FERRITE-BASED OXIDES: PREPARATION, CHARACTERIZATION AND CARBON DIOXIDE ADSORPTION STUDY

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by

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LIST OF SYMBOLS

%	Percentage
±	Plus-minus
°	Degree
Al	Aluminium
°C	Degree Celsius
CO_2	Carbon dioxide
Fe	Ferrite
g	Gram
h	Hour
K	Kelvin
k_1	Kinetic rate constant for pseudo-first order
k_2	Kinetic rate constant for pseudo-second order
m	Meter
mg	Milligram
min	Minute
mL	Milliliter
mmol	Millimole
mol %	Mol percent
N_2	Nitrogen
nm	Nanometer
ppm	Parts per million
R^2	Correlation coefficient
s	Solid
S_{bet}	BET specific surface area
vol %	Volume percent

wt %	Weight percent
θ	Theta
λ	Wavelength

LIST OF ABBREVIATIONS

AC	Activated carbon
AMOST	Aqueous miscible organic solvent treatment
AP	Aminopropyltriethoxysilane
BECCS	Bioenergy with carbon capture and storage
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CA	Citric acid
CCS	CO_2 capture and storage
CCU	Carbon capture and utilization
CCUS	Carbon capture, utilization and storage
CTAB	Cetyl-*N,N,N*-trimethylammonium bromide
CTAC	Cetyltrimethylammonium chloride
DAC	Direct air capture
DETA	Diethylenetriamine
DTG	Derivative thermogravimetry
EIA	Energy Administration
FTIR	Fourier Transform Infrared
FWHM	Full width at half maximum
GHG	Greenhouse gas
HNTs	Halloysite nanotubes
HTlc	Hydrotalcite
IL	Ionic liquid
IL-CP	Ionic liquid-conjugated polymer
IPCC	Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder and Applied Chemistry
LDH	Layered double hydroxides
LTA	Linde-Type A
MEA	Monoethanolamine
MI	Metal ions
MOFs	Metal-organic frameworks

NAD	Nitrogen adsorption-desorption
NMR	Nuclear magnetic resonance
PAA	Polyacrylic acid
PAN	Polyacrylonitrile
PEI	Polyethyleneimine
SEM-EDX	Scanning electron microscopy-energy dispersive X-ray spectroscopy
STP	Standard temperature and pressure
TGA	Thermogravimetric analysis
WMO	World meteorological organization
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

OKSIDA BERASASKAN FERIT: PENYEDIAAN, PENCIRIAN DAN KAJIAN PENJERAPAN KARBON DIOKSIDA

ABSTRAK

Sebagai tindak balas terhadap permintaan yang semakin meningkat bagi teknologi penangkapan karbon yang berkesan, kajian ini menyelidik sintesis dan pencirian bahan penjerapan pepejal berasaskan ferit disediakan dengan menggunakan kaedah mudah sol-gel. Objektif utama adalah untuk meningkatkan kapasiti penjerapan, kebolehgunaan semula dan sifat struktur bahan penjerap. Selain itu, okdisa berasaskan ferit ternar dan kuaterner telah melihat pejelajahan yang terhad dalam bidang penangkapan karbon yang sebahagian besarnya disebabkan oleh banyaknya kajian yang memfokuskan kepada oksida logam tunggal yang ringkas. Sistem pelbagai-logam yang kompleks ini menawarkan potensi untuk sifat penjerapan CO_2 yang lebih baik tetapi masih kurang dimanfaatkan. Dalam kajian ini, ferit spinel songsang bersama dengan bahan penjerap heksaferit jenis M dan W telah berjaya disintesis menggunakan kaedah kos rendah, mudah dan berkesan. Kapasiti penjerapan CO_2 oleh bahan penjerap ini dinilai melalui analisis termogravimetri. Oksida berasaskan ferit telah disintesis di bawah keadaan terbaik dengan suhu tindak balas 80 °C, nisbah optimum asid sitrik kepada ion logam (CA:MI) 1.2:1, masa tindak balas 30 minit dan masa pengkalsinan 4 jam. $NiFe_2O_4$, $BaFe_{12}O_{19}$ dan $BaNi_2Fe_{16}O_{27}$ masing-masing menunjukkan kapasiti penjerapan CO_2 sebanyak 11.31 mg g^{-1}, 17.33 mg g^{-1}, and 20.43 mg g^{-1}. $BaNi_2Fe_{16}O_{27}$ yang terdop dengan Al menunjukkan sifat yang dipertingkatkan. Ini menunjukkan prestasi penjerapan yang lebih baik berbanding bahan penjerap yang tidak terdop. Di bawah keadaan penjerapan optimum (3 mg bahan penjerap, kadar aliran 10 mL min^{-1}), $BaNi_2Fe_{16}O_{27}$ yang terdop dengan Al memaparkan

