Design and Optimization of CO$_2$ sorbents for Point Source Emissions and Direct Air Capture

RIBOOGA CHANG

This thesis presents a comprehensive study on the design and optimization of CO₂ sorbents, targeting two distinct applications: CO₂ capture from point source emissions and Direct Air Capture (DAC). The research first introduces Na₂HfO₃ as a potential CO₂ sorbent for point source emissions, using the molten salt effects of Na₂CO₃ and the thermal stability of HfO₂. This combination results in a CO₂ sorbent with impressive thermal and cyclic stability, through various optimization steps to enhance CO₂ capture performance and efficiency. The study then shows into the structural disorder in Na₂ZrO₃, a chemically similar CO₂ sorbent. This investigation fills a knowledge gap, offering new insights into the sorbent's behavior in CO₂ capture. For DAC applications, the thesis explores the design of inorganic anion pillared metal-organic frameworks, focusing on the adjustment of M⁵⁺−F⁻ bond lengths in inorganic anion pillars within M⁵⁺OFFIVE-1-Ni samples. These structural modifications impact the CO₂ capture properties, particularly in terms of capacity and kinetics, demonstrating the potential of structural tuning in enhancing sorbent effectiveness. The synthesized samples exhibit good cyclic and water stability, suggesting their potential for practical DAC applications.

Keywords: CCS, CO₂ Sorbents, Direct Air Capture

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The author also contributed to the following published works which are not included in this thesis:


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Abbreviations

Al₂O₃    Aluminium oxide
CaCO₃   Calcium carbonate
CaO      Calcium oxide
CCS   Carbon capture and storage
CH₄      Methane
CO₂   Carbon dioxide
DAC   Direct air capture
DEA   Diethanolamine
GWP   Global warming potential
H₂     Hydrogen
HFCs   Hydrofluorocarbons
HfO₂   Hafnium oxide
HUMs   Hybrid ultramicroporous materials
MEA   Monoethanolamine
MOFs   Metal-organic frameworks
N₂     Nitrogen
N₂O   Nitrous oxide
Na₂HfO₃  Sodium hafnium oxide
Na₂ZrO₃  Sodium zirconium oxide
O₂     Oxygen
PFCs  Perfluorocarbons
PSD  Pore size distribution
PXRD  Powder X-ray diffraction
SEM  Scanning electron microscopy
SF₆   Sulfur hexafluoride
SSA  Specific surface area
TEM  Transmission electron microscopy
VdW  van der Waals forces
XPS  X-ray photoelectron spectroscopy
ZrO₂  Zirconium oxide
1. Introduction

1.1. Climate change and greenhouse gases

“Climate change” has emerged as a paramount concern of the current century, demanding fundamental research and practical interventions. Numerous theories suggest various causes of climate change, including natural climate cycles, solar activity, and human activities. However, this thesis is founded on the premise that the rise in greenhouse gases, primarily due to human industrial activities, is a major factor driving the changes observed in our climate.\textsuperscript{1-5}

“Greenhouse gases” are atmospheric constituents that possess the capability to absorb and subsequently re-emit infrared radiation, thereby contributing to the greenhouse effect.\textsuperscript{6} Approximately 50% of the solar radiation penetrates the Earth's atmospheric layers, reaching the surface. Upon absorption, this energy is transmuted into heat or long-wavelength infrared radiation, which is then radiated outward.\textsuperscript{7} A part of this re-emitted radiation is intercepted by clouds and greenhouse gases with a subsequent part being absorbed and re-radiated back to the Earth's surface. Intrinsically, the greenhouse effect is an essential nature mechanism, maintaining terrestrial temperatures at levels conducive for life. However, human activities, notably the combustion of fossil fuels, are elevating the levels of greenhouse gases.\textsuperscript{8, 9} It leads to the trapping of much heat in the atmosphere, resulting in rising global temperatures, a phenomenon recognized as global warming.\textsuperscript{8}

![Figure 1. Simplified illustration of the greenhouse effect.](image-url)
The primary greenhouse gases implicated in this enhanced greenhouse effect include carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆). Each of these gases exhibits a unique global warming potential (GWP), a metric that quantifies their relative impact in inducing global warming when compared to CO₂ (as shown in Table 1).

Table 1. Global warming potential (GWP) of seven different gases.

<table>
<thead>
<tr>
<th>Gases</th>
<th>Global warming potential</th>
<th>Gas emissions [%]</th>
<th>Atmospheric life [year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>1</td>
<td>79.4</td>
<td>Variable</td>
</tr>
<tr>
<td>Methane (CH₄), fossil</td>
<td>28</td>
<td>11.5</td>
<td>12</td>
</tr>
<tr>
<td>Methane (CH₄), biogenic</td>
<td>25.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide (N₂O)</td>
<td>265</td>
<td>6.2</td>
<td>114</td>
</tr>
<tr>
<td>Hydrofluorocarbons (HFCs)</td>
<td>160 to 11,700</td>
<td>3</td>
<td>1.4 to 260</td>
</tr>
<tr>
<td>Perfluorocarbons (PFCs)</td>
<td>6,500 to 9,200</td>
<td>3</td>
<td>10,000 to 50,000</td>
</tr>
<tr>
<td>Sulfur hexafluoride (SF₆)</td>
<td>23,500</td>
<td>3</td>
<td>3,200</td>
</tr>
</tbody>
</table>

As shown in Table 1, CO₂ is the primary focus to reduce due to its pronounced impacts for the global warming in other words, climate change. Despite its relatively modest global warming potential (GWP) in comparison to other greenhouse gases (GHGs), the substantial magnitude of CO₂ emissions underscores its significance in the context of global warming. The sources of CO₂ emissions are multifaceted, predominantly stemming from human activities including transportation, power generation, industrial processes, and infrastructure development. Notably, the combustion and subsequent emission of industrial point sources account for a considerable fraction of CO₂ emissions.

A critical shift from using fossil fuels to adopting renewable energy sources is required in progressing towards a sustainable, low-carbon future. Nevertheless, even in a scenario where renewable energy sources dominate, CO₂ emissions remain indispensable in certain industrial processes, including the cement and steel industries. Consequently, numerous technologies for capturing and storing CO₂ have been suggested and developed, with ongoing researches aimed at optimizing their efficacy.

1.2. Carbon capture and storage (CCS)

“Carbon capture and storage (CCS)” refers a suite of technologies designed to reduce atmospheric emissions by capturing and storing greenhouse gases, mainly CO₂, from various sources. Based on the source of the CO₂ emissions,
CCS approaches can in principle be divided into point source emissions and direct air capture techniques.\textsuperscript{19}

1.2.1 CO\textsubscript{2} capture from point source emissions

CO\textsubscript{2} capture from point sources can be delineated into four distinct processes: (i) capture and separation, (ii) regeneration, (iii) compression, and (iv) transportation.\textsuperscript{20, 21}

(i) Capture and separation: CO\textsubscript{2} capture from point sources aims to remove CO\textsubscript{2} before it is released into the atmosphere. Two primary methods are; Pre-combustion capture and Post-combustion capture for this process.\textsuperscript{22, 23} However, the methods target different stages of the combustion process.

- **Pre-combustion capture**: this method involves capturing CO\textsubscript{2} prior to fuel combustion.\textsuperscript{23} Initially, the fuel undergoes a process known as gasification for solid fuels or reforming for gaseous fuels. This results in the production of a mixture comprising hydrogen (H\textsubscript{2}) and CO\textsubscript{2}, referred to as syngas. The subsequent water-gas shift reaction transforms carbon monoxide (CO) into CO\textsubscript{2}. After this step, CO\textsubscript{2} is isolated, leaving H\textsubscript{2}, which is then combusted to generate electricity. The gas which is subjected to CO\textsubscript{2} separation process predominantly consists of H\textsubscript{2} and CO\textsubscript{2}, with CO\textsubscript{2} often being a major component. Solvents capable of selectively absorbing CO\textsubscript{2} from this high-pressure syngas are typically employed.

- **Post-combustion capture**: this method captures CO\textsubscript{2} after the combustion of fossil fuels. The resulting flue gas, which is emitted post-combustion, predominantly contains nitrogen (N\textsubscript{2}) and CO\textsubscript{2}, complemented by other constituents like water vapor, oxygen (O\textsubscript{2}), and trace amounts of various gases. Hence, effective CO\textsubscript{2} capture (removal) necessitates technologies that can either selectively separate CO\textsubscript{2} from this mixture or sorbents adept at its selective capture.\textsuperscript{24} Widely employed techniques and sorbents encompass amine scrubbing, activated carbon, and metal oxides.\textsuperscript{25} A comprehensive discussion on these sorbents are discussed in Section 1.3.

(ii) Regeneration: after the capture and separation process, the CO\textsubscript{2} captured by a sorbent is released under appropriate conditions, such as increased temperature or pressure (i.e. temperature swing or pressure swing).\textsuperscript{25} Subsequently, the CO\textsubscript{2} sorbent is recycled back into the capture and separation process.

(iii) Compression: once CO\textsubscript{2} is regenerated, it typically remains in a gaseous state and necessitates compression to reduce its volume for efficient transportation and storage feasibility.
(iv) Transportation: compressed CO\textsubscript{2} is then conveyed, primarily via pipelines or alternative transport methods, to designated storage sites.

This thesis mainly focuses on the development of CO\textsubscript{2} sorbents, which are materials used to capture CO\textsubscript{2}. When selecting a suitable sorbent, it is important to consider the specific conditions under which it will be used, including temperature, pressure, and gas composition. Generally, the CO\textsubscript{2} capture mechanism demonstrates higher efficiency under conditions of reduced temperatures and elevated pressures. However, flue gas (600 to 1600 °C) cooling before/in the capture process incurs energy expenses, thereby influencing the efficiency and economic viability of the entire process.\textsuperscript{26} Moreover, re-elevating temperatures for regeneration also implies an energy consumption. Hence, in the development of sorbents for CO\textsubscript{2} capture from point sources, accounting for both the capture and regeneration temperatures, is important. Equally critical is ensuring the stability of the sorbents under the various conditions of the capture and regeneration processes, guaranteeing consistent CO\textsubscript{2} capture capacity throughout multiple capture/regeneration cycles. Currently, one of the challenges is developing these ideal sorbents. A detailed discussion on CO\textsubscript{2} sorbents tailored for CO\textsubscript{2} capture from point source can be found in Section 1.3.

1.2.2 CO\textsubscript{2} capture from air (direct air capture; DAC)

“Direct Air Capture (DAC)” represents an emergent technology which is tailored to remove CO\textsubscript{2} directly from ambient air, rather than from point source emissions such as the cement and steel industries.\textsuperscript{27} The primary goal of DAC is to decrease the elevated atmospheric CO\textsubscript{2} concentrations originating. The operational process of DAC can be described using four different processes: (i) air intake, (ii) capture, (iii) regeneration, and (iv) storage.

(i) Air Intake: since DAC targets to capture CO\textsubscript{2} from the atmosphere, it can be considered a location-independent technology. However, DAC needs to be incorporated in a system which can draw a large volume of ambient air using large fans or blowers since the concentration of CO\textsubscript{2} in the atmosphere is lower (about 0.04%) than the point sources (15%).

(ii) Capture: the drawn air is passed through a filtration system, eliminating contaminants and substances that could potentially decrease the efficacy of the CO\textsubscript{2} capture capacity or deteriorate the performance of the CO\textsubscript{2} sorbent. Various filter types are employed in DAC systems, including particulate, activated carbon, chemical, and CO\textsubscript{2} adsorbent filters.

