\(_2\),\(^{3}\)Ni-MOF-74\(^{4}\) and HKUST-1\(^{5}\) were synthesised according to literature procedures.

B.1 Synthesis of Hybrid Ultramicroporous Materials

Preparation of \{[Ni(pyrazine)\(_2\)-(TiF\(_6\))]\(_n\)\} (TIFSIX-3-Ni). Nickel hexafluorotitanate (0.500 g, 2.27 mmol) and pyrazine (2.50 g, 31.2 mmol) were dissolved in 1 mL of deionised water and stirred for 48 h at room temperature to yield an as yet uncharacterised polycrystalline precursor of TIFSIX-3-Ni (blue colour powder). The precursor was air dried and heated at 160 °C for 24 h to obtain the desired TIFSIX-3-Ni. Activation of TIFSIX-3-Ni was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 160 °C with a ramp rate of 10 °C/min).

Preparation of \{[Ni(pyrazine)\(_2\)-(NbOF\(_5\))]\(_n\)\} (NbOFFIVE-1-Ni). The compound NbOFFIVE-1-Ni was synthesised and activated using a reported synthesis method.\(^{6}\) Nickel nitrate hexahydrate (0.175 g, 0.602 mmol), niobium(V) oxide (0.0790 g, 0.297 mmol), pyrazine (0.384 g, 4.79 mmol) and hydrofluoric acid (0.26 mL, aqueous 48%, 7.17 mmol) were added to 3 mL of deionized water in a Teflon bomb and heated at 130 °C for 24 h. Violet coloured crystals were obtained upon cooling the reaction mixture to room temperature. The crystals obtained were washed with methanol to remove any traces of unreacted hydrofluoric acid. Activation of NbOFFIVE-1-Ni was carried out by degassing the methanol-washed sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 105 °C with a ramp rate of 10 °C/min).
B.2 Experimental Section

**Powder X-ray Diffraction (PXRD).** Diffractograms were recorded using a PANalytical Empyrean™ diffractometer equipped with a PIXcel³D detector operating in scanning line detector mode with an active length of 4 utilizing 255 channels. The diffractometer is outfitted with an Empyrean Cu LFF (long fine-focus) HR (9430 033 7310x) tube operated at 40 kV and 40 mA and CuKα radiation (λα = 1.540598 Å) was used for diffraction experiments. Continuous scanning mode with the goniometer in the theta-theta orientation was used to collect the data. Incident beam optics included the Fixed Divergences slit with anti-scatter slit PreFIX module, with a 1/8° divergence slit and a 1/4° anti-scatter slit, as well as a 10 mm fixed incident beam mask and a Soller slit (0.04 rad). Divergent beam optics included a P7.5 anti-scatter slit, a Soller slit (0.04 rad), and a Ni-β filter. In a typical experiment, 20 mg of sample was dried, ground into a fine powder and was loaded on a zero background silicon disks. The data was collected from 5° - 45° (2θ) with a step-size of 0.02626° and a scan time of 29 seconds per step. Crude data was analysed using the X’Pert HighScore Plus™ software V 4.1 (PANalytical, The Netherlands). Plots of stacked PXRD spectra for each adsorbent displaying the diffraction pattern for calculated and as synthesized materials are provided below (Figure B2-B3). Additional plots of stacked PXRD spectra displaying patterns for calculated, pristine sample, and post-humidity chamber exposure (after 1, 7, and 14 d) are provided for each sorbent. (Figure B22 and B24)

**Thermogravimetric Analysis (TGA).** Thermograms were recorded under nitrogen using TGA instrument TA Q50 V20.13 Build 39. Platinum pans and a flow rate of 60 mL/min for the nitrogen gas were used for the experiments. The data was collected in the High Resolution Dynamic mode with a sensitivity of 1.0, a resolution of 4.0, and a temperature ramp of 20 °C/min up to 500 °C. The data was evaluated using the T.A.
Universal Analysis suite for Windows XP/Vista Version 4.5A. Plots of stacked thermograms for each microporous sorbent are provided below (Figure B7–B9).

**Gas Sorption Measurements.** Ultra-high-purity grade N\textsubscript{2} and CO\textsubscript{2} were used for gas sorption experiments. Adsorption experiments (up to 1 bar) for different pure gases were performed on Micromeritics TriStar II PLUS and Micromeritics 3 Flex surface area and pore size analyser. Measurements with N\textsubscript{2} at 77 K were conducted on a Micromeritics TriStar II PLUS instrument. Brunauer-Emmett-Teller (BET) surface areas were determined from the N\textsubscript{2} adsorption isotherms at 77 K using the Micromeritics Microactive software except for NbOFFIVE-1-Ni and TIFSIX-3-Ni whose BET surface areas were determined from the CO\textsubscript{2} adsorption isotherms collected at 298 K. About 200 mg of activated samples were used for the measurements. Very low pressure CO\textsubscript{2} measurements were performed on a Micromeritics 3 Flex surface area and pore size analyser at 273, 283, 293 and 298 K. A Julabo temperature controller was used to maintain a constant temperature in the bath through the duration of the experiment. Samples were degassed on a Smart VacPrep instrument prior to the analysis.

**TGA-Temperature-Programmed Desorption (TPD) Studies.** Gas mixing rig coupled independently with a TGA instrument TA Q50 V20.13 Build 39 and mass spectrometer (MS) Agilent 5975 MSD was used for the TGA-TPD studies, see Figure B1. A typical test involved activating the sample by heating at desired temperature under a 60 mL/min flow of nitrogen gas and then cooling it down to 30 °C before the introduction of the desired gas mixture. Gas ratios was controlled and monitored by mass flow controller whereas moisture was introduced by passing the pre-mixed gas mixture through a gas bubbler containing water. Increase in weight was monitored until it began to plateau along with exposure time and gas flow conditions. Composition of the adsorbed species was analysed during the desorption cycle using the mass spectrometer. Custom-made fixed-bed flow
system consisting of gas delivery system, a reactor housed in a furnace and a mass spectrometer detection system was used for the TPD experiments. Amount of guest adsorbed and the temperature at which desorption occurs can be figured out using the TPD profiles. A typical CO$_2$ TPD profile tells us about the amount of CO$_2$ adsorbed and the range of desorption temperature. It is carried out by placing the sorbent in a quartz tubular reactor and the sample is fixed within it using quartz wool. Helium is passed through the reactor until a constant signal is recorded by the mass spectrometer followed by increase in temperature at the rate of 10 °C/min to the desired temperature so as to remove the impurities. Once the impurities are flushed out, the sample is cooled down to 30 °C and the gas mixture is introduced till the desired loading is obtained. Once the desired adsorption parameters are obtained, gas flow is switched to nitrogen to flush out the excessive CO$_2$ in the system. Once the CO$_2$ concentration reaches the background levels, carrier gas is switched to helium (it is not detected by the MS, ensuring that all desorbed species from the adsorbents are detected) and the temperature of the reactor is raised at the rate of 10 °C/min. Composition of the desorbed gas was monitored by MS thus helping us to figure out the identity and quantity of each component present in the desorbed gas.

A typical direct air capture (DAC) test, involves activation of sample as per the reported conditions followed by exposure to the laboratory environment for 24 h. Analysis of the exposed sample is carried out using TPD studies to determine the composition of the adsorbed gas.

**Accelerated Stability Protocol.** In pharmaceutical industry, there exists a well-established criteria for the determination of a compound’s stability to long-term and accelerated storage conditions.[7] The procedure incorporates all possible storage conditions from different regions around the globe. Approved as a unified testing condition by
International Conference of Harmonization (ICH) it consists of long-term, intermediate and accelerated storage conditions valid for the USA, EU and Japan. Proven by Arrhenius equation to be a valid model, accelerated stability conditions mimic an acceleration of the storage at ambient conditions and accelerated stability testing for 6 months is similar to two years of long-term storage conditions.\(^{[8]}\) In a typical experiment, pristine sample of the adsorbent under investigation was prepared and placed into an environment where relative humidity temperature and were controlled. To achieve 75% relative humidity at 40 °C, saturated aq. NaCl solution is placed in a desiccator stored at 40 °C. Adsorbents were placed in a separate, open glass vial and stored within the desiccator. They were exposed to this temperature and humidity continuously and aliquots were removed for analysis (PXRD, TGA, and gas sorption) after 1, 7, and 14 d.
B.3 Scheme of Thermogravimetric-Temperature-Programmed Desorption

Figure B1. Schematic of gas mixing system, TGA uptake analysis and TPD analysis units.
B.4 Powder X-Ray Diffraction of Sorbents

Figure B2. PXRD of TIFSIX-3-Ni.

Figure B3. PXRD of NbOFFIVE-1-Ni.
Figure B4. PXRD of Mg-MOF-74 as synthesised and after sorption vs. the calculated pattern.

Figure B5. PXRD of UiO-66-NH₂ as synthesised and after sorption vs. the calculated pattern.
Figure B6. PXRD of HKUST-1 as synthesised and after sorption vs. the calculated pattern.
B.5 Thermogravimetric Analysis of Sorbents

Figure B7. TGA of TIFSIX-3-Ni.

Figure B8. TGA of NbOFFIVE-1-Ni.
Figure B9. TGA of SIFSIX-3-Ni.
B.6 Sorption Isotherms of Sorbents

Figure B10. CO$_2$ sorption isotherms for TIFSIX-3-Ni.

Figure B11. CO$_2$ (black) and N$_2$ (red) sorption isotherms for TIFSIX-3-Ni
Figure B12. CO\textsubscript{2} (black) and N\textsubscript{2} (red) sorption isotherms for NbOFFIVE-1-Ni.

Figure B13. CO\textsubscript{2} isosteric heat of adsorption for TIF SIX-3-Ni.
B.7 Low Pressure Isosteric Heat of Adsorption ($Q_{st}$) Calculation of Sorbents

The $Q_{st}$ of CO$_2$ for TIFSIX-3-Ni, SIFSIX-3-Ni, NbOFFIVE-1-Ni, UiO-66-NH$_2$, Zeolite 13X, HKUST-1, Mg-MOF-74 were calculated from the low pressure CO$_2$ adsorption isotherms collected at 273, 283 and 293 K.

The Clausius-Clapeyron equation was used for the calculation of $Q_{st}$ where virial-type equations were used to fit ten points in the adsorption data between 0 and 3000 ppm (0.3 mbar) at multiple temperatures (Equation 1). The fit for each of the compounds is shown below. All fitting was performed using Origin Pro 8.

\[
\ln P = \ln n + \left(\frac{1}{T^2}\right) \sum_{i=0}^{j} a_i n^i + \sum_{i=0}^{k} b_i n^i
\]

The $Q_{st}$ was then calculated from the virial model using Equation 2.

\[
-Q_{st} = -R \sum_{i=0}^{j} a_i n^i
\]
**Qst Calculation - Virial Fitting for HKUST-1**

![Graph showing fitting of isotherm data of HKUST-1 to the virial equation.](image)

Figure B14. Fitting of the isotherm data of HKUST-1 to the virial equation.