kapasiti penjerapan sebanyak 40.66 mg g^{-1} berbanding 20.46 mg g^{-1} yang dicapai oleh $BaNi_2Fe_{16}O_{27}$ tanpa dop pada suhu 30 °C. Pendopan meningkatkan luas permukaan dan isipadu liang, seperti yang disahkan melalui analisi BET yang menunjukkan peningkatan luas permukaan spesifik daripada 57.230 to 78.704 m^2 g^{-1} dan isipadu liang daripada 0.20141 kepada 0.42930 cm^3 g^{-1}, sekaligus menyediakan permukaan yang lebih besar dan lebih mudah diakses untuk molekul CO_2 berinteraksi. Pendopan Al ke dalam $BaNi_2Fe_{16}O_{27}$ membawa kepada peningkatan bilangan tapak asas aktif, yang menguatkan interaksi antara bahan penjerap dan molekul CO_2. Bahan penjerap terdop Al menunjukkan kebolehgunaannya semula yang baik dengan mengekalkan aktiviti penjerapan yang tinggi sepanjang lima kitaran., serupa dengan prestasi bahan penjerap yang tanpa dop. Walaupun lima kitaran menunjukkan kebolehlaksanaan dan kecekapan regenerasi yang baik bagi kedua-dua $BaNi_2Fe_{16}O_{27}$ yang didop and tidak didop, bahan penjerap yang diimpregnasi HNT telah meningkatkan prestasi penjanaan semula yang lebih baik. Oleh itu, $BaNi_2Fe_{16}O_{27}$ yang didop dengan Al kemudiannya diimpregnasi ke dalam HNT untuk meningkatkan keupayaan penjerapannya dan kestabilan sepanjang kitaran yang berpanjangan. Bahan penjerap komposit HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ menunjukkan prestasi penjerapan CO_2 yang lebih tinggi dengan kapasiti sebanyak 58.61 mg g^{-1} pada 30 °C dan 70.17 mg g^{-1} pada 50°C berbanding dengan kedua dua varian $BaNi_2Fe_{16}O_{27}$ yang tanpa dop dan terdop. Prestasi penjerapan CO_2 tertinggi dicapai dengan menggunakan 12 wt % HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$. Penjerapan yang unggul oleh HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ adalah disebabkan oleh luas permukaan yang lebih besar (90.53 m^2 g^{-1}), dan isipadu liang (0.4229 cm^3 g^{-1}) berbanding varian tidak didop dan didop, serta peningkatan ketersediaan tapak aktif berasas. Tambahan pula, kebesan HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ adalah jauh lebih tinggi pada 2.770 mmol g^{-1}, berbanding 0.843 mmol g^{-1} bagi yang tidak didop dan 1.412

mmol g^{-1} bagi $BaNi_2Fe_{16}O_{27}$ yang didop, yang turut menyumbang kepada prestasi penjerapan CO_2 yang lebih unggul. Penjerapan oleh semua bahan penjerap mengikut model kinetik tertib pseudo-kedua. Tambahan lagi, bahan penjerap komposit HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ menunjukkan kebolehgunaan semula yang lebih tinggi dan mengekalkan kecekapan lebih daripada 95 % selepas lima kitaran. Semua bahan penjerap oksida berasaskan ferit menunjukkan keupayaan untuk penjerapan CO_2, menawarkan potensi besar dalam pemulihan alam sekitar bagi mengurangkan pelepasan gas rumah hijau dan menangani perubahan iklim.