- Particulate filters: these filters are designed to eliminate particles like dust and pollen, which could clog the system or disrupt the CO\textsubscript{2} capture. Materials commonly used for these filters include fiberglass and polypropylene.
• Activated carbon filters: these filters target contaminants such as volatile organic chemicals (VOCs) due to the large surface area which can adsorb a wide range of contaminants.
• Chemical filters: these filters are tasked with specific contaminants that might impede the capture process, such as sulfur compounds. In order to remove this, materials such as alumina combined with potassium permanganate are frequently employed.
• CO₂ adsorbent filters: these filters are unique as they play a direct role in the CO₂ capture process. Notable materials utilized in these filters are amines-modified silica, metal-organic frameworks (MOFs), zeolites, and etc. Since these sorbents can selectively interact with CO₂, they have the distinctive ability to both filter and concurrently capture CO₂ from the drawn air mixture. This implies that the sorbent can significantly influence the capacity and efficiency of the CO₂ process. Consequently, developing the suitable sorbent is one of the ongoing research topics in DAC technology.

(iii) Regeneration: the bound CO₂ is released under pre-determined conditions, typically involving heat or pressure parameters. As explained in Section 1.2.1, the parameters employed in this step influence the energy expenditure, which, in turn, impacts the operational costs of the process. Consequently, the investigation of efficient CO₂ sorbents emerges as an important research topic of CO₂ capture for both point source emission and DAC.

(iv) Storage: the released CO₂ requires compression to streamline subsequent transportation and storage processes as explained in Section 1.2.1.

Figure 2. Simplified illustration of Direct Air Capture (DAC) process.

Key differences in CO₂ sorbents targeted between point source emissions and DAC relate to the targeted CO₂ concentrations and the temperatures associated with capture/regeneration processes. As mentioned earlier, CO₂ concentrations in flue gases are around 15%, clearly contrasting with atmospheric CO₂ concentrations, which is approximately 0.04%. Concurrently, the temperature...
of the flue gases is between 600 to 1600 °C, markedly higher than ambient air temperatures. These disparities underscore the imperative for specialized sorbents tailored for CO$_2$ capture from both point sources and the atmosphere. A detailed discussion on these CO$_2$ sorbents is presented in the upcoming Section 1.3.

1.3. Sorbents for CO$_2$ capture and storage

Various criteria can be used to distinguish CO$_2$ sorbents, in this thesis, these sorbents will first be divided into physical and chemical sorbents for comparison.

1.3.1. Physisorbents vs Chemisorbents

Physisorbents and chemisorbents work based on two distinct sorption mechanisms: physisorption and chemisorption. These represent different ways by which molecules or atoms attach to the surface of sorbents, differentiated primarily by the nature and strength of the interaction between the adsorbate and the adsorbent.

![Figure 3. Simplified illustration of physisorption and chemisorption interaction between the adsorbent (substrate surface) and the adsorbate molecules.](image)

Physisorption, commonly known as physical adsorption, is characterized by the weak intermolecular forces between the adsorbate and adsorbent, such as van der Waals forces (VdW) and dipole-dipole interactions. Owing to the non-permanent (transient) nature of these interactions, physisorption often exhibits reversible and multilayer adsorption behaviours. It typically takes place under relatively mild conditions of temperature and pressure, without causing significant chemical changes in the adsorbate. On the other hand, chemisorption involves the formation of strong chemical bonds, either covalent or ionic, which involve the sharing or transfer of electrons between the adsorbate and the adsorbent. This bond formation leads to notable electronic and chemical modifications in the adsorbate, resulting in an essentially irreversible adsorption process. Furthermore, due to the strength of these bonds, adsorption usually occurs as a monolayer. Contrary to physisorption, chemisorption often
requires higher temperatures and pressures, reflecting the increased energy demands for bond creation or disruption.

When investigating suitable and efficient sorbents, it is important to consider the inherent characteristics of both physisorption and chemisorption. In essence, physisorbents and chemisorbents represent two distinct categories of sorbents, each associated with a unique adsorption mechanism: the former utilizes weak intermolecular forces, while the latter forms stronger chemical bonds with the adsorbate. In fact, as explained above, the required conditions for physisorption and chemisorption can be differed. Therefore, a clear understanding of the distinctions and the required conditions is crucial for developing adsorbents tailored to specific applications and conditions.

1.3.2. CO$_2$ Sorbents for point source emissions

**Amines**, such as monoethanolamine (MEA) and diethanolamine (DEA), are prevalently employed as sorbents owing to their notable affinity for CO$_2$. This pronounced affinity engenders high selectivity, facilitating the efficient removal of CO$_2$ from flue gases. Specifically, MEA undergoes a chemical reaction with CO$_2$, resulting in the formation of carbamate. Despite the presence of strong chemisorption, the interaction between CO$_2$ and MEA remains reversible, enabling both capture and subsequent release of CO$_2$ for potential storage or utilization. Post sorption, the carbamate-laden MEA solution is directed to a stripping unit where it is subjected to heat, prompting the release of CO$_2$ and decomposition of the carbamate. Upon regeneration, the MEA solution is cooled and prepared for the next CO$_2$ sorption cycles. It is pertinent to emphasize the energy-intensive nature of this process, which translates to substantial operational costs. Contemporary research thus gravitates towards enhancing the efficiency and cost-effectiveness of these sorbents.

![Figure 4. Simplified process flow diagram of an amine-based CO$_2$ capture plant.](image)

**Inorganic oxide-based sorbents**, especially those containing alkali metals and/or alkaline earth metals are notable solid sorbents that chemically interact with CO$_2$ to form stable carbonate compounds through carbonation
The mechanism for the reversible carbonation reaction by these inorganic oxide sorbents can be generalized as follows:

$$M_xO + CO_2 \rightleftharpoons M_xCO_3$$

Calcium oxide (CaO) is as a commonly studied inorganic oxide-based sorbent. In the carbonation reaction, CO$_2$ from point source emissions reacts with CaO, forming the more thermodynamically stable calcium carbonate (CaCO$_3$). The subsequent reaction, known as calcination, reverses the carbonation reaction, releasing the previously captured CO$_2$ from CaCO$_3$. During this reaction, CaCO$_3$ is exposed to elevated temperatures, leading to its decomposition into CaO and CO$_2$. The released CO$_2$ can be collected, compressed, and either stored or utilized, while the regenerated CaO is ready for further cycles of carbonation and calcination reaction. One of the reasons inorganic oxide-based sorbents have been considered attractive for CO$_2$ capture from point source emissions is their high carbonation and calcination temperature. Specifically, for CaO, the carbonation process operates at approximately 650 °C, and the calcination process around 900 °C. Given that the exhaust temperatures from industrial processes usually fall between 600°C and 1200°C, this is a key consideration. Performing CCS using inorganic oxide-based sorbents can reduce energy demands, as there would be not need to adjust the temperature of the exhaust gas from, for example, steel plant process.

![Figure 5. Simplified process flow diagram of carbonation and calcination reaction using calcium oxide for CO$_2$ capture.](image)

Indeed, one of the challenges associated with inorganic oxide-based sorbents is the sintering effect. Sintering refers to the agglomeration of the sorbent particles when exposed to elevated temperatures over successive carbonation and calcination cycles. This leads to a reduction in the space between sorbent particles, subsequently diminishing its CO$_2$ capture capacity. Sintering can cause a range of morphological and microstructural changes in the sorbent. Addressing this sintering effect and developing strategies to mitigate its impact is crucial for enhancing the efficiency of inorganic oxide-based sorbents.
in CCS applications. A detail explanation of the sintering effect, its implications, and potential mitigation strategies will be discussed in Section 1.4.

Figure 6. Simplified structure of metal-organic frameworks (MOFs) consisting of metal ions and organic linkers.

**Metal-organic frameworks (MOFs),** also referred to as coordination polymers, represent a unique class of porous materials distinguished by their structural characteristics. They are composed of metal ions or clusters that function as structural nodes, intricately coordinated with organic linkers or ligands. This results in a diverse array of finely structured frameworks, and an unique feature of MOFs is their structural tunability. By selectively pairing specific metal ions and organic linkers, it is feasible to modulate various properties, from pore dimensions, volume, porosity, and surface functionalities to \( \text{CO}_2 \) capture properties and stability. Despite their potential as \( \text{CO}_2 \) sorbents, it is important to note that there are also challenges including issues related to MOF stability, scalability, and cost. MOFs are yet to be deemed suitable for immediate and widespread application into practical CCS applications. Some MOFs can lose their structure or degrade when exposed to moisture and elevated temperatures. Considering that point source emissions are typically humid and hot, the applicability of MOFs as \( \text{CO}_2 \) sorbents can be restricted. Although MOFs can be synthesized at the laboratory scale, their cost-effective industrial scale production poses challenges. Moreover, certain MOFs incorporate rare or costly metals and organic linkers, rendering them economically not viable for extensive CCS applications.

The design and optimization of a \( \text{CO}_2 \) sorbent depends on factors such as the specific industrial process, flue gas composition, temperature, and pressure conditions, as well as economic considerations. \( \text{CO}_2 \) sorbents are a crucial component of CCS technologies aimed at reducing \( \text{CO}_2 \) from point source emissions, and ongoing research and development efforts continue to improve their efficiency and reduce costs.

1.3.3. \( \text{CO}_2 \) Sorbents for direct air capture

**Hybrid ultramicroporous materials (HUMs),** the term “hybrid” refers to the combination of organic and inorganic components, and
“ultramicroporous” indicates that these materials have pore dimensions typically smaller than 10 Å.\textsuperscript{54} As explained in Section 1.3.2, MOFs are finely structured frameworks, resulting from the coordination of metal ions or clusters with organic linkers or ligands. The unique facet of HUMs is the integration of an additional “pillar” amidst the foundational layers of the MOF lattice. This inclusion permits modulation of the pore dimension but also the pore aperture. The ultramicropore dimensions (< 10 Å) closely align with the kinetic diameter of guest molecules which can result in strong electrostatic interactions with polarizable molecules.\textsuperscript{55} The kinetic diameters of common guest gas molecules are approximately 3.30 Å, 3.30 Å, 3.64 Å, 3.80 Å, and 5.50 Å for CO$_2$, N$_2$O, N$_2$, CH$_4$, and SF$_6$, respectively. In the design of HUMs which is capable physisorbents, the kinetic diameters of guest gas molecules are one of the crucial parameters. The deliberate tuning of pore apertures in HUMs is essential to ensure effective adsorption and separation between different molecules.