**Table B1. Fitting parameters for HKUST-1.**

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**Qst Calculation - Virial Fitting for UiO-66-NH₂**

Figure B15. Fitting of the isotherm data of UiO-66-NH₂ to the virial equation.

Table B2. Fitting parameters for UiO-66-NH₂.

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**Q_{st} Calculation - Virial Fitting for Mg-MOF-74**

![Figure B16. Fitting of the isotherm data of Mg-MOF-74 to the virial equation.](image)

Table B3. Fitting parameters for Mg-MOF-74.

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**Qm Calculation - Virial Fitting for Zeolite 13X**

![Graph showing fitting of isotherm data of Zeolite 13X to the virial equation.](image)

Figure B17. Fitting of the isotherm data of Zeolite 13X to the virial equation.

**Table B4. Fitting parameters for Zeolite 13X.**

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Figure B18. Fitting of the isotherm data of SIFSIX-3-Ni to the virial equation.

Table B5. Fitting parameters for SIFSIX-3-Ni.

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**Q_st Calculation - Virial Fitting for TIFSIX-3-Ni**

![Graph showing isotherm fits to the virial equation for TIFSIX-3-Ni](graph)

Figure B19. Fitting of the isotherm data of TIFSIX-3-Ni to the virial equation.

**Table B6. Fitting parameters for TIFSIX-3-Ni.**

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B.8 Temperature-Programmed Desorption Analysis of Sorbents

Figure B20. DAC test TPD for TIFSIX-3-Ni

Figure B21. DAC test TPD for NbOFFIVE-1-Ni
B.9 Accelerated Stability Test of Sorbents

Figure B22. PXRD for TIFSIX-3-Ni after accelerated stability test.

Figure B23. Sorption for TIFSIX-3-Ni after accelerated stability test.
Figure B24. PXRD for NbOFFIVE-1-Ni after accelerated stability test.

Figure B25. Sorption for NbOFFIVE-1-Ni after accelerated stability test.
B.10 Variable temperature powder x-ray diffraction (VT-PXRD) of sorbents

Figure B26. VT-PXRD of TIFSIX-3-Ni. This series of diffractograms shows the temperature-induced transformation {rear to front} of the precursor (red. 25 °C) into TIFSIX-3-Ni (orange. 140 °C).

Figure B27. VT-PXRD of SIFSIX-3-Ni.
B.11 Unit Cell Refinement of TIFSIX-3-Ni.

Powder diffraction data used for structure solution was obtained from beamline i11 at the Diamond Light Source (\( \lambda = 0.82620(6) \) and zero point = -0.0367(1)). Due to the high energy X-ray source, two second scans using a positional scanning detector was used to collect data from a powder sample sealed in a 0.6 mm quartz capillary tube. Analysis of the powder data was carried out in GSAS-II; the lattice parameters were determined and structure factors obtained by use of the Pawley method. A Monte Carlo/simulated annealing method was used for structure solution using free moving rigid bodies obtained from the Cambridge Structural Database (CSD) (CSD refcode PETWIW = TiF₆, AHADUI = pyrazine). (See Table B7 for crystallographic details).

Figure B28. Diffractograms for the Rietveld refinement of TIFSIX-3-Ni. Inset depicts a more detailed view of the high angle data (2Å < d < 1Å)
Table B7. Crystallographic data for TIFSIX-3-Ni

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B.12 References


Appendix C. Supplementary data for chapter four

Zinc hexafluorosilicate hexahydrate \((\text{ZnSiF}_6.6\text{H}_2\text{O})\), Nickel hexafluorosilicate hexahydrate \((\text{NiSiF}_6.6\text{H}_2\text{O})\), Hexafluorotitanic acid, 60 wt.% in \(\text{H}_2\text{O}\) \((\text{H}_2\text{TiF}_6)\), Hexafluorosilicic acid, 35 wt.% in \(\text{H}_2\text{O}\) \((\text{H}_2\text{SiF}_6)\), Niobium(V) oxide \((\text{Nb}_2\text{O}_5)\), Aqueous hydrofluoric acid, aqueous 48% \((\text{HF})\), Nickel nitrate hexahydrate \((\text{NiNO}_3.6\text{H}_2\text{O})\), Ammonium hexafluorosilicate \((\text{(NH}_4)_2\text{SiF}_6)\) and \text{pyrazine} was obtained from Sigma-Aldrich. Ferrous hexafluorosilicate hexahydrate \((\text{FeSiF}_6.6\text{H}_2\text{O})\) was obtained from Alfa Chemsitry. Zinc carbonate basic \((\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6)\), Nickel(II) carbonate, anhydrous \((\text{NiCO}_3)\) and Cobalt(II) carbonate, anhydrous \((\text{CoCO}_3)\) was purchased from Alfa Aesar.

C.1 Synthesis of Inorganic Salt

Preparation of Zinc hexafluorotitanate hexahydrate \((\text{ZnTiF}_6.6\text{H}_2\text{O})\). Zinc carbonate basic (5.48 g, 10 mmol) and Hexafluorotitanic acid (15 ml, excess) were added to 10 mL of deionised water, and stirred for 4 h at room temperature to yield a colourless clear solution. The solution was transferred to PTFE petridish, and kept in open air for slow evaporation. After a week, colourless crystals of \(\text{ZnTiF}_6.6\text{H}_2\text{O}\) was obtained which was filtered and air dried for further use.

Preparation of Zinc pentafluoroxyjniobate hexahydrate \((\text{ZnNbOF}_5.6\text{H}_2\text{O})\). Niobium(V) oxide (2.65 g, 10 mmol) and hydrofluoric acid, aqueous 48% (8 ml, excess) were placed in a Teflon bomb and heated for 16 h at 100 °C. The clear solution obtained was cooled down to room temperature and reacted with Zinc carbonate basic (2.19 g, 4 mmol) to yield a colourless clear solution. The solution was transferred to PTFE petridish, and kept in open air for slow evaporation. After a week, colourless crystals of \(\text{ZnNbOF}_5.6\text{H}_2\text{O}\) was obtained which was filtered and air dried for further use.
Preparation of Nickel hexafluorotitanate hexahydrate (NiTiF$_6$.6H$_2$O). Nickel carbonate (2.36 g, 20 mmol) and Hexafluorotitanic acid (10 ml, excess) were added to 10 mL of deionised water, and stirred for 4 h at room temperature to yield a green colour solution. The solution was transferred to PTFE petridish, and kept in open air for slow evaporation. After a week, green crystals of NiTiF$_6$.6H$_2$O was obtained which was filtered and air dried for further use.

Preparation of Nickel pentafluorooxyniobate hexahydrate (NiNbOF$_5$.6H$_2$O). Niobium(V) oxide (2.65 g, 10 mmol) and hydrofluoric acid, aqueous 48% (8 ml, excess) were placed in a Teflon bomb and heated for 16 h at 100 °C. The clear solution obtained was cooled down to room temperature and reacted with Nickel carbonate (2.36 g, 20 mmol) to yield a green colour solution. The solution was transferred to PTFE petridish, and kept in open air for slow evaporation. After a week green crystals of NiNbOF$_5$.6H$_2$O was obtained which was filtered and air dried for further use.

Preparation of Cobalt hexafluorosilicate hexahydrate (CoSiF$_6$.6H$_2$O). Cobalt carbonate (2.36 g, 20 mmol) and Hexafluorosilicic acid (30 ml, excess) were added to 10 mL of deionised water, and stirred for 4 h at room temperature to yield a red-brown colour solution. The solution was transferred to PTFE petridish, and kept in open air for slow evaporation. After a week, red-brown crystals of CoSiF$_6$.6H$_2$O was obtained which was filtered and air dried for further use.

Preparation of Cobalt hexafluorotitanate hexahydrate (CoTiF$_6$.6H$_2$O). Cobalt carbonate (2.36 g, 20 mmol) and Hexafluorotitanic acid (10 ml, excess) were added to 10 mL of deionised water, and stirred for 4 h at room temperature to yield a red-brown colour solution. The solution was transferred to PTFE petridish, and kept in open air for slow evaporation.
evaporation. After a week, red-brown crystals of \( \text{CoTiF}_6\cdot6\text{H}_2\text{O} \) was obtained which was filtered and air dried for further use.

**Preparation of Cobalt pentafluoroxygeniobate hexahydrate**

(\( \text{CoNbOF}_5\cdot6\text{H}_2\text{O} \)). Niobium(V) oxide (2.65 g, 10 mmol) and hydrofluoric acid, aqueous 48% (8 ml, excess) were placed in a Teflon bomb and heated for 16 h at 100 °C. The clear solution obtained was cooled down to room temperature and reacted with Cobalt carbonate (2.36 g, 20 mmol) to yield a red-brown colour solution. The solution was transferred to PTFE petridish, and kept in open air for slow evapouration. After a week red-brown crystals of \( \text{NiNbOF}_5\cdot6\text{H}_2\text{O} \) was obtained which was filtered and air dried for further use.

**C.2 Synthesis of Hybrid Ultramicroporous Materials by Traditional Method**

**Preparation of \([\text{Ni(pyrazine)}_2\text{(SiF}_6\text{)}_n]\) (SIFSIX-3-Ni) (Slurry).**

Nickel nitrate (0.870 g, 3 mmol), ammonium silicate (0.510 g, 3 mmol) and pyrazine (0.540 g, 6.75 mmol) were dissolved in 4 mL of deionised water and stirred for 48 h at room temperature to yield a polycrystalline \( \text{sql} \) precursor of \( \text{SIFSIX-3-Ni} \) (blue colour powder). The precursor was air dried and heated at 100 °C for 24 h to obtain the desired \( \text{SIFSIX-3-Ni} \). Activation of \( \text{SIFSIX-3-Ni} \) was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 100 °C with a ramp rate of 10 °C/min).

**Preparation of \([\text{Ni(pyrazine)}_2\text{(TiF}_6\text{)}_n]\) (TIFSIX-3-Ni) (Slurry).**

Nickel hexafluorotitanate (0.500 g, 2.27 mmol) and pyrazine (2.50 g, 31.2 mmol) were dissolved in 1 mL of deionised water and stirred for 48 h at room temperature to yield a polycrystalline \( \text{sql} \) precursor of \( \text{TIFSIX-3-Ni} \) (blue colour powder). The precursor was air dried and heated
at 160 °C for 24 h to obtain the desired TIFSIX-3-Ni. Activation of TIFSIX-3-Ni was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 160 °C with a ramp rate of 10 °C/min).