FERRITE–BASED OXIDES: PREPARATION, CHARACTERIZATION AND CARBON DIOXIDE ADSORPTION STUDY

ABSTRACT

In response to the growing demand for effective carbon capture technologies, this study investigates the synthesis and characterization of ferrite–based oxides solid adsorbents prepared using a facile sol-gel method. The primary aim is to enhance the adsorption capacity, reusability and structural properties of the adsorbent. Besides, ternary and quaternary ferrite–based oxides have seen limited exploration in the field of carbon capture, largely due to the prevalence of studies focusing on simpler single metal oxides. These complex multi-metal systems offer the potential for enhanced CO_2 adsorption properties yet remain underutilized. In this study, inverse spinel ferrite along with M-type and W-type hexaferrite adsorbents, were successfully synthesized using low-cost, facile and efficient method. The CO_2 adsorption capacity of the adsorbent was evaluated through thermogravimetric analysis. The ferrite–based oxides were synthesized under best conditions with a reaction temperature of 80 °C, the optimal citric acid to metal ion (CA:MI) of 1.2:1, a reaction time of 30 minutes and a calcination time of 4 hours. $NiFe_2O_4$, $BaFe_{12}O_{19}$ and $BaNi_2Fe_{16}O_{27}$ displayed CO_2 adsorption capacities of 11.31 mg g^{-1}, 17.33 mg g^{-1}, and 20.43 mg g^{-1}, respectively. The Al–doped $BaNi_2Fe_{16}O_{27}$ exhibited enhanced properties. It showed superior adsorption performance compared to the undoped adsorbent. Under optimum adsorption conditions, (3 mg adsorbents, 10 mL min^{-1} of flow rate), the Al–doped $BaNi_2Fe_{16}O_{27}$ displayed 40.66 mg g^{-1} of adsorption capacity at 30 °C. Al-doping increases the surface area and pore volume, as confirmed by BET analysis showing an increase from 57.230 to 78.704 m^2 g^{-1} and pore volume from 0.20141 to 0.42930 cm^3

g^{-1} providing a larger and more accessible surface for CO_2 adsorption. The doping of Al into the $BaNi_2Fe_{16}O_{27}$ leads to an increased number of active basic sites, which strengthens the interaction between the adsorbent and CO_2 molecules. The Al-doped adsorbent showed better reusability, maintaining high adsorption activity over five cycles, similar to the performance of the undoped adsorbent. Although five cycles demonstrate good viability and regeneration efficiency for both doped and undoped $BaNi_2Fe_{16}O_{27}$, impregnating the adsorbent with HNTs significantly enhanced its long-term performance. Therefore, the Al-doped $BaNi_2Fe_{16}O_{27}$ was further impregnated into HNTs to improve its adsorption capacity. The HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ composite adsorbent demonstrated higher CO_2 adsorption performance achieving a capacity of 58.61 mg g^{-1} at 30 ℃ and 70.17 mg g^{-1} at 50 ℃ compared to both the undoped and doping variants of $BaNi_2Fe_{16}O_{27}$. The highest CO_2 adsorption performance was achieved by using 12 wt % of $BaNi_2Fe_{16-x}Al_xO_{27}$ loading. The superior adsorption of HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ is attributed to its significantly higher surface area (90.53 m^2 g^{-1}) and pore volume (0.4229 cm^3 g^{-1}) compared to the undoped and doped variants along with enhanced availability of basic active sites. In addition, the basicity of HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ is significantly higher at 2.770 mmol g^{-1}, compared to 0.843 mmol g^{-1} for undoped and 1.412 mmol g^{-1} for the doped $BaNi_2Fe_{16}O_{27}$ which further contributing to its superior CO_2 capture performance. The adsorption by all adsorbents followed the pseudo-second order kinetic model. Furthermore, HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ composite adsorbent exhibited greater reusability and maintain over 95 % efficiency after five cycles. All ferrite–based oxide adsorbents demonstrated capability for CO_2 adsorption, serving as a great potential in environmental remediation for reducing greenhouse gas emissions and combating climate change.

CHAPTER 1

INTRODUCTION

1.1 Background

1.1.1 Climate change and CO_2 emission

Global warming has attracted the attention of many researchers and environmental scientists. It is mainly due to the rapid increase in population and energy consumption worldwide. High magnitudes of greenhouse gases released into the air has contributed to climate disasters. According to the Energy Administration (EIA), energy consumption is expected to increase by 57 % in 2030 (Santamouris and Vasilakopoulou, 2021). The emission of greenhouse gases contributes to most environmental problems and CO_2 is the major greenhouse gas that contributes to global warming (Kabir *et al*., 2023; Filonchyk *et al*., 2024). In addition, approximately 60 % of global warming effects are attributed to CO_2 emissions (WMO, 2023).