Table 2. The kinetic diameter of the typical guest gas molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kinetic diameter [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide (CO$_2$)</td>
<td>3.30</td>
</tr>
<tr>
<td>Nitrous oxide (N$_2$O)</td>
<td>3.30</td>
</tr>
<tr>
<td>Oxygen (O$_2$)</td>
<td>3.46</td>
</tr>
<tr>
<td>Nitrogen (N$_2$)</td>
<td>3.64</td>
</tr>
<tr>
<td>Methane (CH$_4$)</td>
<td>3.80</td>
</tr>
<tr>
<td>Sulfur hexafluoride (SF$_6$)</td>
<td>5.50</td>
</tr>
</tbody>
</table>

By tuning the pore aperture to correspond with the kinetic diameter of the target gas molecule particularly at low-concentration, HUMs can be optimized for enhanced adsorption capacity. HUMs containing the inorganic anion pillar (SiF$_6^{2-}$) coordinated with transition metals such as zinc (Zn$^{2+}$) and nickel (Ni$^{2+}$), with pyrazine as the bridging organic linker, stand as one of the classic HUMs.\textsuperscript{56-58} Despite the variation in metal ions (M’), these HUMs maintain an isostructure. Notably, within this series, the M’−N bond length associated with the pyrazine linker exhibits a contraction when transitioning from Zn$^{2+}$ to Ni$^{2+}$. Accompanying this bond shortening is a concomitant decrease in the pore aperture size, specifically the fluorine to fluorine distance (F−⋯F−). Consequentially, the pore aperture reduced from 3.84 Å in SIFSIX-3-Zn (SIFSIX=SiF$_6^{2-}$, 3=pyrazine, Zn=Zinc) to 3.66 Å in SIFSIX-3-Ni (SIFSIX=SiF$_6^{2-}$, 3=pyrazine, Ni=Nickel). The CO$_2$ adsorption capacity increase from 0.13 mmol g$^{-1}$ (SIFSIX-3-Zn) to 0.4 mmol g$^{-1}$ (SIFSIX-3-Ni) at 500 ppm.\textsuperscript{59,60} The fine-tuning of pore apertures emerges as a central topic in HUMs research, highlighting the adsorption property changes particularly when these distances of pore aperture approach the kinetic diameter of CO$_2$. 
1.4. Inorganic oxide-based CO\(_2\) sorbents

A concise overview of inorganic oxide-based sorbents was provided in Section 1.3.2. Building upon that foundation, this section discusses deeper into the sintering effect inherent to these sorbents. Herein, it will be elucidated the mechanisms driving sintering effect in inorganic oxide-based sorbents, detail its repercussions on sorbent performance, and outline promising strategies that have been proposed to minimize these effects. Understanding these intricacies is pivotal for the design of effective and sustainable inorganic oxide-based sorbents. As delineated earlier, sintering is a thermal-driven phenomenon whereby particles undergo coalescence and growth. Such thermal processes can drastically reduce not only the surface area of the sorbents but also the space between the sorbent particles. The porosity provides not only an expansive reactive surface but also ensures efficient pathways for CO\(_2\) molecule diffusion.\(^{44, 48}\) However, the sintering effect threatens this pathway. Space
between particles become blocked, which in turn stifles the CO$_2$ capture efficiency. Consequently, this can lead to the masking of activation sites, hindering the carbonation kinetics during ensuing carbonation and calcination (CO$_2$ capture and regeneration) cycles. This sintering effect amplifies with repeated carbonation and calcination cycles, resulting in poor performance after a number of cycles. Furthermore, sintered sorbents may necessitate increase regeneration temperatures, thereby higher energy consumption and lower efficiency of process.

Figure 8. The cyclic stabilities of the carbonation and calcination reactions for (a) pure CaO and (b) CaO modified with ZrO$_2$, along with a simplified illustration of the carbonation reactions of the pure inorganic oxide-sorbent and the inorganic oxide-sorbent with additives.

Several mitigation strategies have been proposed to address the sintering effect observed in inorganic oxide-based sorbents. One of the strategies involves the incorporation of specific additives into the sorbents as shown in above. These additives, often in the form of metal, can enhance the thermal stability of the sorbents, preventing or at least delaying the sintering effect even under prolonged exposure to high temperatures. Moreover, these additives can also act as physical barriers that prevent the agglomeration of sorbent particles, thereby preserving the surface area and porosity, which safeguards the reaction sites from being masked or becoming inaccessible. The utilization of
additives such as aluminium oxide (Al$_2$O$_3$) or zirconium oxide (ZrO$_2$) in conjunction with CaO exemplifies a strategic approach to enhance the thermal stability of inorganic oxide-based sorbents. Not only the choice of additive but also the ratio of additive integrated into the sorbent is important. There is an inverse relationship between the quantity of additive and CO$_2$ capture capacity: as the amount of additive increases, the CO$_2$ capture capacity often decreases. This is attributed to the potential blocking of reaction sites or alterations in the structure of sorbent which can impede the carbonation reaction. Optimal additive concentration is thus important to find a balance between improved thermal stability and maintained or enhanced CO$_2$ capture capacity.

Figure 9. Simplified illustration of the molten inorganic oxide-sorbent and the inorganic oxide-sorbent with additives.

Another possible strategy is the incorporation of specific promotors into the sorbents. The capture capacity and cyclic stability of inorganic oxide-based sorbents can be significantly promoted by the presence and migration of alkali metals typically, sodium (Na$^+$), lithium (Li$^+$), and potassium (K$^+$). At high temperatures, alkali metal ions have been observed to migrate not only between particles of the sorbent but also within the structure of the inorganic oxide. During this migration, alkali metal ions can either occupy existing vacancies in the oxide lattice or replace other cations. This migration can beneficially impact the sorbent by influencing particle boundary movements, subsequently reducing the propensity for particles to aggregate. The phenomenon wherein alkali metal ions migrate within the inorganic oxide-based sorbent at elevated temperatures, is referred to as “molten salt effects”, “cation mobility” or specifically “sodium diffusion” for Na$^+$. Moreover, alkali metals act as a catalytic promoter, improving the capability of sorbent to adsorb targeted gases. This promotional effect can be attributed to the creation of new reaction sites by alkali metal ions. The creation of this new reaction site is significant as it enables the transformation of inorganic oxides, which were traditionally non-reactive to CO$_2$, into effective CO$_2$ sorbents.
1.5. Inorganic anion pillared metal-organic frameworks

A concise overview of HUMs was provided in Section 1.3.3. Building upon that foundation, this section discusses deeper into one of the types of HUMs is inorganic anion pillared metal-organic frameworks and its CO$_2$ adsorption properties. 1st generation of inorganic anion pillared metal-organic frameworks, SIFSIX-3-M (M’=Zn, Ni, and Cu) series demonstrate significant CO$_2$ adsorption capacity at 500 ppm however, their adsorption property is decreased in the presence of water. Addressing this drawback, the incorporation of NbOF$_5^{2-}$ as an alternative anion pillar has been investigated. This can be attributed to the larger atomic radius of niobium compared to silicon, which extends the Nb$^{5+}$-F$^-$ bond lengths, thereby conferring increased steric bulk to the NbOF$_5^{2-}$ pillar compared to SiF$_6^{2-}$ pillar. The NbOF$_5^{2-}$ pillar, with a greater nucleophilicity than SiF$_6^{2-}$, contributes to the formation of a water stable sorbent while maintaining the framework structure. The resultant NbOFFIVE-1-Ni (NbOFFIVE=NbOF$_5^{2-}$, 1=pyrazine, Ni=Nickel), referred to as KAUST-7, exhibits enhanced water stability.

Figure 10. 1st generation of inorganic anion pillared metal-organic frameworks crystal structure (a) SIFSIX-3-Ni (SIFSIX=SiF$_6^{2-}$, 3=pyrazine, Ni=Nickel) and 2nd generation of inorganic anion pillared metal-organic frameworks crystal structure (b) NbOFFIVE-1-Ni (NbOFFIVE=NbOF$_5^{2-}$, 1=pyrazine, Ni=Nickel).

Additionally, the extended Nb$^{5+}$–F$^-$ length of NbOFFIVE-1-Ni as compared to Si$^{6+}$–F$^-$ of SIFSIX-3-Ni (Nb$^{5+}$–F$^-$ vs Si$^{6+}$–F$^-$ = 1.899 and 1.613 Å) reduced the pore aperture from 3.66 Å to 3.2 Å. This change led NbOFFIVE-1-Ni to have CO$_2$ adsorption capacity of 1.3 mmol g$^{-1}$ at 500 ppm which is three times higher than SIFSIX-3-Ni. Based on the insights gathered from Section 1.3.3 and the current section, it becomes evident that the CO$_2$ adsorption capacity of inorganic anion pillared metal-organic frameworks are highly dependent on their constitutive elements, which include the metal nodes and inorganic anion pillars. This tunability provides the opportunity to fine-tune the
CO₂ adsorption properties, proving the significance of strategic structural design.

1.6. Aim on this thesis

In this thesis, the primary goal is to design and optimize CO₂ sorbents tailored for two distinct applications: point source emissions and direct air capture. As mentioned in Section 1.4, one of the crucial research topics is the improvement of inorganic oxide-based sorbents, which typically suffer from low cyclic and thermal stability. One approach involves combining the molten salt effects with thermally stable inorganic oxides like HfO₂ and ZrO₂ to mitigate the sintering effect, a key factor reducing cyclic stability. Therefore, a new CO₂ sorbent, Na₂HfO₃, was synthesized using HfO₂ and Na₂CO₃. The goal is not only to develop a novel CO₂ sorbent but also to enhance its CO₂ capture properties by optimizing various synthesis parameters and operational conditions for real-life applications. The study of Na₂HfO₃ revealed structural disorders in Na₂ZrO₃, which have not been previously discussed in the previous literature. Consequently, a comprehensive structural analysis of Na₂ZrO₃, chemically similar to Na₂HfO₃, was conducted to deepen the understanding of inorganic oxide-based sorbents, specifically Na₂HfO₃ and Na₂ZrO₃. As discussed in Section 1.5, tuning the pore apertures of inorganic anion pillared metal-organic frameworks is considered a primary research focus for improving CO₂ adsorption properties. Hence, this thesis aims to adjust the pore aperture by modifying the bond length of anion pillars (M₅⁺−F⁻; M₅⁺ = V₅⁺ and Ta₅⁺) and using different linkers (pyrazine and aminopyrazine). This approach is expected to lead to the investigation of new inorganic anion pillared metal-organic frameworks (isoreticular series of NbOFFIVE-1-Ni) potentially suitable for effective direct air capture.

By addressing these aims, this thesis seeks to contribute to the field of CO₂ capture, presenting new sorbents and insights for the design and optimization of more efficient CO₂ sorbents.
2. Characterization methods

2.1. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) is a characterization technique that employs X-rays to elucidate the atomic-scale geometry within the crystal structure of a material. Upon interaction with atoms in the crystal lattice, X-rays undergo scattering by the electrons associated with those atoms. The scattered X-rays, propagating in various directions, are collected by a detector and manifest with varying intensities. The measured intensity of X-ray diffraction provides insights into the relative positions of the atoms in the material, thereby yielding information about its structural geometry. X-ray diffraction phenomena are often described by Bragg's law ($n\lambda = 2d \cdot \sin \theta$), which relates X-ray reflection to lattice planes. In the aforementioned equation, $n$ represents an integer multiple ($n = 0, \pm 1, \pm 2, \text{etc}$), $\lambda$ denotes the incident wavelength, $d$ signifies the interplanar spacing of lattice (crystal) planes, and $2\theta$ corresponds to the angle of diffraction, which is the angle between the incident and reflected X-ray waves.

![Diagram of PXRD pattern](image)

Figure 11. Information from a PXRD pattern of the synthesized CO$_2$ sorbents.

It is worth noting that crystal structures are not always perfect; occasional imperfections in the lattice arrangement can arise due to disorder. In the case of disordered materials, the diffracted intensity can be observed in all directions away from the reciprocal lattice points, resulting in diffuse scattering, as
discussed in Section 4.1.2. The background of the PXRD patterns was utilized to identify diffuse scattering. Conversely, reflections in the PXRD patterns were leveraged to determine lattice parameters, space group, quantitative phase, and atom analysis, as well as peak shapes and crystal structure via peak positions, intensity, and profile characteristics, such as peak shape and full width at half maximum (FWHM).

In this thesis, PXRD was employed to extract diverse information related to all the synthesized CO$_2$ sorbents using a Bruker D8 powder diffractometer (Karlsruhe, Germany).

### 2.2. Electron microscopy

#### 2.2.1 Scanning electron microscopy

The scanning electron microscope (SEM) is an indispensable tool to observe the morphology and chemical compositions of materials with high resolution. It employs a focused beam of electrons to scan the surface of the materials and detect signals arising from interactions between the electrons and the material. These interactions can be classified as elastic or inelastic. Elastic interactions occur when the incident electrons are deflected by the atomic nucleus or outer shell electrons of the material. When the scattering angle exceeds 90°, it is referred to as backscattered electrons, which are useful for morphology observation (imaging). Inelastic interactions encompass various interactions between the incident electrons and atoms, leading to energy losses that depend on the binding energy of the electron to the atom. These interactions manifest as Auger electrons, X-rays, and secondary electrons. Among these, secondary electrons are utilized for imaging and analysing the chemical compositions of materials. Energy-dispersive spectroscopy (EDS) utilizes secondary electrons to provide chemical (elemental) compositions in conjunction with imaging.