Preparation of \([\text{Ni(pyrazine)}_2(\text{NbOF}_5)]_n\) (NbOFFIVE-1-Ni) (Solvothermal). The compound NbOFFIVE-1-Ni was synthesised and activated using a reported synthesis method. Nickel nitrate hexahydrate (0.175 g, 0.602 mmol), niobium(V) oxide (0.0790 g, 0.297 mmol), pyrazine (0.384 g, 4.79 mmol) and hydrofluoric acid (0.26 mL, aqueous 48%, 7.17 mmol) were added to 3 mL of deionized water in a Teflon bomb and heated at 130 °C for 24 h. Violet coloured crystals were obtained upon cooling the reaction mixture to room temperature. The crystals obtained were washed with methanol to remove any traces of unreacted hydrofluoric acid. Activation of NbOFFIVE-1-Ni was carried out by degassing the methanol-washed sample on a SmartVacPrep™ using dynamic vacuum and heating for 24 h (sample heated from RT to 105 °C with a ramp rate of 10 °C/min).

C.3 Synthesis of Hybrid Ultramicroporous Materials by Ball Milling

Preparation of \([\text{Zn(pyrazine)}_2(\text{SiF}_6)]_n\) (SIFSIX-3-Zn) (Ball Milling). Zinc hexafluorosilicate (1.8 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 60 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline sql precursor of SIFSIX-3-Zn (white colour powder). The precursor was heated at 60 °C for 6 h to obtain the desired SIFSIX-3-Zn. Activation of SIFSIX-3-Zn was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 40 °C with a ramp rate of 2 °C/min).
Preparation of \{[Zn(pyrazine)\(_2\)(TiF\(_6\))]\(_n\)\} (TIFSIX-3-Zn) (Ball Milling). Zinc hexafluorotitanate (2.0 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 60 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline sql precursor of TIFSIX-3-Zn (light yellow colour powder). The precursor was heated at 100 °C for 6 h to obtain the desired TIFSIX-3-Zn. Activation of TIFSIX-3-Zn was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 80 °C with a ramp rate of 5 °C/min).

Preparation of \{[Zn(pyrazine)\(_2\)(NbOF\(_5\))]\(_n\)\} (NbOFFIVE-1-Zn) (Ball Milling). Zinc oxypentafluoroniobate (2.3 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 60 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline NbOFFIVE-1-Zn (white colour powder). Activation of NbOFFIVE-1-Zn was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 120 °C with a ramp rate of 10 °C/min).

Preparation of \{[Ni(pyrazine)\(_2\)(SiF\(_6\))]\(_n\)\} (SIFSIX-3-Ni) (Ball Milling). Nickel hexafluorosilicate (1.8 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 150 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline sql precursor of SIFSIX-3-Ni (blue colour powder). The precursor was heated at 100 °C for 6 h to obtain the desired SIFSIX-3-Ni. Activation of SIFSIX-3-Ni was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 100 °C with a ramp rate of 10 °C/min).
Preparation of \([\text{[Ni(pyrazine)\textsubscript{2}(TiF\textsubscript{6})\textsubscript{n}]}}\) (TIFSIX-3-Ni) (Ball Milling). Nickel hexafluorotitanate (2 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 150 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline \textbf{sql} precursor of TIFSIX-3-Ni (blue colour powder). The precursor was heated at 120 °C for 6 h to obtain the desired TIFSIX-3-Ni. Activation of TIFSIX-3-Ni was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 160 °C with a ramp rate of 10°C/min).

Preparation of \([\text{[Ni(pyrazine)\textsubscript{2}(NbOF\textsubscript{5})\textsubscript{n}]}}\) (NbOFFIVE-1-Ni) (Ball Milling). Nickel oxypentafluoroniobate (2.3 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 150 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline NbOFFIVE-1-Ni (blue colour powder). Activation of NbOFFIVE-1-Ni was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 120 °C with a ramp rate of 10 °C/min).

Preparation of \([\text{[Co(pyrazine)\textsubscript{2}(SiF\textsubscript{6})\textsubscript{n}]}}\) (SIFSIX-3-Co) (Ball Milling). Cobalt hexafluorosilicate (1.8 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 90 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline \textbf{sql} precursor of SIFSIX-3-Co (orange colour powder). The precursor was heated at 100 °C for 6 h to obtain the desired SIFSIX-3-Co. Activation of SIFSIX-3-Co was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 100 °C with a ramp rate of 10 °C/min).
Preparation of \{{[\text{Co(pyrazine)}_2(\text{TiF}_6)]_n}\} (TIFSIX-3-Co) (Ball Milling). Cobalt hexafluorotitanate (2 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 90 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline sql precursor of TIFSIX-3-Co (blue colour powder). The precursor was heated at 120 °C for 6 h to obtain the desired TIFSIX-3-Co. Activation of TIFSIX-3-Co was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 160 °C with a ramp rate of 10°C/min).

Preparation of \{{[\text{Co(pyrazine)}_2(\text{NbOF}_5)]_n}\} (NbOFFIVE-1-Co) (Ball Milling). Cobalt oxypentafluoroniobate (2.3 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 90 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline NbOFFIVE-1-Co (orange colour powder). Activation of NbOFFIVE-1-Co was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 120 °C with a ramp rate of 10 °C/min).

Preparation of \{{[\text{Fe(pyrazine)}_2(\text{SiF}_6)]_n}\} (SIFSIX-3-Fe) (Ball Milling). Iron hexafluorosilicate (1.8 g, 6 mmol) and pyrazine (1.040 g, 13 mmol) were placed into a 35 mL teflon jar with two 10 mm teflon steel core grinding balls. The mixture was then ground for 60 min at 25 Hz in a Retsch MM400 laboratory ball mill to form a polycrystalline sql precursor of SIFSIX-3-Fe (yellow colour powder). The precursor was heated at 70°C for 6 h to obtain the desired SIFSIX-3-Fe. Activation of SIFSIX-3-Fe was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heating for 16 h (sample heated from RT to 70 °C with a ramp rate of 5 °C/min).
C.4 Experimental Section

**Powder X-ray Diffraction (PXRD).** Diffractograms were recorded using a PANalytical Empyrean™ diffractometer equipped with a PIXcel3D detector operating in scanning line detector mode with an active length of 4 utilizing 255 channels. The diffractometer is outfitted with an Empyrean Cu LFF (long fine-focus) HR (9430 033 7310x) tube operated at 40 kV and 40 mA and CuKα radiation (λα = 1.540598 Å) was used for diffraction experiments. Continuous scanning mode with the goniometer in the theta-theta orientation was used to collect the data. Incident beam optics included the Fixed Divergences slit with anti-scatter slit PrefIX module, with a 1/8° divergence slit and a 1/4° anti-scatter slit, as well as a 10 mm fixed incident beam mask and a Soller slit (0.04 rad). Divergent beam optics included a P7.5 anti-scatter slit, a Soller slit (0.04 rad), and a Ni-β filter. In a typical experiment, 20 mg of sample was dried, ground into a fine powder and was loaded on a zero background silicon disks. The data was collected from 5° - 40° (2θ) with a step-size of 0.02626° and a scan time of 29 seconds per step. Crude data was analysed using the X’Pert HighScore Plus™ software V 4.1 (PANalytical, The Netherlands). Plots of stacked PXRD spectra for each adsorbent displaying the diffraction pattern for calculated and as synthesized materials are provided below (Figure C1-C7, C9, C11, C13-C16). Additional plots of stacked PXRD spectra displaying patterns for classical vs ball milling approach (Figure C8, C10 and C12), and for pristine sample, and post-humidity chamber exposure (after 1, 7, and 14 d) are provided for each sorbent (Figure C68, C70, C72, C74, C76, C78, C80, C82, C84, C86).

**Thermogravimetric Analysis (TGA).** Thermograms were recorded under nitrogen using TGA instrument TA Q50 V20.13 Build 39. Platinum pans and a flow rate of 60 mL/min for the nitrogen gas were used for the experiments. The data was collected in the High Resolution Dynamic mode with a sensitivity of 1.0, a resolution of 4.0, and a temperature ramp of 20 °C/min up to 500 °C. The data was evaluated using the T.A.
Universal Analysis suite for Windows XP/Vista Version 4.5A. Plots of stacked thermograms for each microporous sorbent are provided below (Figure C17–C26).

**Gas Sorption Measurements.** Ultra-high-purity grade N₂, CH₄ and CO₂ were used for gas sorption experiments. Adsorption experiments (up to 1 bar) for different pure gases were performed on Micromeritics TriStar II PLUS and Micromeritics 3 Flex surface area and pore size analyser. Brunauer-Emmett-Teller (BET) surface areas were determined from the CO₂ adsorption isotherms collected at 298 K. About 200 mg of activated samples were used for the measurements. Very low pressure CO₂ measurements were performed on a Micromeritics 3 Flex surface area and pore size analyser at 273 and 298 K. A Julabo temperature controller was used to maintain a constant temperature in the bath through the duration of the experiment. Samples were degassed on a Smart VacPrep instrument prior to the analysis. (Figure C27–C42)

**Isosteric Heats of Adsorption Calculations.**

The \( Q_{st} \) of CO₂ for HUMs were calculated from the low pressure CO₂ adsorption isotherms collected at 273 and 298 K. The Clausius-Clapeyron equation was used for the calculation of \( Q_{st} \) where virial-type equations were used to fit points in the adsorption data between 0 and 3000 ppm (0.3 mbar) at multiple temperatures (Equation 1). The fit for each of the compounds is shown (Figure C43–C52). All fitting was performed using Origin Pro 8.

\[
\ln P = \ln n + \left( \frac{1}{T} \right) \sum_{i=0}^{j} a_i n^i + \sum_{i=0}^{k} b_i n^i \quad (\text{Equation 1})
\]

The \( Q_{st} \) was then calculated from the virial model using Equation 2. The plot is shown below (Figure C53)

\[
-Q_{st} = -R \sum_{i=0}^{j} a_i n^i \quad (\text{Equation 2})
\]
Ideal Absorbed Solution Theory (IAST) Selectivity Calculations.

Gas separation selectivities were calculated using the ideal adsorbed solution theory (IAST) as implemented in the program pyIAST.\textsuperscript{4,5}

Isotherm fitting parameters are summarised in Figures C54-C63. Experimental isotherms were fitted with adsorption models, \(n_i^*(P)\), that provided the best root mean square error (RMSE) and observable fitting such as Quadratic ((Equation 3), Dual-Site Langmuir ((Equation 4) and Henry isotherms ((Equation 5). Where experimental data could not be appropriately fitted to an adsorption model, the experimental data was linearly interpolated with the spreading pressure calculated using numerical quadrature.

**Quadratic Isotherm Model**

\[
n_i^*(P) = M \frac{(K_A + 2K_B P)P}{1 + K_AP + K_B P^2}
\]  
\text{(Equation 3)}

Where \((P)\) is pressure, \(2M\) is the saturation loading and \(K_A\) (units. pressure\textsuperscript{-1}) and \(K_B\) (units. pressure\textsuperscript{-2}) are constants.

**Dual-Site Langmuir Isotherm Model**

\[
n_i^*(P) = M_1 \frac{K_1P}{1 + K_1P} + M_2 \frac{K_2P}{1 + K_2P}
\]  
\text{(Equation 4)}

Where \((P)\) is pressure, \(M_i\) is the number of adsorption sites of type \(i\) that has constants \(K_i\) (units. pressure\textsuperscript{-1}) for sites 1 and 2.

**Henry Isotherm Model**

\[
n_i^*(P) = K_H P
\]  
\text{(Equation 5)}

Where \((P)\) is pressure and \(K_H\) is the Henry coefficient (units. loading/pressure).

**Interpolator Isotherm model**

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Here, experimental data was linearly interpolated to approximate $n_i^*(P)$. To calculate spreading pressure between full vacuum and lowest loading, Henry’s law was assumed in order to extrapolate the data.

**Accelerated Stability Protocol.** In pharmaceutical industry, there exists a well-established criteria for the determination of a compound’s stability to long-term and accelerated storage conditions.\(^6\)\(^7\) The procedure incorporates all possible storage conditions from different regions around the globe. Approved as a unified testing condition by International Conference of Harmonization (ICH) it consists of long-term, intermediate and accelerated storage conditions valid for the USA, EU and Japan. Proven by Arrhenius equation to be a valid model, accelerated stability conditions mimic an acceleration of the storage at ambient conditions and accelerated stability testing for 6 months is similar to two years of long-term storage conditions. In a typical experiment, pristine sample of the adsorbent under investigation was prepared and placed into an environment where relative humidity temperature and were controlled. To achieve 75% relative humidity at 40 °C, saturated aq. NaCl solution is placed in a desiccator stored at 40 °C. Adsorbents were placed in a separate, open glass vial and stored within the desiccator. They were exposed to this temperature and humidity continuously and aliquots were removed for analysis (PXRD and gas sorption) after 1, 7, and 14 d. The experimental data is provided below (Figure C68-C87).
C.5 Powder X-Ray Diffraction of Hybrid Ultramicroporous Materials

Figure C1. PXRD of SIFSIX-3-Ni (Slurry).

Figure C2. PXRD of TIFSIX-3-Ni (Slurry).
Figure C3. PXRD of NbOFFIVE-1-Ni (Solvothermal).

Figure C4. PXRD of SIFSIX-3-Zn (Ball Milling).
Figure C5. PXRD of TIFSIX-3-Zn (Ball Milling).

Figure C6. PXRD of NbOFFIVE-1-Zn (Ball Milling).
Figure C7. PXRD of SIFSIX-3-Ni (Ball Milling).

Figure C8. PXRD of SIFSIX-3-Ni (Slurry vs Ball Milling).
Figure C9. PXRD of TIFSIX-3-Ni (Ball Milling).

Figure C10. PXRD of TIFSIX-3-Ni (Slurry vs Ball Milling).
Figure C11. PXRD of NbOFFIVE-1-Ni (Ball Milling).

Figure C12. PXRD of NbOFFIVE-1-Ni (Solvothermal vs Ball Milling).
Figure C13. PXRD of SIFSIX-3-Co (Ball Milling).

Figure C14. PXRD of TIFSIX-3-Co (Ball Milling).
Figure C15. PXRD of NbOFFIVE-1-Co (Ball Milling).

Figure C16. PXRD of SIFSix-3-Fe (Ball Milling).
C.6 Thermogravimetric Analysis of Hybrid Ultramicroporous Materials

Figure C17. TGA of SIFSIX-3-Zn (Ball Milling).

Figure C18. TGA of TIFSIX-3-Zn (Ball Milling).
Figure C19. TGA of NbOFFIVE-1-Zn (Ball Milling).

Figure C20. TGA of SIFSIX-3-Ni (Ball Milling).
Figure C21. TGA of TIFSIX-3-Ni (Ball Milling).

Figure C22. TGA of NbOFFIVE-1-Ni (Ball Milling).
Figure C23. TGA of SIFSIX-3-Co (Ball Milling).

Figure C24. TGA of TIFSIX-3-Co (Ball Milling).
Figure C25. TGA of NbOFFIVE-1-Co (Ball Milling).

Figure C26. TGA of SIFSIX-3-Fe (Ball Milling).
C.7 Sorption Isotherms of Hybrid Ultramicroporous Materials

Figure C27. Sorption Isotherms for SIFSIX-3-Ni (Slurry).

Figure C28. Sorption Isotherms for TIFSIX-3-Ni (Slurry).
Figure C29. Sorption Isotherms for NbOFFIVE-1-Ni (Solvothermal).

Figure C30. Sorption Isotherms for SIFSIX-3-Zn (Ball Milling).
Figure C31. Sorption Isotherms for TIFSIX-3-Zn (Ball Milling).

Figure C32. Sorption Isotherms for NbOFFIVE-1-Zn (Ball Milling).
Figure C33. Sorption Isotherms for SIFSIX-3-Ni (Ball Milling).

Figure C34. Sorption Isotherms for SIFSIX-3-Ni (Slurry vs Ball Milling).
Figure C35. Sorption Isotherms for SIFSIX-3-Ni (Ball Milling).

Figure C36. Sorption Isotherms for TIFSIX-3-Ni (Slurry vs Ball Milling).
Figure C37. Sorption Isotherms for NbOFFIVE-1-Ni (Ball Milling).

Figure C38. Sorption Isotherms for NbOFFIVE-1-Ni (Solvo thermal vs Ball Milling).
Figure C39. Sorption Isotherms for SIFSIX-3-Co (Ball Milling).

Figure C40. Sorption Isotherms for TIFSIX-3-Co (Ball Milling).
Figure C41. Sorption Isotherms for NbOFFIVE-1-Co (Ball Milling).

Figure C42. Sorption Isotherms for SIFSix-3-Fe (Ball Milling).
C.8 Isosteric Heat of Adsorption ($Q_{st}$) Calculation of Hybrid Ultramicroporous Materials

![Graph A](image1.png)  ![Graph B](image2.png)

**Figure C43.** *A*) Fitting of the isotherm data of SIFSIX-3-Zn (Ball Milling) to the virial equation. *B*) Fitting parameters for SIFSIX-3-Zn (Ball Milling).

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![Graph A](image3.png)  ![Graph B](image4.png)

**Figure C44.** *A*) Fitting of the isotherm data of TIFSIX-3-Zn (Ball Milling) to the virial equation. *B*) Fitting parameters for TIFSIX-3-Zn (Ball Milling).

<table>
<thead>
<tr>
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<th>Standard Error</th>
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Figure C45. A) Fitting of the isotherm data of SIFSIX-3-F NbOFFIVE-1-Zn (Ball Milling) to the virial equation. B) Fitting parameters for NbOFFIVE-1-Zn (Ball Milling).

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Figure C46. A) Fitting of the isotherm data of SIFSIX-3-Ni (Ball Milling) to the virial equation. B) Fitting parameters for SIFSIX-3-Ni (Ball Milling).

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Figure C47. A) Fitting of the isotherm data of TIFSIX-3-Ni (Ball Milling) to the virial equation. B) Fitting parameters for TIFSIX-3-Ni (Ball Milling).

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Figure C48. A) Fitting of the isotherm data of NbOFFIVE-1-Ni (Ball Milling) to the virial equation. B) Fitting parameters for NbOFFIVE-1-Ni (Ball Milling).

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Figure C49. A) Fitting of the isotherm data of SIFSIX-3-Co (Ball Milling) to the virial equation. B) Fitting parameters for SIFSIX-3-Co (Ball Milling).

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Figure C50. A) Fitting of the isotherm data of TIFSIX-3-Co (Ball Milling) to the virial equation. B) Fitting parameters for TIFSIX-3-Co (Ball Milling).

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Figure C51. A) Fitting of the isotherm data of NbOFFIVE-1-Co (Ball Milling) to the virial equation. B) Fitting parameters for NbOFFIVE-1-Co (Ball Milling).

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Figure C52. A) Fitting of the isotherm data of SIFSIX-3-Fe (Ball Milling) to the virial equation. B) Fitting parameters for SIFSIX-3-Fe (Ball Milling).

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Figure C53. CO$_2$ isosteric heat of adsorption ($Q_{st}$) for HUMs.
C.9 Ideal Adsorbed Solution Theory Selectivity Calculation. Fitting of CO₂, CH₄ and N₂ Sorption Data of Hybrid Ultramicroporous Materials

Figure C54. Fitting of CO₂, CH₄ and N₂ isotherm data of SIFSIX-3-Zn (Ball Milling).

Figure C55. Fitting of CO₂, CH₄ and N₂ isotherm data of TIFSIX-3-Zn (Ball Milling).
Figure C56. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of NbOFFIVE-1-Zn (Ball Milling).

Figure C57. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of TIFSIX-3-Ni (Ball Milling).
Figure C58. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of TIFSIX-3-Ni (Ball Milling).

**Figure C58.**

- **NbOFFIVE-1-Ni CO$_2$ 298 K Fitting**
  - Quadratic model parameters:
    - $M = 1.183669$
    - $K_a = 42.087581$
    - $K_b = 497.954529$
    - RMSE = 0.0552025377258

- **NbOFFIVE-1-Ni CH$_4$ 298 K Fitting**
  - Henry model parameters:
    - $K_H = 0.001121$
    - RMSE = 0.00135128360746

- **NbOFFIVE-1-Ni N$_2$ 298 K Fitting**
  - Henry model parameters:
    - $K_H = 0.001580$
    - RMSE = 0.0012624163876

Figure C59. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of NbOFFIVE-1-Ni (Ball Milling).

**Figure C59.**

- **SIFSIX-3-Co CO$_2$ 298 K Fitting**
  - Quadratic model parameters:
    - $M = 1.205872$
    - $K_a = 3.115776$
    - $K_b = 3.070223$
    - RMSE = 0.0230617111541

- **SIFSIX-3-Co CH$_4$ 298 K Fitting**
  - Henry model parameters:
    - $K_H = 0.006706$
    - RMSE = 0.00409703146312

- **SIFSIX-3-Co N$_2$ 298 K Fitting**
  - Henry model parameters:
    - $K_H = 0.001830$
    - RMSE = 0.002115691698

Figure C60. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of SIFSIX-3-Co (Ball Milling).
Figure C61. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of TIFSIX-3-Co (Ball Milling).