In this thesis, SEM images were utilized to discern the morphology, homogeneity, and size of inorganic oxide-based sorbents and inorganic anion pillarated metal-organic frameworks. Additionally, EDS was employed to examine the elemental composition and abundance in both bulk and selected areas of the aforementioned sorbents. All the sorbents were analysed using either the Zeiss LEO 1530 or Zeiss Merlin Field Emission SEM systems. In order to enhance conductivity for high-resolution imaging, some sorbents were sputter-coated with Ag/Pd.
2.2.2. Transmission electron microscopy\textsuperscript{80, 81}

Transmission electron microscopy (TEM) is a potent technique to examine the internal structure of materials through imaging and diffraction. In this thesis, electron diffraction was employed to observe the crystal structure of inorganic oxide-based sorbents. Similar to PXRD patterns, materials scatter electrons through Bragg diffraction, resulting in diffraction patterns. While PXRD provides diffraction patterns for the entire sample, TEM enables the acquisition of selected area electron diffraction (SAED) patterns by using an aperture. This confers the advantage of obtaining crystal structure information for a single crystal within a heterogeneous sample. It is akin to single X-ray diffraction (SCXRD) analysis, allowing for the observation of the crystal structure of a single crystal. However, TEM possesses the additional advantage of not requiring a specific crystal size, which is a prerequisite for SCXRD analysis.

Nevertheless, sample preparation for TEM often presents challenges, particularly in achieving thin sample thickness to mitigate dynamic effects and prevent damage to the crystal structure caused by grinding or solvents. Despite the numerous advantages of SAED, substantial efforts and time are required to collect all the SAED patterns necessary for constructing the crystal structure. An alternative approach is three-dimensional electron diffraction (3D ED), which involves collecting electron diffraction data from consecutive orientations of a single crystal by tilting it in the electron microscope. The
diffraction patterns acquired at various angles are subsequently combined to construct a complete 3D structure.

In this thesis, all TEM images and 3D ED patterns were collected using the JEOL JEM-2100 TEM equipped with a Timepix detector from Amsterdam Scientific Instruments.

2.3. Thermogravimetry-differential scanning calorimetry

Thermogravimetry-differential scanning calorimetry analysis (TG-DSC) comprises two main techniques: thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA is a significant tool for monitoring the mass changes of materials as they are subjected to controlled temperature and specific time intervals under different gases. In this thesis, a sorbent is placed in a suitable pan, such as an alumina ceramic or sapphire pan, and positioned on a balance within a furnace. The furnace is then heated or cooled, with or without the presence of inert gases. These gases flow over the sample, initiating chemical reactions depending on the specific gas environment. TGA provides valuable information regarding the thermal stability, decomposition, and potential chemical reactions of the sorbents. TGA was employed for several purposes:

(i) Synthesis: TGA was used to synthesize certain inorganic oxide-based sorbents. The starting materials for these sorbents were placed in sapphire pans and heated under a nitrogen (N$_2$) gas environment

(ii) Determination: TGA was utilized to examine the decomposition temperature of the sorbents, enabling the calculation of their chemical compositions. This information was essential for establishing suitable calcination temperatures

(iii) CO$_2$ capture property: TGA was employed to evaluate the CO$_2$ capture properties of the synthesized inorganic oxide-based sorbents and inorganic anion pillared metal-organic frameworks under CO$_2$ gas environment.

The measured mass changes, corresponding to CO$_2$ capture capacity, were also utilized for adsorption kinetic analysis. In this thesis, five different kinetic models, including the Pseudo-first order (PFO), Pseudo-second order (PSO), Elovich, Avrami, and Avrami-Erofeev models, in both non-linear and linear versions, were applied to analyse the CO$_2$ capture process of the synthesized inorganic oxide-based sorbents. These kinetic models provided the CO$_2$ capture property and provided insights into the adsorption kinetics of the sorbents.
• Pseudo-first order non-linear: \( q_t = q_e (1 - e^{k_1 t}) \)
  Linear: \( \ln \left( \frac{C_t}{C_i} \right) = k_1 t \)

• Pseudo-second order non-linear: \( q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \)
  Linear: \( \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \)

• Elovich non-linear: \( q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \)
  Linear: \( q_t = \frac{1}{\alpha} \ln(\alpha \beta) + \frac{1}{\alpha} \ln t \)

• Avrami non-linear: \( \ln[\ln(q_e / q_e - q_t)] = n \ln k + n \ln t \)
  Linear: \( V_v = 1 - \exp(-kt^n) \)

• Avrami-Erofeev non-linear: \( \ln[-\ln(1 - \alpha)] = \ln k + n \ln t \)

The result of the adsorption kinetic analysis is discussed in Section 4.2.1. Conversely, DSC analysis observes heat flow as a sorbent is exposed to controlled temperatures under CO\(_2\) gas environments. It quantifies the disparity in heat flow between the sorbent and a reference pan. DSC analysis yields valuable information regarding thermal properties, including chemical reactions, melting, and crystallization phenomena. In this thesis, the TGA data were recorded using a Mettler Toledo TGA2 thermogravimetric analyser (Schwerzenbach, Switzerland), while the DSC data were acquired using a Netzsch DSC 214 Polyma instrument.

2.4. Accelerated surface area and porosimetry system\(^{85, 86} \)

The accelerated surface area and porosimetry system is an essential technique utilized for the characterization and quantification of the surface area and porosity properties of porous materials, such as specific surface area (SSA), pore volume, and pore size distribution (PSD). The measurement principle is based on the adsorption and desorption of gas molecules on the surface and within the pores of materials. By exposing the material to a gas, typically N\(_2\) and CO\(_2\), and monitoring the changes in the gas uptake at different pressures.

In this thesis, the accelerated surface area and porosimetry system was employed to investigate the surface area and CO\(_2\) adsorption capacity of the synthesized sorbents. The surface area is calculated by Brunauer-Emmett-Teller
The BET (BET) model. The BET assumes that the surface sites have multiple layers of adsorbed molecules, with each layer having a specific adsorption potential. According to the BET model, the relationship between the relative pressure \( \frac{P}{P_0} \), which represents the gas pressure at equilibrium, and the quantity of adsorbed gas \( N \) can be described by the following equation:

\[
v \frac{1}{v[P_0(P/P_0) - 1]} = \frac{c - 1}{v_m c} \times \frac{P}{P_0} + \frac{1}{v_m c}
\]

Here, \( v \) is the volume of gas adsorbed, \( P \) is the equilibrium pressure, \( P_0 \) is the saturation pressure of the adsorbate at the temperature of adsorption, \( v_m \) is the monolayer adsorbed gas quantity, \( c \) is the BET constant, related to the energy of adsorption.

In this thesis, the SSA and CO\(_2\) adsorption capacities were recorded on the synthesized sorbents using a Micromeritics ASAP 2020 surface area analyser.

### 2.5. X-ray photoelectron spectroscopy\(^{87-89}\)

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy, is a surface analysis method employed to determine the chemical compositions of elements, their bonding states, and oxidation states. It relies on the measurement of the kinetic energy of photoelectrons emitted from the surface of a material.

![X-ray photoelectron spectroscopy](image)

Figure 13. X-ray photoelectron spectroscopy (XPS).

The photoelectrons are generated by irradiating the surface with characteristic x-rays such as Al K\(\alpha\). Al K\(\alpha\) rays provide information about elements within a few nm of the surface. The depth of analysis can be adjusted by performing surface etching using a sputter ion gun. Surface etching serves multiple purposes, including analysing element composition, bonding states, and removing surface contamination. In some cases, depth profiling, which involves alternating between surface etching and measurement, is conducted to evaluate the thickness of materials with multiple layers. The obtained elements in the XPS analysis provide insights into the atomic locations on the surface, atomic valence charges, interatomic distances, and chemical shifts resulting from...
changes in bond energies, enabling the determination of chemical compositions. The X-ray parameters, such as the X-ray energy, scan range, and analysis type (e.g., multi-point analysis, line analysis, and area analysis), can be tailored to suit the specific material under investigation.

In this thesis, XPS was employed for qualitative and quantitative analysis of elements in the synthesized inorganic oxide-based sorbents, utilizing a PHI Quantera II Scanning XPS Microprobe. Prior to analysis, all samples underwent surface etching using argon ions to ensure cleanliness. Furthermore, all measured spectra of the target elements were calibrated using the C-C peak of C1s.

2.6. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a widely used analytical method that provides the molecular composition and structure of materials. It operates based on the principle that molecules absorb infrared radiation at specific frequencies, which are characteristic of their functional groups and chemical bonds. By analysing the absorption patterns, FTIR enables the identification and characterization of organic and inorganic compounds. In FTIR spectroscopy, a beam of infrared light is passed through a material, and the transmitted or reflected light is measured. The resulting spectrum represents the absorption of infrared energy as a function of wavelength or wavenumber. The spectrum contains characteristic bands corresponding to the vibrational modes of the molecules present in the material. FTIR is sensitive enough to detect low concentrations of chemical bonds for both qualitative and quantitative analysis.

In this thesis, FTIR spectroscopy was utilized to investigate not only the molecular composition and structural properties of the synthesized inorganic anion pillared metal-organic frameworks but also CO\textsubscript{2} capture kinetic analysis. Varian 670-IR FT-IR spectrometer was used with a mercury cadmium telluride (MCT) detector.
3. Synthesis methods

3.1. Synthesis of inorganic oxide-based CO\(_2\) sorbents

3.1.1. Sodium hafnium oxide

The synthesis of sodium hafnium oxide (Na\(_2\)HfO\(_3\)) was conducted using sodium carbonate (Na\(_2\)CO\(_3\)) and hafnium oxide (HfO\(_2\)) purchased from Sigma-Aldrich. Na\(_2\)CO\(_3\) (anhydrous for analysis EMSURE® ISO) and HfO\(_2\) (98%) were dried at 130 °C for 3 h before synthesis. An extensive investigation of the synthesis parameters was tested to optimize the formation of Na\(_2\)HfO\(_3\) according to equation below

\[
\text{Na}_2\text{CO}_3(\text{s}) + \text{HfO}_2(\text{s}) \leftrightharpoons \text{Na}_2\text{HfO}_3(\text{s}) + \text{CO}_2(\text{g})
\]

This included variations in the molar ratios of the starting materials, Na\(_2\)CO\(_3\) and HfO\(_2\), synthesis temperature, synthesis time, and heating rates. The specified molar ratios investigated for Na\(_2\)CO\(_3\):HfO\(_2\) = 0.5:1, 0.75:1, 1:1, 1.25:1, and 1.5:1. These were mechanically mixed by hand before synthesis. The mixtures were heated using a Mettler Toledo thermogravimetric analyzer (TGA) to target temperatures of 800, 850, 900, and 1050 °C for four different synthesis time from 1 to 4 h. The heating rates were employed 2, 5, or 10 °C/min, all under a constant flow rate of nitrogen (N\(_2\)) at 50 cm\(^3\)/min.