Figure C62. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of NbOFFIVE-1-Co (Ball Milling).
Figure C63. Fitting of CO$_2$, CH$_4$ and N$_2$ isotherm data of SIFSIX-3-Fe (Ball Milling).

SIFSIX-3-Fe CO$_2$ 298 K Fitting

Quadratic model parameters:
- $M = 1.287470$
- $K_s = 1.246660$
- $K_i = 0.467922$
- $RMSE = 0.00603545264372$

SIFSIX-3-Fe CH$_4$ 298 K Fitting

Henry model parameters:
- $KH = 0.099722$
- $RMSE = 0.0298676857844$

SIFSIX-3-Fe N$_2$ 298 K Fitting

Data Interpolated
C.10 Ideal Adsorbed Solution Theory Selectivity of Hybrid Ultramicroporous Materials

Figure C64. IAST selectivity of CO$_2$/N$_2$ (0.04/99.96) for HUMs.

Figure C65. IAST selectivity of CO$_2$/N$_2$ (1.99) for HUMs.
Figure C66. IAST selectivity of CO$_2$/N$_2$ (15.85) for HUMs.

Figure C67. IAST selectivity of CO$_2$/CH$_4$ (50.50) for HUMs.
C.11 Accelerated Stability Test of Hybrid Ultramicroporous Materials

Figure C68. PXRD for SIFSIX-3-Zn after accelerated stability test.

Figure C69. Sorption for SIFSIX-3-Zn after accelerated stability test.
Figure C70. PXRD for TIFSIX-3-Zn after accelerated stability test.

Figure C71. Sorption for TIFSIX-3-Zn after accelerated stability test.
Figure C72. PXRD for NbOFFIVE-1-Zn after accelerated stability test.

Figure C73. Sorption for NbOFFIVE-1-Zn after accelerated stability test.
Figure C74. PXRD for SIFSIX-3-Ni after accelerated stability test.

Figure C75. Sorption for SIFSIX-3-Ni after accelerated stability test.
Figure C76. PXRD for TIFSIX-3-Ni after accelerated stability test.

Figure C77. Sorption for TIFSIX-3-Ni after accelerated stability test.
Figure C78. PXRD for NbOFFIVE-1-Ni after accelerated stability test.

Figure C79. Sorption for NbOFFIVE-1-Ni after accelerated stability test.
Figure C80. PXRD for SIFSIX-3-Co after accelerated stability test.

Figure C81. Sorption for SIFSIX-3-Co after accelerated stability test.
Figure C82. PXRD for TIFSIX-3-Co after accelerated stability test.

Figure C83. Sorption for TIFSIX-3-Co after accelerated stability test.
Figure C84. PXRD for NbOFFIVE-1-Co after accelerated stability test.

Figure C85. Sorption for NbOFFIVE-1-Co after accelerated stability test.
Figure C86. PXRD for SIFSIX-3-Fe after accelerated stability test.

Figure C87. Sorption for SIFSIX-3-Fe after accelerated stability test.
C.12 Variable Temperature Powder X-Ray Diffraction of Hybrid Ultramicroporous Materials

Figure C88. VT-PXRD of SIFSIX-3-Zn.

Figure C89. VT-PXRD of TIFSIX-3-Zn.
Figure C90. VT-PXRD of NbOFFIVE-1-Zn.

Figure C91. VT-PXRD of SIFSIX-3-Ni.
Figure C92. VT-PXRD of TIFSIX-3-Ni.

Figure C93. VT-PXRD of NbOFFIVE-1-Ni.
Figure C94. VT-PXRD of SIFSIX-3-Co.

Figure C95. VT-PXRD of TIFSIX-3-Co.
Figure C96. VT-PXRD of NbOFFIVE-1-Co.

Figure C97. VT-PXRD of SIFSIX-3-Fe.
C.13 Scanning Electron Microscope Image of Hybrid Ultramicroporous Materials

Figure C98. SEM image of SIFSIX-3-Zn (Ball Milling).

Figure C99. SEM image of TIFSIX-3-Zn (Ball Milling).
Figure C100. SEM image of NbOFFIVE-1-Zn (Ball Milling).

Figure C101. SEM image of SIFSIX-3-Ni (Ball Milling).
Figure C102. SEM image of TIFSIX-3-Ni (Ball Milling).

Figure C103. SEM image of NbOFFIVE-1-Ni (Ball Milling).
Figure C104. SEM image of SIFSIX-3-Co (Ball Milling).

Figure C105. SEM image of TIFSIX-3-Co (Ball Milling).
Figure C106. SEM image of NbOFFIVE-1-Co (Ball Milling).

Figure C107. SEM image of SIFSIX-3-Fe (Ball Milling).
C.14 Particle Size Distribution of Hybrid Ultramicroporous Materials

Figure C108. Particle size distribution plot of SIFSIX-3-Zn (Ball Milling).

Figure C109. Particles around the mean length of SIFSIX-3-Zn (Ball Milling).
Figure C110. Particle size distribution plot of TIFSIX-3-Zn (Ball Milling).

Figure C111. Particles around the mean length of TIFSIX-3-Zn (Ball Milling).
Figure C112. Particle size distribution plot of NbOFFIVE-1-Zn (Ball Milling).

Figure C113. Particles around the mean length of NbOFFIVE-1-Zn (Ball Milling).
Figure C114. Particle size distribution plot of SIFSIX-3-Ni (Ball Milling).

Figure C115. Particles around the mean length of SIFSIX-3-Ni (Ball Milling).
Figure C116. Particle size distribution plot of TIFSIX-3-Ni (Ball Milling).

Figure C117. Particles around the mean length of TIFSIX-3-Ni (Ball Milling).
Figure C118. Particle size distribution plot of NbOFFIVE-1-Ni (Ball Milling).

Figure C119. Particles around the mean length of NbOFFIVE-1-Ni (Ball Milling).
Figure C120. Particle size distribution plot of SIFSIX-3-Co (Ball Milling).

Figure C121. Particles around the mean length of SIFSIX-3-Co (Ball Milling)
Figure C122. Particle size distribution plot of TIFSIX-3-Co (Ball Milling).

Figure C123. Particles around the mean length of TIFSIX-3-Co (Ball Milling).
Figure C124. Particle size distribution plot of NbOFFIVE-1-Co (Ball Milling).

Figure C125. Particles around the mean length of NbOFFIVE-1-Co (Ball Milling).
Figure C126. Particle size distribution plot of SIFSIX-3-Fe (Ball Milling).

Figure C127. Particles around the mean length of SIFSIX-3-Fe (Ball Milling).
C.15 Particle Size Distribution Data of Hybrid Ultrimicroporous Materials

Table C1. Particle size distribution data for HUMs.

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<th>Length minimum (µm)</th>
<th>Length Maximum (µm)</th>
<th>Length STDV (µm)</th>
<th>Length RSD (%)</th>
<th>Length D[3,2] (µm)</th>
<th>Length D[4,2] (µm)</th>
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C.16 Unit Cell Refinement of Hybrid Ultramicroporous Materials

Unit Cell refinement for TIFSIX-3-Zn.

Laboratory powder X-ray diffractograms were collected between 4.01313 < 2θ < 40.00587 with a stepsize of 0.0262601 on PANalytical Empyrean X-ray diffractometer in continuous Bragg-Brentano geometry with a Cu Kα radiation source (40 kV, 40 mA, Empyrean Cu long fine focus high resolution tube) and PIXcel 3D detector.

All analysis of diffractograms was carried out in GSAS-II. Profile fitting was carried out using the full range of diffraction data and a background was fitted to each diffractogram. Lattice Parameter calculations indicated that all structures best corresponded to primitive tetragonal systems. The LeBail method was used to refine the lattice parameters of each structure.

Figure C128. Diffractograms for the unit cell refinement of TIFSIX-3-Zn.
Table C2. Crystallographic data for TIFSIX-3-Zn

<table>
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Unit Cell refinement for NbOFFIVE-3-Zn.

Laboratory powder X-ray diffractograms were collected between $4.01313 < 2\theta < 40.00587$ with a stepsize of 0.0262601 on PANalytical Empyrean X-ray diffractometer in continuous Bragg-Brentano geometry with a Cu Kα radiation source (40 kV, 40 mA, Empyrean Cu long fine focus high resolution tube) and PIXcel 3D detector.

All analysis of diffractograms was carried out in GSAS-II. Profile fitting was carried out using the full range of diffraction data and a background was fitted to each diffractogram. Lattice Parameter calculations indicated that all structures best corresponded to primitive tetragonal systems. The LeBail method was used to refine the lattice parameters of each structure.

![Diffractogram image](image)

Figure C129. Diffractograms for the unit cell refinement of NbOFFIVE-3-Zn.

Table C3. Crystallographic data for NbOFFIVE-3-Zn

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Unit Cell refinement for TIFSIX-3-Co.

Laboratory powder X-ray diffractograms were collected between $4.01313 < 2\theta < 40.00587$ with a stepsize of 0.0262601 on PANalytical Empyrean X-ray diffractometer in continuous Bragg-Brentano geometry with a Cu Kα radiation source (40 kV, 40 mA, Empyrean Cu long fine focus high resolution tube) and PIXcel 3D detector.

All analysis of diffractograms was carried out in GSAS-II. Profile fitting was carried out using the full range of diffraction data and a background was fitted to each diffractogram. Lattice Parameter calculations indicated that all structures best corresponded to primitive tetragonal systems. The LeBail method was used to refine the lattice parameters of each structure.

![Figure C130. Diffractograms for the unit cell refinement of TIFSIX-3-Co.](image)

Table C4. Crystallographic data for TIFSIX-3-Co

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<td>Goodness-of-fit</td>
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Unit Cell refinement for NbOFFIVE-3-Co.

Laboratory powder X-ray diffractograms were collected between $4.01313 < 2\theta < 40.00587$ with a stepsize of 0.0262601 on PANalytical Empyrean X-ray diffractometer in continuous Bragg-Brentano geometry with a Cu Kα radiation source (40 kV, 40 mA, Empyrean Cu long fine focus high resolution tube) and PIXcel 3D detector.

All analysis of diffractograms was carried out in GSAS-II. Profile fitting was carried out using the full range of diffraction data and a background was fitted to each diffractogram. Lattice Parameter calculations indicated that all structures best corresponded to primitive tetragonal systems. The LeBail method was used to refine the lattice parameters of each structure.

![Diffractograms for the unit cell refinement of NbOFFIVE-3-Co.](image)

Figure C131. Diffractograms for the unit cell refinement of NbOFFIVE-3-Co.