3.1.2. Sodium zirconium oxide

The synthesis of sodium zirconium oxide (Na\(_2\)ZrO\(_3\)) was conducted using sodium carbonate (Na\(_2\)CO\(_3\)) and zirconium oxide (ZrO\(_2\)) purchased from Sigma-Aldrich. Na\(_2\)CO\(_3\) (anhydrous for analysis EMSURE® ISO) and ZrO\(_2\) (98%) were dried at 130 °C for 3 h before synthesis. The various molar ratios of Na\(_2\)CO\(_3\):ZrO\(_2\) = 0.75:1, 1:1, 1.25:1, and 1.5:1 were mechanically mixed by hand and heated using TGA to 900 °C with a heating rate of 5 °C/min under a 100 mL/min flow of 100% nitrogen (N\(_2\)) for 2 h and 5 h.
3.2 Synthesis of inorganic anion pillared metal-organic frameworks

Isoreticular series of NbOFFIVE-1-Ni (NbOFFIVE=NbOF\(_5^{2-}\), 1=pyrazine, Ni=Nickel) was synthesized as TaOFFIVE-1-Ni, VOFFIVE-1-Ni, NbOFFIVE-2-Ni, and TaOFFIVE-2-Ni using Tantalum oxide (Ta\(_2\)O\(_5\)), Vanadium oxide (V\(_2\)O\(_5\)), and Niobium oxide (Nb\(_2\)O\(_5\)) purchased from Thermo Fisher scientific, and Hydrofluoric acid (HF), Nickel nitrate hexahydrate (Ni(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O), Pyrazine, Aminopyrazine, and Methanol purchased from Sigma-Aldrich. All chemicals were used without further purifications for all the synthesis.

In order to synthesize TaOFFIVE-1-Ni and VOFFIVE-1-Ni, 0.3 mmol (133 mg) of Ta\(_2\)O\(_5\) (99% purity) and 0.3 mmol (55 mg) of V\(_2\)O\(_5\) (> 99% purity) were mixed with 0.4 ml of HF in 20 ml of Teflon vessels respectively. Each mixture was sealed in hydrothermal synthesis reactors and heated at 130 °C for overnight. After cooling down the pre-heated mixtures to room temperature, 3 ml of deionized water, 4.8 mmol (384 mg) of pyrazine (≥ 99% purity), and 0.6 mmol (174 mg) of Ni(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O (99 < x < 102%) were added into the pre-heated mixtures and mixed on a shaker at 250 ppm for 3 h. After mixing, the mixtures were sealed and reacted at 130 and 85 °C, respectively, for 48 h. After the reaction, pastel light-blue and light-emerald fine powders were collected by centrifugation at 3800 rpm for 10 min and washed twice using methanol. After washing, TaOFFIVE-1-Ni and VOFFIVE-1-Ni were soaked in methanol for solvent exchange for 24 h. The soaked powders were centrifuged and then dried at 70 °C for 24 h.

In order to synthesize NbOFFIVE-2-Ni and TaOFFIVE-2-Ni, the same pre-heated mixture step was performed as above, mixtures of 0.3 mmol (79.74 mg) of Nb\(_2\)O\(_5\) (99.99% purity) and Ta\(_2\)O\(_5\) (133 mg) were mixed in 0.4 ml of HF in 20 ml of Teflon vessels respectively. Each mixture was heated at 130 °C for overnight. After cooling down, the same amount of Ni(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O, deionized water, and 4.8 mmol (456.48 mg) of Aminopyrazine (98% purity) were added into the pre-heated mixtures and mixed on a shaker at the same condition as above. After mixing, the mixtures were sealed and reacted at 130 and 85 °C for 36 and 48 h, respectively. After the reaction, the same washing and dry steps were performed to the mixtures. As final products, dark-brown and pastel light-blown fine powers were collected as NbOFFIVE-2-Ni and TaOFFIVE-2-Ni.

Figure 14. Colour of the synthesized samples: VOFFIVE-1-Ni, NbOFFIVE-1-Ni, TaOFFIVE-1-Ni, NbOFFIVE-2-Ni, TaOFFIVE-2-Ni (NbOFFIVE=NbOF\(_5^{2-}\), 1=pyrazine, 2=aminopyrazine, Ni=Nickel)
4. Results and Discussion

4.1. Characterization of inorganic oxide-based CO$_2$ sorbents

Characterization of sodium hafnium oxide (Na$_2$HfO$_3$) and sodium zirconium oxide (Na$_2$ZrO$_3$) were conducted using PXRD, SEM, TEM, and Micromeritics ASAP 2020 surface area analyser.$^{91,92}$

4.1.1. Sodium hafnium oxide

Synthesis temperature, a range of temperatures including 800, 850, 900, and 1050 °C were tested to optimize. Among these temperatures, the sample synthesized at 900 °C exhibited clear Na$_2$HfO$_3$ peaks compared to the samples synthesized at other temperatures. As a result, 900 °C was selected to be the suitable synthesis temperature for Na$_2$HfO$_3$.

![Figure 15. PXRD patterns of the synthesized NHO-1.25 at the different synthesis temperatures (a) 800 (b) 850 (c) 1050 °C for 3 h under N$_2$.](image)

To optimize the molar ratio of Na$_2$CO$_3$ to HfO$_2$ for the synthesis of Na$_2$HfO$_3$, various ratios were explored. Based on previous finding, the synthesis was conducted at the optimal temperature of 900 °C. The specific molar ratios of Na$_2$CO$_3$ to HfO$_2$ tested were 0.5:1, 0.75:1, 1:1, 1.25:1, and 1.5:1. The samples
are referred to as NHO-X, where X is the molar ratio of Na$_2$CO$_3$ with respect to HfO$_2$ (NHO-0.5, NHO-0.75, NHO-1, NHO-1.25, and NHO-1.5).

PXRD patterns of the synthesized NHO-Xs were collected at ambient temperature from a 2θ range between 10 and 60° with 0.01° step size.

As shown in above, two distinct types of PXRD patterns were observed 1) in NHO-0.5 and NHO-0.75, more peaks related with HfO$_2$ which was in excess in the reaction mixture were seen in the PXRD patterns 2) in NHO-1, NHO-1.25, and NHO-1.5, the PXRD patterns predominantly exhibited peaks associated with Na$_2$HfO$_3$ at specific angles (2θ ~16.2, 17.6, 18.5, 32.5, 39, and 42.5 degrees). Na$_2$HfO$_3$ peaks were identified in all the samples, indicating the presence of Na$_2$HfO$_3$. Notably, among these samples, NHO-1.25 revealed Na$_2$HfO$_3$ peaks with particularly high intensity. This suggests that the NHO-1.25 sample exhibited a more pronounced presence of Na$_2$HfO$_3$ thus, it was selected as the suitable molar ratio.

The observed peaks of Na$_2$HfO$_3$ were found to be comparable in position of Na$_2$ZrO$_3$, which is a chemically similar inorganic oxide-based CO$_2$ sorbent. Na$_2$ZrO$_3$ has been reported in the literature to exist in three different phases: monoclinic, hexagonal, and cubic. Therefore, it was expected that Na$_2$HfO$_3$ would exhibit similar phases.
Figure 17. 3D electron diffraction (3D ED) data of the synthesized NHO-1.25 viewed slightly off-axis from c*, showing well-resolved reflections (black) that can be indexed to a rhombohedral cell (a = 3.4 Å, c = 16.6 Å), as well as streaks (grey) along the c*-axis.

Structural analysis on the synthesized NHO-1.25 was carried transmission electron microscopy (TEM), in particular 3-dimensional electron diffraction (3D ED). 3D ED data includes clear reflections and lines of diffuse scattering, which are common in disordered materials with stacking faults. The clear reflections were indexed with specific unit cell parameters (a = b = 3.37 Å, c = 17.16 Å, α = β = 90°, and γ = 120°) and consistent with the space group R-3m due to the systematic absence of certain reflections. The overall structure of Na₂HfO₃ is similar to other disordered mixed metal oxides such as Li₂MnO₃ and Li₂TiO₃.⁹⁷,⁹⁸ The 3D ED data shows that both Na⁺ and Hf⁴⁺ ions are surrounded by six oxygen atoms (octahedrally coordinated). The structure of Na₂HfO₃ consists of alternating layers of metal cations (one with only Na⁺ and another with both Na⁺ and Hf⁴⁺) separated by oxide layers (O²⁻). ³⁰ It is assumed that in the mixed metal layer, Hf⁴⁺ and Na⁺ are present in a ratio of 2:1. Each unit cell has three such mixed metal layers stacked along the c-axis. There are four potential stacking sequences for these layers, resulting in Na₂HfO₃ with different space groups (P₃₁₂, P₃₂₁₂ (trigonal), C2/m or C2/c (monoclinic)) as shown in below.
Figure 18. Structures of $\text{Na}_2\text{HfO}_3$ and four different stacking orders of (a) the average structure (b) a single ordered $\text{Na}^+ + \text{Hf}^{4+}$ layer (e-h) various space groups. Arrows indicate the translation between neighbouring layers in the stacking orders.

PXRD patterns of $\text{Na}_2\text{HfO}_3$ consisting the four different stacking orders (different space groups) were simulated and appeared to be very similar as shown in below.

Figure 19. Simulated PXRD patterns of $\text{Na}_2\text{HfO}_3$ depends on the different space groups (a) C2/m, (b) P312, and (c) P3212, respectively.

The similarities in the simulated PXRD patterns which making it hard to identify the specific stacking order within a sample. The NHO-X samples discussed in this thesis exhibit more than one type of stacking sequence within each crystal, leading to a disordered structure characterized by stacking faults and diffuse scattering along the $c^*$-axis. This kind of disorder is also seen in similar compounds such as $\text{Li}_2\text{TiO}_3$ and $\text{Li}_2\text{MnO}_3$.97, 98 In the next section of the study, a more in-depth analysis was conducted focusing on the structural disorder observed in the materials. The unexpected discovery of structural disorder in $\text{Na}_2\text{HfO}_3$ revealed a necessity for further structural analysis. This
analysis extended not only to $\text{Na}_2\text{HfO}_3$ but also to $\text{Na}_2\text{ZrO}_3$, given its chemical similarity to $\text{Na}_2\text{HfO}_3$. The further analysis aimed to understand implications of the disorder within these mixed metal oxides. The detailed findings will be discussed in Section 4.1.2.

Figure 20. SEM images of the synthesized NHO-Xs at 900 °C for 3 h under $\text{N}_2$ (a) NHO-0.5 (b) NHO-0.75 (c) NHO-0.75 (d) NHO-1 (e) NHO-1.25 (f) NOH-1.5 and the starting materials (g) $\text{Na}_2\text{CO}_3$ (h) HfO$_2$.

Echoing the findings from the PXRD patterns of the synthesized NHO-Xs, the SEM images of NHO-0.5 and NHO-0.75 revealed two distinct types of particle morphologies. The first type was small globular-shaped particles resembling the morphology of HfO$_2$. The second type was polyhedral-like particles that had clumped together. The SEM images of NHO-1 and NHO-1.25 showed a morphology similar to the polyhedral-like particles which was also observed in NHO-0.5 and NHO-0.75, but without the presence of small globular-shaped particles. The particles in NHO-1.5, however, showed a distinctly different appearance from the other NHO-Xs, lacking both globular and polyhedral-like particles. They were highly aggregated and covered on the surface, bearing resemblance to pure $\text{Na}_2\text{CO}_3$. This finding is also evident in the BET specific surface area of NHO-1.5, measured at 2.83 m$^2$/g through $\text{N}_2$ sorption. This is lower compared to the other NHO-Xs, with values of 3.83,
3.77, 3.51, and 3.66 m²/g for NHO-0.5, NHO-0.75, NHO-1, and NHO-1.25, respectively, as listed in table below.

Table 3. BET specific surface area of the synthesized NHO-Xs.

<table>
<thead>
<tr>
<th>NHO-X</th>
<th>BET surface area [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.83</td>
</tr>
<tr>
<td>0.75</td>
<td>3.76</td>
</tr>
<tr>
<td>1</td>
<td>3.51</td>
</tr>
<tr>
<td>1.25</td>
<td>3.66</td>
</tr>
<tr>
<td>1.5</td>
<td>2.83</td>
</tr>
</tbody>
</table>

In Section 4.2.1, optimization processes were discussed for each synthesized NHO-X, focusing on parameters such as heating rate, carbonation temperature, and carbonation time. These factors are known to influence CO₂ capture properties. The focus was to tune these parameters to enhance the performance of the sample. Following this optimization, a thorough evaluation was conducted to identify the most practical CO₂ sorbent from the synthesized NHO-Xs.

4.1.2. Sodium zirconium oxide

The further analysis to understand the disorder within mixed metal oxides, structural analysis on the synthesized Na₂ZrO₃ samples was carried out using PXRD and 3D ED. PXRD patterns of Na₂ZrO₃ samples (Na₂CO₃:ZrO₂ = 1.5:1) synthesized at 900 °C under 100% N₂ for 2 h and 5 h were collected at ambient temperature, covering a 2θ range between 10° and 60° with a step size of 0.01°.

Figure 21. PXRD patterns of the synthesized Na₂ZrO₃ samples for (a) 2 h and (b) 5 h.

The PXRD patterns of the synthesized Na₂ZrO₃ samples revealed a high degree of similarity to the synthesized NHO-Xs samples discussed in the previous section.
The PXRD patterns of the two Na$_2$ZrO$_3$ samples showed that they had the same peak positions, but the highest relative peak intensities were different, occurring at $2\theta = 16.2^\circ$ and $38.7^\circ$. It was assumed that the phase of the samples could be different.

Previous literature on Na$_2$ZrO$_3$ indicates that its CO$_2$ capture capacity and cyclic stability change based on different phases. Therefore, many literatures have been directed toward controlling the phase, with a specific focus on comparing and optimizing their CO$_2$ capture properties across different phases. The literature presented that hexagonal Na$_2$ZrO$_3$ (NZO-H) exhibits excellent cyclic stability at elevated temperatures which makes it a potential sorbent for high temperature CO$_2$ capture applications. Conversely, monoclinic Na$_2$ZrO$_3$ (NZO-M) is considered for higher CO$_2$ capture capacity than NZO-H. This comparative analysis aimed to elucidate the relationship between phase and CO$_2$ capture capacity, thereby informing the design and optimization of Na$_2$ZrO$_3$ for enhanced CO$_2$ capture performance.

The phase of Na$_2$ZrO$_3$ has been discussed since 1966, leading to believe that it manifests in three distinct phases: monoclinic, hexagonal and cubic. However, the definitive phase of this so-called “hexagonal” remained unconfirmed. Notably, the PXRD patterns of the monoclinic and hexagonal forms exhibit closely aligned peak positions in the literature. The hexagonal form is theoretically expected to display additional PXRD peaks distinct from the monoclinic variant, but such distinctions have not been extensively explored in the literature. Conventionally, differences between NZO-M and NZO-H has been reliant on the relative intensity of two specific PXRD peaks. The NZO-M shows its highest relative intensity at $2\theta = 38.7^\circ$, whereas for the NZO-H, the highest peak intensity appears at $2\theta = 16.2^\circ$. However, the use of other peak intensities for phase identification has not been widely adopted. Instances where samples have been labeled as NZO-H based on the peak at $2\theta = 16.2^\circ$ being the most intense, irrespective of the intensity variations at $2\theta = 38.7^\circ$, exemplify the need for more precise methodologies for phase determination in Na$_2$ZrO$_3$.

Figure 22. 3D electron diffraction (3D ED) data and TEM image of the synthesized NZO-H viewed slightly off-axis from $c^*$, showing well-resolved reflections (black) that can be indexed to a trigonal cell ($a = b = 3.393$ Å, $c = 17.029$ Å), as well as streaks (grey) along the $c^*$-axis.
To investigate the structural complexities of hexagonal Na$_2$ZrO$_3$ (NZO-H), 3D ED analysis was conducted as shown in above. Intriguingly, the reconstructed 3D ED data for NZO-H revealed a composite pattern characterized by distinct diffraction reflections alongside pronounced lines of diffuse scattering along the c* axis. As discussed in Chapter 4.1.1, the occurrence of such diffuse scattering is indicative of structural disorder within the crystal lattice, specifically pointing to the presence of stacking faults. These faults are attributable to the irregular arrangement of Na$^+$ and Zr$^{4+}$ ions in alternating layers along the stacking direction, reflecting a deviation from periodic order in the crystal structure. It can be deduced that Na$_2$ZrO$_3$ not only shares a similar structure with the previously discussed Na$_2$HfO$_3$ but also exhibits an identical stacking sequence. The systematic absence of certain reflections indicated the same space group symmetry as NHO, R-3m. As it initially expected, Na$^+$ and Zr$^{4+}$ cations are each octahedrally coordinated to O$^{2-}$ anions, forming a structure with alternating layers of Na$^+$ and combined Na$^+$ + Zr$^{4+}$. The stacking of Na$^+$ + Zr$^{4+}$ layers in NZO-Xs can occur in multiple configurations, akin to those observed in NHO-Xs. Consequently, if NZO were to exhibit perfect structural order, it could potentially crystallize in the same space groups: C2/m, C2/c, P3$_1$12, and P3$_2$12. However, the simulated PXRD patterns of each space group for these hypothetical, idealized Na$_2$ZrO$_3$ structures do not align with the observed highest relative peak intensity at 20 = 16.2°. This discrepancy led to the hypothesis that structural disorder within the Na$^+$ + Zr$^{4+}$ layers might influence the observed peak intensities, and necessitate a more in-depth structural investigation.
(i) Stacking faults

Figure 23. Simulated PXRD patterns of Na$_2$ZrO$_3$ with 0 to 100% of stacking faults at $2\theta = 10^\circ$ to 60$^\circ$.

To elucidate the impact of stacking faults on the PXRD pattern of Na$_2$ZrO$_3$, simulations were conducted, modelling a range of stacking fault degrees from 0% to 100%, as shown above.

Figure 24. Simulated PXRD patterns of Na$_2$ZrO$_3$ with 0 to 100% of stacking faults at $2\theta = 18^\circ$ to 30$^\circ$.

A notable observation was the broadening of peaks, particularly at $2\theta$ between 18$^\circ$ and 30$^\circ$. The peak at $2\theta = 18.2^\circ$ exhibited an asymmetric character as the degree of stacking faults increased. This trend was confirmed by the
experimental PXRD patterns of NZO-M and NZO-H with the peaks at 2θ = 18.2° and 19.0° displaying significant asymmetry. Based on the simulated PXRD patterns, it was deduced that NZO-M and NZO-H contain approximately 30-50% and over 60% stacking faults, respectively. Interestingly, the relative intensities of the peaks at 2θ = 16.2° and 38.7° appeared to be invariant to the presence of stacking faults.

(ii) Cation site mixing
Beyond stacking faults, cation site mixing can be involved where Na⁺ and Zr⁴⁺ positions in the Na⁺ + Zr⁴⁺ layers were interchanged. The cation site mixing simulations conducted with 10% to 50% revealed changes in the intensities of the same five peaks impacted by stacking faults. As the cation site mixing percentage increased, peak intensities decreased, yet no significant change in peak shape was observed.

Figure 25. Simulated PXRD patterns of Na₂ZrO₃ with 0 to 50% of cation site mixing at 2θ = 10° to 60°.
Indeed, it is important to note that the discussion of these structural defects, particularly stacking faults and cation site mixing, was not explicitly linked to the CO$_2$ capture properties of Na$_2$ZrO$_3$ in the literature. The potential influence of such defects on the CO$_2$ capture capacity of Na$_2$ZrO$_3$ remains an under-explored area. Typically, structural anomalies like stacking faults or cation site disorder can significantly impact the physicochemical properties of Na$_2$ZrO$_3$, potentially altering its adsorption behaviour. However, the specific effects of these structural irregularities on the CO$_2$ capture capacity of Na$_2$ZrO$_3$ have not been extensively investigated, highlighting a gap in the current understanding and an opportunity for further research in this domain.

Figure 26. Simulated PXRD patterns of Na$_2$ZrO$_3$ with 100 to 0% Na$^+$ site occupancy with a (a) $2\theta$ range from 10° to 50° and (b) $2\theta$ range from 15° to 40°.
(iii) Na⁺ site occupancy
The Na⁺ site occupancy can be influenced by the formation or presence of Na₂CO₃, a by-product of the solid-state synthesis and the product of the subsequent carbonation reaction. Consequently, the Na⁺ site occupancy within the Na layer impacted on the relative intensity of specific PXRD peaks, particularly those at 2θ = 16.2° and 38.7°. As demonstrated in the figure above, a reduction in Na⁺ site occupancy in the Na layer from 100% to 0% led to an increase in the relative intensity of the peak at 2θ = 16.2°, while the intensity of the peak at 2θ = 38.7° decreases inversely. Notably, when the Na⁺ site occupancy falls below 50%, the relative intensity of the peak at 2θ = 16.2° surpasses that of the peak at 2θ = 38.7°. These simulation results suggested that Na₂ZrO₃, with less than 50% Na⁺ site occupancy in the Na layer, would exhibit a PXRD pattern akin to what is typically identified as hexagonal Na₂ZrO₃ in existing literature. This identification is based on the relative intensities of the two aforementioned peaks, implying that Na⁺ site occupancy is a critical factor in determining the perceived phase of Na₂ZrO₃.

In Section 4.2.2, attention is directed toward examining how structural defects, particularly those related to Na⁺ site occupancy, affect the CO₂ capture capabilities of the sorbent. This investigation will provide critical insights into the relationship between the structural features of the sorbent and its functional properties in CO₂ capture and storage.

4.2. CO₂ capture capacity on inorganic oxide-based CO₂ sorbents

4.2.1. Sodium hafnium oxide
CO₂ capture capacity was conducted on the synthesized NHO-Xs. In their first carbonation/calcination cycle, both NHO-1 and NHO-1.25 showed nearly identical CO₂ capture capacities, around 15 wt.%. Interestingly, NHO-0.75, NHO-1, and NHO-1.25 not only shared similar CO₂ capture rates but also reached over 80% of their highest capture capacity within roughly 250 seconds.
The CO₂ capture capacity of the synthesized NHO-Xs, (a) five carbonation/calcination cycles at 750 °C, (b) 1st cycle of the five carbonation/calcination cycles, and (c) the normalized curves of the 1st cycle.

The CO₂ capture capacities recorded for NHO-0.5, 0.75, 1, 1.25, and 1.5 at 250 second were 4.98, 10.05, 10.70, 13.80, and 4.04 wt.%, respectively. It is noteworthy that the CO₂ capture rates of NHO-0.5 and NHO-1.5 were significantly slower compared to the other NHO-Xs.
The CO$_2$ capture capacities of the synthesized NHO-Xs were systematically evaluated over a range of temperatures from 600 to 800 °C, increasing at 50 °C intervals. It was observed that, irrespective of the carbonation temperature, the CO$_2$ capture capacities of all the synthesized NHO-Xs remained relatively consistent. Among the NHO-Xs, NHO-1 and NHO-1.25 consistently exhibited excellent CO$_2$ capture capacities across the entire spectrum of tested temperatures. Specifically, at 750 °C, the order of CO$_2$ capture capacities, from highest to lowest, was as follows: NHO-1 > NHO-1.25 > NHO-0.75 > NHO-0.5 > NHO-1.5, with NHO-1 achieving a maximum of 14.54 wt.% and NHO-1.5 reaching 8.54 wt.%. Notably, with the exception of NHO-1.5, the NHO-Xs demonstrated capture capacity nearing 100% of their theoretical maximum.
capacity. However, the rate of CO$_2$ capture was found to be temperature-dependent, with the highest capture rates typically recorded at 750 and 800 °C for all the synthesized NHO-Xs.