<table>
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<td>Goodness-of-fit</td>
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</table>
C.17 References


Appendix D: Supplementary Data for Chapter Five

Solvents and reagents with the exception of 1,2-bis(4-pyridyl)acetylene (dpa) were purchased from chemical suppliers and used without further purification. Methanol (ACS Reagent Grade > 99%), Ethanol (ACS Reagent Grade 96%), Acetonitrile (HPLC Grade, > 99.7%) and N,N’-Dimethylformamide (HPLC Grade, > 99.7%) were purchased from Sigma Aldrich.

D.1 Synthesis of Sorbents

Preparation of \{[\text{Cu(pyrazine)}_2\text{(SiF}_6\text{)}]_n\} (SIFSIX-3-Cu). The compound SIFSIX-3-Cu was synthesized and activated using a modified synthesis from previous reports.\(^1\) A hot methanol solution (10 mL) of pyrazine (2 mmol) was slowly added into a hot methanol solution (10 mL) of CuSiF\(_6\)•H\(_2\)O (1 mmol). The blue precipitate immmoderately was obtained and suspended in the solution. After stirring this mixture for 1 minute, SIFSIX-3-Cu was harvested by direct filtration. Attention: longer stirring time will introduce more impurity. The sample was then dried in the air and degassed under high vacuum at 50 °C for 12 hours before use for sorption experiments.

Preparation of \{[\text{Cu(dpa)}_2\text{(SiF}_6\text{)}]_n\} (SIFSIX-2-Cu-i). The compound SIFSIX-2-Cu-i was synthesized and activated using a modified synthesis from previous reports.\(^2\) dpa (150 mg, 0.833mmol) was dissolved in 20 mL of acetonitrile and added dropwise to a stirring aqueous solution of Cu(NO\(_3\))\(_2\) (100 mg, 0.416mmol) and (NH\(_4\))\(_2\)SiF\(_6\) (78 mg, 0.416mmol) and the resulting solution was left stirring overnight. Following the reaction, SIFSIX-2-Cu-i was obtained by filtration and washed with acetonitrile. Fine powder obtained after washing was soaked in acetonitrile and the solvent was exchanged twice a day for three days before the SIFSIX-2-Cu-i sample was used for sorption experiments. Activation of SIFSIX-2-Cu-i
was achieved by degassing the acetonitrile-exchanged sample on a SmartVacPrep™ using dynamic vacuum for 36 hours.

Preparation of $\{[\text{Ni}(\text{apy})_2(\text{Cr}_2\text{O}_7)]\}_a$ (DICRO-3-Ni-i). The compound DICRO-3-Ni-i was synthesized and activated using a previous reported method.³ K$_2$Cr$_2$O$_7$ (294 mg, 1.0 mmol) and Ni(NO$_3$)$_2$·xH$_2$O (1.0 mmol, 291 mg) were dissolved in 20 mL of water and stirred at room temperature. Separately, 4,4′-azopyridine (368 mg, 2.0 mmol) was dissolved in 20 mL of acetonitrile. To the stirring aqueous solution of Ni(NO$_3$)$_2$ and K$_2$Cr$_2$O$_7$, the 4,4′-azopyridine solution in acetonitrile was added dropwise, to form an immediate precipitate. The product was left stirring overnight, after which time it was removed from stirring and the mother liquor exchanged with fresh acetonitrile twice a day until the solution became clear. Fine powder obtained by filtration was activated by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heat (373K) for 12 hours.

Preparation of $\{[\text{Ni}(\text{bpe})_2(\text{MoO}_4)]\}_a$ (MOOFOUR-1-Ni). The compound MOOFOUR-1-Ni was synthesized and activated using a previous reported method.⁴ 3 mL of acetonitrile and water (v/v = 1:2) was carefully layered over an aqueous solution (3 mL) of NiCl$_2$·6H$_2$O (19.0 mg, 0.08 mmol) and Na$_2$MoO$_4$·2H$_2$O (19.4 mg, 0.08 mmol) in a long thin test tube. 1,2-bis(4-pyridyl)ethene (bpe) (18.2 mg, 0.1 mmol) in 3 mL of acetonitrile and water (v/v = 2:1) was slowly layered over the buffer layer. The tube was sealed and left undisturbed at room temperature. After 3 days light green block-shaped crystals were isolated from the buffer layer. The obtained crystals was soaked in acetonitrile and the solvent was exchanged twice a day for three days before the MOOFOUR-1-Ni sample was used for sorption experiments. Activation of MOOFOUR-1-Ni was achieved by degassing the acetonitrile-exchanged sample on a SmartVacPrep™ using dynamic vacuum and heat (333K) for 12 hours.
Preparation of $\{[\text{Ni}_9(\mu-\text{H}_2\text{O})_4(\text{H}_2\text{O})_2(\text{C}_6\text{NH}_4\text{O}_2)_{18}]\}_n$ (Ni-4-PyC). The compound Ni-4-PyC was synthesized and activated using a previous reported method.$^5$ NiCO$_3$ (0.119 g; 1 mmol) and pyridine-4-carboxylic acid (0.244 g; 2 mmol) were added in a solution containing 1.5 ml of tetrahydrofuran (THF) + 2.5 ml of water + 2 ml of methanol and heated in a teflon-lined steel bomb at 150 °C for 3 days. A bright blue–coloured polycrystalline product was isolated by filtration and was washed with plenty of water and methanol. The sample was soaked in methanol and solvent exchange was carried out twice a day for three days before the Ni-4-PyC sample was used for sorption experiments. Activation of Ni-4-PyC was achieved by degassing the methanol-exchanged sample on a SmartVacPrep™ using dynamic vacuum and heat (373K) for 24 hours.

Preparation of $\{[\text{Zn(MeIM)}_2]\}_n$ (ZIF-8). The compound ZIF-8 was synthesized and activated using a previous reported method.$^6$ A mixture of Zn(NO$_3$)$_2$·6H$_2$O (0.210 g, 0.803 mmol) and 2-methylimidazole (H-MeIM) (0.060 g, 0.731 mmol) was dissolved in 18 ml of DMF and heated in a teflon-lined steel bomb at 140 °C for 24 hours. After cooling and removal of mother liquor from the mixture, chloroform (20 ml) was added to the vial. Colourless polyhedral crystals were collected from the upper layer, washed with DMF (10 ml) and soaked in methanol. The solvent was exchanged twice a day for three days before the ZIF-8 sample was used for sorption experiments. Activation of ZIF-8 was achieved by degassing the methanol exchanged sample on a SmartVacPrep™ using dynamic vacuum and heat (573K) for 6 hours.

Preparation of $\{[\text{Zn}_2(\text{bdc})_2(\text{dabco})]\}_n$ (DMOF-1). The compound DMOF-1 was synthesized and activated using a previous reported method.$^7$ A mixture of Zn(NO$_3$)$_2$·6H$_2$O (1.0 g, 3.36 mmol), H$_2$bdc (0.560 g, 3.37 mmol), and dabco (0.187 g, 1.67 mmol) was suspended in DMF (40 mL) and heated in a teflon-lined steel bomb at 120 °C for 2 days. The colourless crystalline precipitate formed was collected, washed with DMF and soaked in
methanol. The solvent was exchanged twice a day for three days before the DMOF-1 sample was used for sorption experiments. Activation of DMOF-1 was achieved by degassing the methanol-exchanged sample on a SmartVacPrep™ using dynamic vacuum and heat (403K) for 24 hours.

**Preparation of \{[Cr₃(O)F(bdc)₃(H₂O)₂]ₙ\} (MIL-101(Cr)).** The compound MIL-101 was synthesized and activated using a synthesis method from previous report.⁸ A solution containing Cr(NO₃)₃·9H₂O (400 mg, 1.0 mmol), HF acid (1.0 mmol) and benzene-1,4-dicarboxylic acid H₂bdc (164 mg, 1.0 mmol) in 5 mL H₂O was transferred to the Teflon vessel and heated for 8 hours at 220 °C. The solution was cooled gradually to room temperature at a rate of 30 °C /hour. Following the reaction, the contents of the autoclave was transferred to two centrifuge tubes and the supernatant solution was carefully removed after centrifugation. Water (5 mL) was added in each tube and the solid was evenly dispersed in the aqueous phase. After renewed centrifugation and removal of the supernatant solution, DMF (5 mL) was added to each tube which was placed in a hot (80 °C) ultrasonic bath and sonicated for 1 hour. Centrifugation was again used to separate MIL-101 and DMF. The precipitate was transferred in a 25 mL beaker where it was stirred with 10 mL of water at 70 °C for 5 hour. After separation by centrifugation, the same washing procedure but using ethanol was repeated once more at the same temperature. Final product was obtained by centrifugation and activation of MIL-101 was achieved by degassing the sample on a SmartVacPrep™ using dynamic vacuum and heat (120 °C) for 12 hours.

**Preparation of \{[Zr₆O₄(OH)₄(CO₂)₁₂]ₙ\} (UiO-66).** The compound UiO-66 was synthesized and activated using a synthesis method from previous report.⁹ It was synthesized by dissolving ZrCl₄ (0.053 g, 0.227 mmol) and 1,4-benzenedicarboxylic acid (H₂BDC) (0.034 g, 0.227 mmol) in N,N′-dimethylformamide (DMF) (24.9 g, 340 mmol) at room temperature. The thus obtained mixture was sealed in a Teflon vessel and placed in a
pre-heated oven at 120 °C for 24 hours. Crystallization was carried out under static conditions. After cooling in air to room temperature the resulting solid was filtered, repeatedly washed with DMF and dried at room temperature. The obtained UiO-66 was soaked in acetonitrile and the solvent was exchanged twice a day for three days before the UiO-66 sample was used for sorption experiments. Activation of UiO-66 was achieved by degassing the acetonitrile-exchanged sample on a SmartVacPrep™ using dynamic vacuum and heat (150 °C) for 36 hours.

Preparation of UiO-66-NH₂. The compound UiO-66-NH₂ was synthesized and activated using a synthesis method from previous report.¹⁰ A standard up scaled synthesis of UiO-66-NH₂ was performed by dissolving ZrCl₄ (1.50 g, 6.4 mmol) and 2-amino-1, 4-benzenedicarboxylic acid (H₂N-H₂BDC) (1.56 g, 6.4 mmol) in DMF (180 mL) at room temperature in a volumetric flask. The resulting mixture was placed in a preheated oven at 80 °C for 12 hours and then held at 100 °C for 24 hours. After the solution was cooled to room temperature in air, the resulting solid was filtered and repeatedly washed with absolute ethanol for 3 days while heated at 60 °C in a water bath. The resulting yellow powder was filtered, transferred to a Schlenk flask, and dried under vacuum at ambient temperature. Activation of UiO-66 was achieved by degassing the acetonitrile-exchanged sample on a SmartVacPrep™ using dynamic vacuum and heat (150 °C) for 36 hours.