The optimal synthesis holding time varied slightly among the different NHO-Xs, impacting their CO$_2$ capture capacity. The order of CO$_2$ capture capacity, based on the optimized holding times, was as follows: NHO-1.25 (3 h) with 15.18 wt.%, NHO-1 (2 h) with 15.1 wt.%, NHO-0.75 (3 h) with 13.03 wt.%, NHO-0.5 (1 h) with 11.91 wt.%, and NHO-1.5 (2 h) with 9.95 wt.%.

Despite these variations, PXRD analysis indicated that the synthesis of Na$_2$HfO$_3$ was essentially complete within 1 h. To ensure the reproducibility of these findings, these experiments were conducted multiple times and on different instruments. Interestingly, a prolonged synthesis holding time of 4 hours resulted in comparatively lower CO$_2$ capture capacities than those sorbents obtained with reduced synthesis durations. This decrease in performance for longer holding times was both unexpected and could not be easily explained.

In summary, under different synthesis conditions tested, NHO-1 (2 h) and NHO-1.25
(3 h) demonstrated the highest CO₂ capture capacities, particularly at 650 °C and 750 °C, compared to all other NHO-Xs.

![Figure 30. Relative CO₂ capture capacity over 100 cycles under the optimized carbonation conditions (a) NHO-1.25 (carbonation at 750 °C), (b) NHO-1.25 (carbonation at 800 °C), and (c) NHO-1 (carbonation at 650 °C). The regeneration was performed at 900 °C for 20 min.](image)

Upon optimizing all the relevant parameters (synthesis time, synthesis holding time, synthesis temperature, heating rate, carbonation temperature, and carbonation time), the cyclic performance and stability of NHO-1 and NHO-1.25 were rigorously evaluated over 100 carbonation/calcination cycles. For NHO-1, the testing encompassed 100 cycles with carbonation conducted at 650 °C. This temperature was selected based on the result of carbonation temperature test. NHO-1.25 conducted a similar cyclic test at two different carbonation temperatures, 750 °C and 800 °C. Notably, both sorbents exhibited remarkable stability over the 100 cycles, irrespective of the carbonation temperature. During the initial cycles, the CO₂ capture capacity of NHO-1 exhibited an increase, followed by a phase of stabilization with a marginal decline over the course of 100 cycles. At the completion of the 100th cycle, the CO₂ capture capacity showed a decrease of 4.87% (equivalent to 0.76 wt.%) from the first cycle. In the case of NHO-1.25, the performance remained robust at both 750 °C and 800 °C, with the CO₂ capture at the 100th cycle dropping by only 2.68% and 2.63% (0.4 and 0.37 wt.%, respectively) in comparison to the initial cycle. Overall, the cyclic stability of NHO-1 and NHO-1.25 can be deemed highly satisfactory, especially when benchmarked against other inorganic oxide-based sorbents with similar functionalities. Their ability to maintain CO₂ capture capacity over extended cycles underscores their potential for practical application in CO₂ capture and storage processes.
4.2.2. Sodium zirconium oxide

In the literature, it is well established that NZO-M (monoclinic Na$_2$ZrO$_3$) exhibits a higher CO$_2$ capture capacity compared to the so-called NZO-H (hexagonal Na$_2$ZrO$_3$), while the NZO-H demonstrates excellent cyclic stability. However, the current investigation revealed that what is traditionally labeled as NZO-H is actually Na$_2$ZrO$_3$ with stacking faults, cation site mixing, and reduced Na$^+$ site occupancy, a re-evaluation of the CO$_2$ capture capacities of these two forms was necessary.

![Figure 31](image.png)

Figure 31. CO$_2$ capture capacity over 20 carbonation/calcination cycles on the synthesized NZO-M and NZO-H.

In the experimental setup, NZO-M and NZO-H underwent 20 carbonation/calcination cycles at 750°C and 900°C, respectively. The initial CO$_2$ capture capacities for NZO-M and NZO-H were recorded at 11.35 wt.% and 13.25 wt.%, respectively, confirming that NZO-M has a higher initial CO$_2$ capture capacity. However, fluctuations in capture capacities were observed in subsequent cycles, with stabilized capturer capacity after approximately 13 cycles. Upon the completion of 20 cycles, the stabilized CO$_2$ capture capacities for NZO-M and NZO-H were similar, at 16.90 wt.% and 17.87 wt.%, respectively. This phenomenon can be explained as follows:

(i) Initially, NZO-M and NZO-H had different degrees of Na$^+$ site occupancies, with NZO-M having a higher occupancy. This resulted in NZO-M having more Na$^+$ and O$^{2-}$ available for reaction with CO$_2$ to form Na$_2$CO$_3$.

(ii) After the first cycle, both samples showed a decrease in Na$^+$ site occupancy due to the formation of Na$_2$CO$_3$, which was not fully reversed during calcination. This was indicated by changes in the relative intensities of PXRD peaks at $2\theta = 16.2^\circ$ and $38.7^\circ$.

(iii) After about 13 cycles, the decrease in Na$^+$ site occupancy stabilized for both samples, leading to a stabilization in their CO$_2$ capture capacities.
(iv) Over 20 cycles, NZO-H displayed less variation in CO$_2$ capture capacity compared to NZO-M, likely due to its initially lower Na$^+$ and O$^{2-}$ site occupancy.

Interestingly, this aligns with the general observation from other studies that “hexagonal” Na$_2$ZrO$_3$ possesses higher cyclic stability than the monoclinic Na$_2$ZrO$_3$. While other changes such as increased stacking faults or cation site mixing disorder might occur during the carbonation/calcination cycles, such alterations were not distinctly identifiable within the scope of this thesis.
4.3. Characterization of inorganic anion pillared metal-organic frameworks

The crystallinity of the synthesized samples, namely VOFFIVE-1-Ni, NbOFFIVE-1-Ni, TaOFFIVE-1-Ni, NbOFFIVE-2-Ni, and TaOFFIVE-2-Ni (NbOFFIVE=NdO\textsubscript{5}^{2–}, 1=pyrazine, 2=aminopyrazine, Ni=Nickel) was verified by PXRD patterns as shown below.

![Figure 32. PXRD patterns of all the synthesized samples (a) VOFFIVE-1-Ni (b) NbOFFIVE-1-Ni (c) TaOFFIVE-1-Ni (d) NbOFFIVE-2-Ni (e) TaOFFIVE-2-Ni.](image)

Moreover, the purity of each sample was confirmed by examining the SEM images as shown in below. Among the synthesized samples, VOFFIVE-1-Ni, NbOFFIVE-1-Ni, and TaOFFIVE-1-Ni exhibited a distinct cubic-like morphology with particle sizes range around 1 to 3 µm. Conversely, the NbOFFIVE-2-Ni and TaOFFIVE-2-Ni samples displayed a sheet-like morphology with dimensions around 1 to 2 µm. Despite the variations in morphology was attributed to the choice of organic ligands, each sample was consistently characterized by a singular morphological form.

![Figure 33. SEM images of all the synthesized samples (a) VOFFIVE-1-Ni (b) NbOFFIVE-1-Ni (c) TaOFFIVE-1-Ni (d) NbOFFIVE-2-Ni (e) TaOFFIVE-2-Ni.](image)
The M$^{5+}$−F$^{-}$ bond distances in the synthesized samples, crucial determinants of their pore sizes, were accurately refined through Pawley and Rietveld refinements. The refinement showed good $R_{wp}$ values and demonstrated a close match between the calculated and observed PXRD patterns, with only minor discrepancies as shown below.

![Figure 34](image)

In these structures, each M$^{5+}$ ion is octahedrally coordinated by five F$^{-}$ ions, and the strength of these coordination bonds significantly influences the M$^{5+}$−F$^{-}$ bond lengths. Furthermore, the F$^{-}$⋯F$^{-}$ distance across two opposing inorganic pillars is primarily dictated by the M$^{5+}$−F$^{-}$ bond lengths of these
pillars. This inter-pillar distance is a critical parameter in tuning the pore apertures of the synthesized samples. A contraction in the $M^{5+}$–$F^-$ bond distance leads to an expansion of the $F^-\cdots F^-$ distance, and consequently, the pore aperture. The obtained bond lengths and pore apertures were summarized below.

Table 4. Unit cell parameters and interatomic distances of all the synthesized samples.

<table>
<thead>
<tr>
<th></th>
<th>VOFFIVE-1-Ni</th>
<th>NbFFIVE-1-Ni</th>
<th>TaOFFIVE-1-Ni</th>
<th>NbOFFIVE-2-Ni</th>
<th>TaOFFIVE-2-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$ [Å]</td>
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</tr>
<tr>
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<td>1.94</td>
<td>1.91</td>
</tr>
<tr>
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</tr>
<tr>
<td>$d_{Ni-Ni}$ [Å]</td>
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<td>1.91</td>
<td>2.13</td>
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<td>2.13</td>
<td>2.10</td>
<td>2.22</td>
<td>2.24</td>
</tr>
</tbody>
</table>

In order to evaluate the porosity of the synthesized samples, N$_2$ sorption isotherms were recorded in the pressure range of 0 to 1 bar at 77 K. Subsequently, BET method was employed to calculate the specific surface area. While the BET surface area was calculated for each sample, as detailed below, the reliability of these result warrants caution. This is attributed to the fact that the adjusted pore aperture in the samples are either very similar to or smaller than the kinetic diameter of N$_2$ molecules, potentially impacting the accuracy of the BET analysis in assessing the true surface area and porosity of these samples.
Figure 35. The calculated BET surface area of the synthesized samples (a) VOFFIVE-1-Ni (b) NbFFIVE-1-Ni (c) TaOFFIVE-1-Ni (d) NbOFFIVE-2-Ni (e) TaOFFIVE-2-Ni through N₂ sorption.

In order to conform the water stability of all the synthesized samples, water sorption isotherms were recorded in the pressure range of 0 to 1 bar at 293 K. Additionally, the synthesized samples were soaked in water for three months and monitored by PXRD patterns. This observation indicates the hydrophobicity and the exceptional water stability of all the samples, further enhancing their potential as promising alternatives for effective adsorption in low-concentration CO₂ removal applications.
Figure 36. Water sorption isotherms of all the synthesized samples (a) VOFFIVE-1-Ni (b) NbOFFIVE-1-Ni (c) TaOFFIVE-1-Ni (d) NbOFFIVE-2-Ni (e) TaOFFIVE-2-Ni and (f) water stability of all the synthesized samples.
4.4. CO$_2$ capture capacity on inorganic anion pillared metal-organic frameworks

The adsorption (CO$_2$ capture) experiments were appropriately conducted under conditions that are similar to ambient conditions as the synthesized samples. These conditions included a temperature setting of 20 °C and a CO$_2$ concentration of 400 ppm (0.4 mbar), which are representative of typical atmospheric temperature and CO$_2$ levels for DAC scenarios. This approach ensures that the performance of the sorbent is evaluated under realistic conditions, providing valuable insights into its efficacy and potential for real-world applications in capturing CO$_2$ directly from the air.