D.2 Experimental Section

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction experiments were carried out using a PANalytical Empyrean™ diffractometer equipped with a PIXcel3D detector operating in scanning line detector mode with an active length of 4 utilizing 255 channels. The diffractometer is outfitted with an Empyrean Cu LFF (long fine-focus) HR (9430 033 7310x) tube operated at 40 kV and 40 mA and Cu K-alpha radiation (λα = 1.540598 Å) was used for diffraction experiments. Experiments were conducted in
continuous scanning mode with the goniometer in the theta-theta orientation. Incident beam optics included the Fixed Divergences slit with anti-scatter slit PreFIX module, with a 1/8° divergence slit and a 1/4° anti-scatter slit, as well as a 10 mm fixed incident beam mask and a Soller slit (0.04 rad). Divergent beam optics included a P7.5 anti-scatter slit, a Soller slit (0.04 rad), and a Ni β filter. The samples were typically dry and ground into a fine powder, applied to a low background sample holder and mounted to a bracket flat sample stage. In a typical experiment, data was collected via a continuous scan in the range of 5°-45° (2θ) with a step-size of 0.02626° and a scan time of 29 seconds per step. Raw data was then evaluated using the X’PertHighScore Plus™ software V 4.1 (PANalytical, The Netherlands). Plots of stacked PXRD spectra for each adsorbent displaying patterns for calculated, as synthesized, solvent exchanged, and after sorption analysis are provided below (Figure D3 – D12). Additional plots of stacked PXRD spectra displaying patterns for calculated, pristine sample, and post-humidity chamber exposure (after 1 day, 7 days, and 14 days) are provided for each sorbent.

**TGA-Temperature-Programmed Desorption (TPD) Studies.** TGA-TPD studies were carried out on a gas mixing rig coupled independently with a TGA instrument TA Q50 V20.13 Build 39 and mass spectrometer (MS) Agilent 5975 MSD, see Figure D1. In a typical TGA uptake test the given sample was activated by heating to a desired temperature under a 60 ml/min flow of nitrogen gas. This was then cooled to 30 °C before the chosen gas mixture was introduced to the sample. A mass flow controller was used to control the gas ratios for each test while moisture was introduced by passing the pre-mixed gas through a gas bubbler containing water. The weight increase for each solid was monitored until the weight began to plateau. The exposure time and gas flow conditions were then noted and subsequently applied to samples during TPD studies to analyse the composition of the adsorbed species during the desorption cycle.
TPD tests were carried out using a custom-made fixed-bed flow system. The system consists of a gas delivery system, a reactor housed in a furnace and a mass spectrometer detection system. There are two aims to this testing; to determine the CO$_2$ adsorbed by the sorbents; to examine the temperatures at which the CO$_2$ desorption occurs. Both of these parameters will be investigated using CO$_2$ TPD profiles. In a typical CO$_2$ TPD cycle, the sorbent is placed in a quartz tubular reactor. The sample is fixed in the reactor using quartz wool. Helium is then passed through the reactor at room temperature until a constant signal is observed using an Agilent 5975 MSD mass spectrometer (MS). The temperature is then increased at a rate of 10 °C/min to an appropriate temperature to remove impurities in the sample. The sample is then cooled to 30 °C. A gas mixture is then introduced to the sorbent for the required length of time. When the required adsorption parameters have been achieved, the gas flow is switched to nitrogen gas until the carbon dioxide concentrations are returned to background levels. The carrier gas is then switched to helium and heated to the required temperature at a rate of 10 °C/min in a flow of helium. The gas composition leaving the reactor is continuously monitored by MS for the identity and quantity of each component of the desorbed gas. Helium is used as a carrier gas as this is not detected by the MS, ensuring that all desorbed species from the adsorbents are detected.

During a direct air capture (DAC) test, a sample is activated under vacuum as per the conditions previously outlined. This sample is then exposed to the laboratory environment for 24 hours. The sample is then analyzed using TPD studies to analyze the composition of the exhaust gas from the sorbent.

For calibration, a gas syringe (Valco precision sampling syringe, 2 ml, from Aldrich) was used to introduce pure CO$_2$, taken directly from a gas cylinder, into the system. Known volumes of CO$_2$ gas, between 0.2 ml and 5 ml, were injected at a location before the reactor which contained several grams of adsorbent material. The gas flows were continuously
monitored using the Agilent 5975 MS. The MS allowed the operator to monitor specific ions continuously throughout the run cycle as well as retrieve complete mass spectra of ions over 12 hours for any given time during a test. The material adsorbed all the injected CO\textsubscript{2}. Helium gas was allowed to flow through the sample for a further 10 minutes to ensure all the injected CO\textsubscript{2} was adsorbed. If no CO\textsubscript{2} was detected by the MS, the sample was then heated to 200°C at 10°C/min while continuously monitoring the level of the desorbed CO\textsubscript{2}. The area of the subsequent CO\textsubscript{2} desorption peak was used as a measure of the known volume of injected CO\textsubscript{2}. This was repeated several times with different volumes of CO\textsubscript{2} gas. The peak areas associated with the different volumes of injected CO\textsubscript{2} were then used to determine the mass of CO\textsubscript{2} adsorbed in milligrams using the ideal gas law. The culmination of these injections was used to generate a calibration graph seen in Figure D2. This graph was used to calculate the amount of CO\textsubscript{2} desorbed during a typical TPD run. The H\textsubscript{2}O uptake was determined from the overall weight loss/gain observed during gravimetric analysis.

**Gas Sorption Measurements.** Ultra-high-purity grade N\textsubscript{2} and CO\textsubscript{2} were used for adsorption experiments. Low-pressure N\textsubscript{2} adsorption measurements (up to 1 bar) were performed on Micromeritics TriStar II PLUS and Micromeritics 3 Flex surface area and pore size analyzer. About 200 mg of activated samples were used for the measurements. BET surface areas for were determined from the N\textsubscript{2} adsorption isotherms collected at 77 K by applying the Brunauer-Emmett-Teller (BET) model.
D.3 Scheme of Thermogravimetric-Temperature-Programmed Desorption

Figure D1. Schematic of gas mixing system, TGA uptake analysis and TPD analysis units.

Figure D2. CO₂ calibration graph.
D.4 Powder X-Ray Diffraction of Sorbents

Figure D3. PXRD of pristine SIFSIX-3-Cu.

Figure D4. PXRD of pristine SIFSIX-2-Cu-i.
Figure D5. PXRD of pristine DICRO-3-Ni-i.

Figure D6. PXRD of pristine MOOFOUR-1-Ni.
Figure D7. PXRD of pristine Ni-4-PyC.

Figure D8. PXRD of pristine ZIF-8.
Figure D9. PXRD of pristine DMOF-1.

Figure D10. PXRD of pristine MIL-101.
Figure D11. PXRD of pristine UiO-66.

Figure D12. PXRD of pristine UiO-66-NH$_2$.  

D.5 Sorption Isotherms of Sorbents

Figure D13. CO$_2$ sorption isotherm on pristine SIFSIX-3-Cu.

Figure D14. CO$_2$ and N$_2$ sorption isotherms on pristine SIFSIX-2-Cu-i.
Figure D15. CO$_2$ and N$_2$ sorption isotherms on pristine DICRO-3-Ni-i.

Figure D16. CO$_2$ sorption isotherms on pristine MOOFOUR-1-Ni.
Figure D17. CO$_2$ and N$_2$ sorption isotherms on pristine Ni-4-PyC.

Figure D18. CO$_2$ and N$_2$ sorption isotherms on pristine ZIF-8.
Figure D19. CO$_2$ and N$_2$ sorption isotherms on pristine DMOF-1.

Figure D20. CO$_2$ and N$_2$ sorption isotherms on pristine MIL-101.
Figure D21. CO$_2$ and N$_2$ sorption isotherms on pristine UiO-66.

Figure D22. CO$_2$ and N$_2$ sorption isotherms on pristine UiO-66-NH$_2$. 
D.6 Temperature-Programmed Desorption Analysis of Sorbents

TGA-TPD analysis for SIFSIX-3-Cu.

Figure D23. TPD profiles and composition for SIFSIX-3-Cu DAC test.

Figure D24. Dry 1.0 atm CO₂ uptake test using TGA for SIFSIX-3-Cu.
Figure D25. Moist 0.15 atm CO$_2$ uptake test using TGA for SIFSIX-3-Cu.

Figure D26. TPD profiles and composition for SIFSIX-3-Cu moist 0.15 atm CO$_2$ test.
Figure D27. Dry 0.15 atm CO$_2$ uptake test using TGA for SIFSIX-3-Cu.
TGA-TPD analysis for SIFSIX-2-Cu-i.

Figure D28. TPD profiles and composition for SIFSIX-2-Cu-i DAC test.

Figure D29. Moist N₂ uptake test using TGA for SIFSIX-2-Cu-i.
Figure D30. Moist 1.0 atm CO₂ uptake test using TGA for SIFSIX-2-Cu-i.

Figure D31. TPD profiles and composition for SIFSIX-2-Cu-i moist 1.0 atm CO₂ test.

- 32.7 mg CO₂ g⁻¹
- ~85% CO₂
- ~15% H₂O
Figure D32. Dry 1.0 atm CO$_2$ uptake test using TGA for SIFSIX-$2$-Cu-$i$.

Figure D33. Moist 0.15 atm CO$_2$ uptake test using TGA for SIFSIX-2-Cu-i.
Figure D34. TPD profiles and composition for SIFSIX-2-Cu-i moist 0.15 atm CO₂ test.

Figure D35. Dry 0.15 atm CO₂ uptake test using TGA for SIFSIX-2-Cu-i.
TGA-TPD analysis for DICRO-3-Ni-i.

Figure D36. TPD profiles and composition for DICRO-3-Ni-i DAC test.

- 1.9 mg CO$_2$ g$^{-1}$
- ~2% CO$_2$
- ~97% H$_2$O

Figure D37. Moist N$_2$ uptake test using TGA for DICRO-3-Ni-i.

- 16.3 mg H$_2$O g$^{-1}$
- 100% H$_2$O
Figure D38. Moist 1.0 atm CO$_2$ uptake test using TGA for DICRO-3-Ni-i.

Figure D39. TPD profiles and composition for DICRO-3-Ni-i moist 1.0 atm CO$_2$ test.