![CO$_2$ sorption isotherms](image)

Figure 37. The CO$_2$ sorption isotherms of all the synthesized samples VOFFIVE-1-Ni, NbOFFIVE-1-Ni, TaOFFIVE-1-Ni, NbOFFIVE-2-Ni, and TaOFFIVE-2-Ni from 0 to 3 mbar at 293 K.
CO$_2$ sorption isotherms revealed distinct adsorption capacities among the samples. NbOFFIVE-1-Ni exhibited the highest CO$_2$ adsorption capacity at 1.45 mmol g$^{-1}$. This was followed by TaOFFIVE-1-Ni with 1.18 mmol g$^{-1}$, and VOFFIVE-1-Ni with 0.67 mmol g$^{-1}$. Notably lower uptakes were observed in NbOFFIVE-2-Ni and TaOFFIVE-2-Ni, at 0.02 mmol g$^{-1}$ and 0.01 mmol g$^{-1}$, respectively. The excellent CO$_2$ adsorption in NbOFFIVE-1-Ni can be attributed to its optimal pore aperture, which enhances electrostatic interactions between the framework and CO$_2$ molecules, enabling efficient adsorption. The guest CO$_2$ molecules are ideally situated in proximity to the adsorption sites. Interestingly, despite having a smaller pore aperture, TaOFFIVE-1-Ni showed a slightly reduced CO$_2$ adsorption capacity compared to NbOFFIVE-1-Ni. This suggests that the pores in TaOFFIVE-1-Ni might be too narrow for effective diffusion and adsorption of CO$_2$ molecules. In the case of VOFFIVE-1-Ni, its larger pore aperture relative to NbOFFIVE-1-Ni and TaOFFIVE-1-Ni likely results in weaker electrostatic interactions with CO$_2$, leading to its lower adsorption capacity. Moreover, the amino-functional groups in MOFFIVE-2-Ni series, which generally have a strong affinity for CO$_2$, could impede the diffusion of CO$_2$ through the pores in NbOFFIVE-2-Ni and TaOFFIVE-2-Ni due to the narrowness of these apertures. Consequently, the minimal CO$_2$ adsorption capacity observed in NbOFFIVE-2-Ni and TaOFFIVE-2-Ni aligns with expectations, underscoring the critical influence of pore dimensions on the adsorption characteristics of these materials.

VOFFIVE-1-Ni demonstrated the fastest CO$_2$ physisorption kinetics among the tested samples, with NbOFFIVE-1-Ni and TaOFFIVE-1-Ni closely following. In situ IR spectroscopy, performed at 0.13 kPa (1.3 mbar) and monitored at intervals of 0.3 seconds for a duration of 3600 seconds, revealed that the asymmetric stretching of CO$_2$ ($\nu_3$, approximately 2320-2360 cm$^{-1}$) was most pronounced in VOFFIVE-1-Ni. The appearance of more than one binding site indicates the likelihood of multiple binding sites within the framework, possibly arising from the disordered structure of its inorganic pillars. Theoretically, the MOF $5^{2-}$ pillar could offer up to six different configurations of O$^2-$ and F$^-$ atoms, each representing a distinct binding site. However, detailed identification of the most favourable binding sites would require advanced computational studies like density functional theory (DFT) simulations, which consider it as future work. Despite the lower CO$_2$ adsorption capacity of VOFFIVE-1-Ni at 400 ppm compared to NbOFFIVE-1-Ni and TaOFFIVE-1-Ni, it exhibited faster adsorption rates. This observation corresponds with the sizes of the pore apertures, where VOFFIVE-1-Ni has the largest, followed by TaOFFIVE-1-Ni and NbOFFIVE-1-Ni. The analysis of the kinetics of CO$_2$ adsorption suggests that larger pore apertures, as seen in VOFFIVE-1-Ni, may confer kinetic advantages in CO$_2$ adsorption, potentially enhancing the overall efficiency of the adsorption process.
In order to evaluate the cyclic (thermal) stability of all the synthesized samples, multiple adsorption/desorption cycles were conducted. Remarkably, all the samples demonstrated outstanding cyclic stability, exhibiting less than 0.3% decrease in CO$_2$ adsorption capacity after 10 cycles. This minimal degradation in performance underscores their robustness under repeated adsorption/desorption conditions. The demonstrated high cyclic stability, coupled with excellent water stability, markedly position them as good candidates for DAC applications. The dual resilience of these HUMs to thermal cycling and exposure to moisture not only improve their durability but also significantly bolsters their suitability for practical use across a wide range of environmental conditions. This versatility enhances the potential for their deployment in various CO$_2$ capture and storage scenarios.
Figure 39. Cyclic stability of all the synthesized samples; VOFFIVE-1-Ni, NbFFIVE-1-Ni, TaOFFIVE-1-Ni, NbOFFIVE-2-Ni, and TaOFFIVE-2-Ni.

The M’OFFIVE-1-Ni (M’ = V$^{5+}$, Nb$^{5+}$, and Ta$^{5+}$) samples, characterized by their exceptional cyclic (thermal) and water stability, leaded an investigation into their potential for capturing CO$_2$ from flue gas at point sources however, at reduced temperatures. To this end, adsorption/desorption cyclic experiments were conducted using a gas mixture comprising 15% CO$_2$ and 85% N$_2$. These tests were performed at elevated temperatures of 50 and 100 °C, a significant increase from the initial experimental condition of 25 °C. The findings from these experiments revealed a discernible decrease in the overall CO$_2$ capture capacity at these heightened temperatures when compared to the results obtained at the lower temperature. However, a critical observation was the consistent cyclic stability of the sorbent, which remained unaltered despite the temperature increase. This enduring stability across varying temperatures is showed in the figure below, highlighting the robust nature of the M’OFFIVE-1-Ni samples for potential applications in CO$_2$ capture from flue gases, even under varied thermal conditions.
Figure 40. CO₂ capture capacity of (a) VOFFIVE-1-Ni (b) NbOFFIVE-1-Ni (c) TaOFFIVE-1-Ni at 50°C and 100°C.
4.5. Conclusion and Future work

This thesis was devoted to the development and optimization of CO\textsubscript{2} sorbents suitable for two distinct applications: capturing CO\textsubscript{2} from point sources and DAC. First of all, Na\textsubscript{2}HfO\textsubscript{3} was proposed as a potential sorbent for CO\textsubscript{2} capture from point sources. The fundamental concept behind this design combined the molten salt effects on inorganic oxide, which inherently lack CO\textsubscript{2} capture capacity, to induce CO\textsubscript{2} capture properties. In this process, Na\textsubscript{2}HfO\textsubscript{3} was synthesized as a CO\textsubscript{2} sorbent exhibiting commendable thermal and cyclic stability. This was achieved by combining Na\textsubscript{2}CO\textsubscript{3}, known for its molten salt properties, with HfO\textsubscript{2} which recognized for its thermal stability. Throughout the thesis, the synthesized Na\textsubscript{2}HfO\textsubscript{3} underwent various optimization steps based on a variety of synthesis and operational parameters. These optimization steps were critical in enhancing the sorbent’s performance and efficiency. Despite the various optimizations, further studies involving CO\textsubscript{2} capture experiments with real-life flue gas and additional cyclic stability tests are required as future work. This will not only validate the practical applicability of the developed Na\textsubscript{2}HfO\textsubscript{3} sorbent, but also contribute to the broader understanding of its performance in real-world industrial settings, particularly for CO\textsubscript{2} capture from point sources.

The process of optimizing Na\textsubscript{2}HfO\textsubscript{3} as a CO\textsubscript{2} sorbent revealed structural disorder. It led a deeper investigation into Na\textsubscript{2}ZrO\textsubscript{3} which is a chemically analogous CO\textsubscript{2} sorbent. The first comprehensive study to address the structural disorder in Na\textsubscript{2}ZrO\textsubscript{3}, thereby significantly improving our understanding of this sorbent. The structural disorder of Na\textsubscript{2}ZrO\textsubscript{3} not only provided new insights into its behaviour in CO\textsubscript{2} capture but also bridged a 60-year knowledge gap in the field.

Finally, the design of HUMs specifically tailored as a CO\textsubscript{2} sorbent was successfully conducted for DAC application. A key focus was on adjusting the M\textsuperscript{5+-}F\textsuperscript{-} bond lengths (where M = V\textsuperscript{5+}, Nb\textsuperscript{5+}, and Ta\textsuperscript{5+}) in the inorganic pillars. The variations in these bond lengths resulted in distinct pore aperture sizes for the MOFFIVE-1-Ni samples. These structural modifications were found to influence the CO\textsubscript{2} capture properties, particularly the capacity and kinetics of CO\textsubscript{2} capture, due to the presence of different inorganic pillars. This finding offers new insights into how structural tuning can enhance not only the CO\textsubscript{2} capture capacity but also the adsorption kinetics. In addition, all the synthesized samples exhibited outstanding cyclic and water stability, reinforcing their potential as effective sorbents for practical DAC applications. However, despite the literature research conducted, the dynamics of inorganic pillars and linkers, particularly the behaviour of M\textsuperscript{5+-}F\textsuperscript{-} bonding and pyrazine upon CO\textsubscript{2} capture, remain under-explored. We posit that further investigation into the interactions between M\textsuperscript{5+-}F\textsuperscript{-} bonding and pyrazine could be a crucial area of research, providing a deeper understanding of the behaviour of HUMs and
potentially unveiling new avenues for the development of more efficient CO₂ capture technologies.

4.6. Svensk smmanfattning


Processen med att optimera Na₂HfO₃ som CO₂-sorbent avslöjade strukturella störningar. Det ledde till en djupare undersökning av Na₂ZrO₃, som är en kemiskt analog CO₂-sorbent. Den första omfattande studien som behandlar strukturella störningar i Na₂ZrO₃, vilket avsevärt förbättrar vår förståelse av denna sorbent. Den strukturella störningen i Na₂ZrO₃ gav inte bara nya insikter om dess beteende vid koldioxidavskiljning utan också bidrog till en bredare förståelse av dess prestanda i verkliga industrial miljöer, särskilt för CO₂-avskiljning från punktkällor.

Slutligen genomfördes framgångsrikt utformningen av HUMs specifikt skråddarsydda som en CO₂-sorbent för DAC-tillämpning. Ett viktigt fokus var att justera bindningslängderna M⁵⁺−F⁻ (där M = V⁵⁺, Nb⁵⁺ och Ta⁵⁺) i de oorganiska pelarna. Variationerna i dessa bindningslängder resulterade i olika poröppningsstorlekar för MOFFIVE-1-Ni-proverna. Dessa strukturella modifieringer visade sig påverka CO₂-avskiljningsegenskaperna, särskilt kapaciteten och kinetiken för CO₂-avskiljning, på grund av närvaron av olika oorganiska pelare. Detta resultat ger nya insikter om hur strukturella justeringar kan förbättra inte bara CO₂-avskiljningskapaciteten utan även adsorptionskinetiken. Dessutom uppvisade alla syntetiserade prover enastående cyklisk stabilitet och vattenstabilitet, vilket förstärker deras potential som effektiva sorbenter för praktiska DAC-tillämpningar. Trots den
litteratursökningar som genomförts är dock dy-namiken hos oorganiska pelare och länkare, särskilt beteendet hos $\text{M}^5\text{F}^-$ bindning och pyrazin vid CO$_2$-fångst, fortfarande underutforskad. Vi menar att ytterligare undersökningar av interaktionen mellan $\text{M}^5\text{F}^-$ bindning och pyrazin kan vara ett viktigt forskningsområde, som ger en djupare förståelse av HUMs beteende och potentiellt avslöjar nya vägar för utveckling av effektivare teknik för koldioxidavskiljning.
I want to thank my main supervisor, Ocean Cheung, for your support and guidance throughout my PhD journey. Your advice and discussions have been foundational to my works. I am grateful for the close mentorship and the care you have shown. I'll be rooting for you on your journey, just as you have for mine.

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Ken Inge, who is sometimes my colleague and always my best friend. Meeting you has been one of the biggest blessings of my entire PhD journey. When we worked together, I learned a lot from your passion and mindset, and your knowledge of structures has been nothing short of amazing. But more than that, I'm so thankful for all the support you've given me. You've been there for me more than anyone else, and I'll be there for you always!
사랑하는 모든가족들, 항상 편안한 사랑과 밤들을 보내시길 캐나다합니다. 
네가 편안하게 자는 모습을 보는 것만으로도 마음이 편안해질 수 있었어. 매번 지하철 주 화물에서 
가만히, 무침없이 지내시는 모습이 얼마나 아름답고, 매번 당신을 보며, 당신의 모습을 청취해주던 
모든 것을 돌려 보고 싶었어. 운전히, 당신의 모습을 보며, 당신의 모습을 청취해주던 
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