- 37.3 mg CO$_2$ g$^{-1}$
- ~76.3% CO$_2$
- ~23.7% H$_2$O
Figure D40. Dry 1.0 atm CO₂ uptake test using TGA for DICRO-3-Ni-i.

Figure D41. Moist 0.15 atm CO₂ uptake test using TGA for DICRO-3-Ni-i.
Figure D42. TPD profiles and composition for DICRO-3-Ni-i moist 0.15 atm CO₂ test.

Figure D43. Dry 0.15 atm CO₂ uptake test using TGA for DICRO-3-Ni-i.

- 19.2 mg CO₂ g⁻¹
- ~52.7% CO₂
- ~47.3% H₂O
TGA-TPD analysis for MOOFOUR-1-Ni.

Figure D44. TPD profiles and composition for MOOFOUR-1-Ni DAC test.

- 2.5 mg CO$_2$ g$^{-1}$
- ~5% CO$_2$
- ~95% H$_2$O

Figure D45. Moist N$_2$ uptake test using TGA for MOOFOUR-1-Ni.

- 65 mg H$_2$O g$^{-1}$
- 100% H$_2$O
Figure D46. Moist 1.0 atm CO$_2$ uptake test using TGA for MOOFOUR-1-Ni.

Figure D47. TPD profiles and composition for MOOFOUR-1-Ni moist 1.0 atm CO$_2$ test.

- 78.3 mg CO$_2$ g$^{-1}$
- ~89% CO$_2$
- ~11% H$_2$O
Figure D48. Dry 1.0 atm CO$_2$ uptake test using TGA for MOOFOUR-1-Ni.

Figure D49. Moist 0.15 atm CO$_2$ uptake test using TGA for MOOFOUR-1-Ni.
Figure D50. TPD profiles and composition for MOOFOUR-1-Ni moist 0.15 atm CO₂ test.

- 39 mg CO₂ g⁻¹
- ~60% CO₂
- ~40% H₂O

Figure D51. Dry 0.15 atm CO₂ uptake test using TGA for MOOFOUR-1-Ni.

- 58 mg CO₂ g⁻¹
- 100% CO₂
TGA-TPD analysis for Ni-4-PyC.

Figure D52. TPD profiles and composition for Ni-4-PyC DAC test.

Figure D53. Moist N\textsubscript{2} uptake test using TGA for Ni-4-PyC.
Figure D54. Moist 1.0 atm CO$_2$ uptake test using TGA for Ni-4-PyC.

Figure D55. TPD profiles and composition for Ni-4-PyC moist 1.0 atm CO$_2$ test.

- 28.0 mg CO$_2$ g$^{-1}$
- $\sim$68% CO$_2$
- $\sim$32% H$_2$O
Figure D56. Dry 1.0 atm CO₂ uptake test using TGA for Ni-4-PyC.

- 36.3 mg CO₂ g⁻¹
- 100% CO₂

Figure D57. Moist 0.15 atm CO₂ uptake test using TGA for Ni-4-PyC.
Figure D58. TPD profiles and composition for Ni-4-PyC moist 0.15 atm CO\textsubscript{2} test.

- 15.6 mg CO\textsubscript{2} g\textsuperscript{-1}
- \textasciitilde 61% CO\textsubscript{2}
- \textasciitilde 39% H\textsubscript{2}O

Figure D59. Dry 0.15 atm CO\textsubscript{2} uptake test using TGA for Ni-4-PyC.

- 26 mg CO\textsubscript{2} g\textsuperscript{-1}
- 100% CO\textsubscript{2}
TGA-TPD analysis for DMOF-1.

Figure D60. TPD profiles and composition for DMOF-1 DAC test.

- 1.3 mg CO\textsubscript{2} g\textsuperscript{-1}
- \sim 2\% CO\textsubscript{2}
- \sim 98\% H\textsubscript{2}O

Figure D61. Moist N\textsubscript{2} uptake test using TGA for DMOF-1.

- 51.6 mg H\textsubscript{2}O g\textsuperscript{-1}
- 100\% H\textsubscript{2}O
Figure D62. Moist 1.0 atm CO$_2$ uptake test using TGA for DMOF-1.

Figure D63. TPD profiles and composition for DMOF-1 moist 1.0 atm CO$_2$ test.

- 19.4 mg CO$_2$ g$^{-1}$
- $\sim$67% CO$_2$
- $\sim$33% H$_2$O
Figure D64. Dry 1.0 atm CO\textsubscript{2} uptake test using TGA for DMOF-1.

Figure D65. Moist 0.15 atm CO\textsubscript{2} uptake test using TGA for DMOF-1.
Figure D66. TPD profiles and composition for DMOF-1 moist 0.15 atm CO$_2$ test.

- 9.7 mg CO$_2$ g$^{-1}$
- ~56% CO$_2$
- ~44% H$_2$O

Figure D67. Dry 0.15 atm CO$_2$ uptake test using TGA for DMOF-1.

- 17.3 mg CO$_2$ g$^{-1}$
- 100% CO$_2$
TGA-TPD analysis for ZIF-8.

Figure D68. TPD profiles and composition for ZIF-8 DAC test.

- 2.3 mg CO₂ g⁻¹
- ~23% CO₂
- ~77% H₂O

Figure D69. Moist N₂ uptake test using TGA for ZIF-8.

- 1 mg H₂O g⁻¹
- 100% H₂O
Figure D70. Moist 1.0 atm CO$_2$ uptake test using TGA for ZIF-8.

Figure D71. TPD profiles and composition for ZIF-8 moist 1.0 atm CO$_2$ test.
Figure D72. Dry 1.0 atm CO$_2$ uptake test using TGA for ZIF-8.

Figure D73. Moist 0.15 atm CO$_2$ uptake test using TGA for ZIF-8.
Figure D74. TPD profiles and composition for ZIF-8 moist 0.15 atm CO\(_2\) test.

- $3 \text{ mg CO}_2 \text{ g}^{-1}$
- $\sim 75\% \text{ CO}_2$
- $\sim 25\% \text{ H}_2\text{O}$

Figure D75. Dry 0.15 atm CO\(_2\) uptake test using TGA for ZIF-8.

- $1.8 \text{ mg CO}_2 \text{ g}^{-1}$
- $100\% \text{ CO}_2$

Figure D76. TPD profiles and composition for MIL-101 DAC test.

- 1.0 mg CO$_2$ g$^{-1}$
- $\sim$1% CO$_2$
- $\sim$99% H$_2$O

Figure D77. Moist N$_2$ uptake test using TGA for MIL-101.

- 33 mg H$_2$O g$^{-1}$
- 100% H$_2$O

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Figure D78. Moist 1.0 atm CO$_2$ uptake test using TGA for MIL-101.

Figure D79. TPD profiles and composition for MIL-101 moist 1.0 atm CO$_2$ test.

- 17.2mg CO$_2$ g$^{-1}$
- $\sim$41% CO$_2$
- $\sim$59% H$_2$O
Figure D80. Dry 1.0 atm CO₂ uptake test using TGA for MIL-101.

Figure D81. Moist 0.15 atm CO₂ uptake test using TGA for MIL-101.
Figure D82. TPD profiles and composition for MIL-101 moist 0.15 atm CO\textsubscript{2} test.

- 15.8 mg CO\textsubscript{2} g\textsuperscript{-1}
- \(~40\%\) CO\textsubscript{2}
- \(~60\%\) H\textsubscript{2}O

Figure D83. Dry 0.15 atm CO\textsubscript{2} uptake test using TGA for MIL-101.

- 33.1 mg CO\textsubscript{2} g\textsuperscript{-1}
- 100\% CO\textsubscript{2}
TGA-TPD analysis for UiO-66.

Figure D84. TPD profiles and composition for UiO-66 DAC test.

- 1.0 mg CO$_2$ g$^{-1}$
- ~1% CO$_2$
- ~99% H$_2$O

Figure D85. Moist N$_2$ uptake test using TGA for UiO-66.

- 50.1 mg H$_2$O g$^{-1}$
- 100% H$_2$O
Figure D86. Moist 1.0 atm CO$_2$ uptake test using TGA for UiO-66.

Figure D87. TPD profiles and composition for UiO-66 moist 1.0 atm CO$_2$ test.

- 20 mg CO$_2$ g$^{-1}$
- $\sim$57% CO$_2$
- $\sim$43% H$_2$O
Figure D88. Dry 1.0 atm CO$_2$ uptake test using TGA for UiO-66.

Figure D89. Moist 0.15 atm CO$_2$ uptake test using TGA for UiO-66.
Figure D90. TPD profiles and composition for UiO-66 moist 0.15 atm CO$_2$ test.

- 8.4 mg CO$_2$ g$^{-1}$
- ~29.6% CO$_2$
- ~70.4% H$_2$O

Figure D91. Dry 0.15 atm CO$_2$ uptake test using TGA for UiO-66.

- 31.8 mg CO$_2$ g$^{-1}$
- 100% CO$_2$
TGA-TPD analysis for UiO-66-NH$_2$.

Figure D92. TPD profiles and composition for UiO-66-NH$_2$ DAC test.

Figure D93. Moist N$_2$ uptake test using TGA for UiO-66-NH$_2$. 

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Figure D94. Moist 1.0 atm CO\textsubscript{2} uptake test using TGA for UiO-66-NH\textsubscript{2}.

Figure D95. TPD profiles and composition for UiO-66-NH\textsubscript{2} moist 1.0 atm CO\textsubscript{2} test.

- 54 mg CO\textsubscript{2} g\textsuperscript{-1}
- ~51% CO\textsubscript{2}
- ~49% H\textsubscript{2}O
Figure D96. Dry 1.0 atm CO$_2$ uptake test using TGA for UiO-66-NH$_2$.

Figure D97. Moist 0.15 atm CO$_2$ uptake test using TGA for UiO-66-NH$_2$. 
Figure D98. TPD profiles and composition for UiO-66-NH₂ moist 0.15 atm CO₂ test.

- 51.3 mg CO₂ g⁻¹
- ~46.7% CO₂
- ~53.3% H₂O

Figure D99. Dry 0.15 atm CO₂ uptake test using TGA for UiO-66-NH₂.

- 59 mg CO₂ g⁻¹
- 100% CO₂
D.7 Accelerated Stability Test of SIFSIX-3-Cu

Figure D100. Powder X-ray diffraction patterns for SIFSIX-3-Cu after 1 day accelerated stability testing (40 °C, 75% RH) compared with TPD studies sample.

Figure D101. % of pristine materials surface area after accelerated stability (40 °C, 75% RH) for SIFSIX-3-Cu compared with SIFSIX-3-Ni and Zeolite 13X.
D.8 Lab Temperature and Relative Humidity During Direct Air Capture Experiment

Figure D102. Lab temperature and relative humidity during DAC experiment.
D.9 References


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