In the past, the total amount of CO_2 was relatively maintained at 280 ± 10 ppm and the atmospheric sink was considered large enough to accommodate any additional CO_2. This was until the industrial revolution. The amount of CO_2 has risen by more than a third since the industrial revolution. In the year 2000, the amount of CO_2 reached 368 ppm and this increased to 388 ppm in 2010 (Rackley, 2017). Currently, the amount of CO_2 is increasing by two ppm per year in the atmosphere, suggesting that CO_2 emitted remains in the atmosphere. The atmosphere may contain up to 570 ppm of CO_2 in 2100 causing a rise of approximately 3.2 °C in the mean global temperature and an increase of 3.8 m in the mean sea level according to the Intergovernmental Panel on Climate Change (IPCC). There are four potential sources of CO_2 emission

which are from the industrial processes, fossil-fueled power plants, de-carbonization and transportation. Among the CO_2 emission sources, fossil-fueled power plants are the main source of CO_2 with 81 % of the world's commercial energy supply (Carpanez *et al*., 2024). The fossil fuel emission level is shown in Table 1.1.

Table 1.1. Fossil fuel emission levels (IEA, 2024).

Pollutant	Natural Gas	Coal	Oil
Carbon dioxide	117000	208000	164000
Carbon monoxide	40	208	33
Nitrogen oxides	92	457	448
Sulphur dioxide	1	2591	1122
Particulates	7	2744	84
Mercury	0	0.016	0.007
Total	**117140**	**214000**	**165687**

1.1.2 CO_2 capture

There are several approaches that can be implemented to reduce the total CO_2 emission in the atmosphere such as improving energy efficiency to lower energy intensity, reducing carbon intensity through the use of alternatives fuels such as hydrogen and renewable energy source and enhancing CO_2 sequestration by developing advanced carbon capture materials (Min *et al*., 2022). CO_2 capture and storage (CCS) have been receiving significant attention in recent years and are being recognized as promising options for CO_2 emission reduction (Turgut *et al*., 2022). Adsorption is the most suitable technologies for CO_2 capture from atmosphere than other technologies that is widely used in CCS process. Recently, the capture of CO_2 directly from atmosphere has generated extensive research interest (Wu *et al*., 2024). Two approaches are currently being used to capture CO_2 from the atmosphere which is through solid and liquid adsorbents. Liquid adsorbent relies on an aqueous basic solution such as potassium hydroxide operating at high temperature (300–900 ℃). Meanwhile, solid adsorbent is based on solid materials that function effectively at

ambient temperature and pressure. Unlike liquid systems, solid adsorbents do not pose issues related to corrosion or water loss, making them a more practical and energy-efficient alternative for atmospheric CO_2 capture.

In recent years, CO_2 adsorption using dry regenerable solid adsorbents has emerged as an advanced strategy for carbon capture. Various microporous and mesoporous solid adsorbents have been explored for CO_2 capture including, metal oxides, hydrotalcite like compounds, carbon-based materials, zeolites and metal-organic frameworks (MOFs) (Petrovic *et al*., 2021). These studies not only focus on enhancing the material properties and performance but also with functional group modification and stability enhancement of the materials with the help of effective methods (Khosrowshahi *et al*., 2024). An ideal adsorbent should exhibit high CO_2 adsorption performances, while also being cost-effective, scalable and fast kinetic performance. Metal oxides have shown great potential and emerged as promising materials for CO_2 adsorption due to their favorable structural and chemical properties. Many metal oxides possess a large specific surface area and a high number of active sites which facilitate effective interaction with CO_2 molecules and advantageous in adsorption (Ong *et al*., 2018). Their surface basicity is particularly important for binding acidic CO_2 molecules through chemisorption or carbonate formation. Furthermore, metal oxides are widely available and making them attractive candidates for large-scale CO_2 capture technologies (Gao *et al*., 2024; Ma *et al*., 2025). The remarkably high CO_2 capture capacities in metal oxides can be ascribed to the strong affinity of metal cations towards CO_2 molecules as well as the Lewis basic sites presented on the surface of metal oxides.

The doping and structural modification have attracted continuous research interest as a method to enhance the performance of metal oxides (Wu *et al*., 2025). The limited adsorption capacity on metal oxides is the main reason driving these efforts as introducing dopants or modifying the crystal structure can increase the surface area, creates additional active sites and improves pore structure. However, excess additional active sites give pore-blockage during surface functionalization modification. This blockage can cause steric hindrance, impeding the diffusion of CO_2 molecules into the adsorbent. Consequently, the overall efficiency of CO_2 adsorption can be compromised. Thus, several supports were used as impregnated for CO_2 adsorbents such as activated carbon (AC), silica, carbon nanotubes and halloysite nanotubes (HNTs) (Jena *et al*., 2019; Khandaker *et al*., 2020; Sharma *et al*., 2021; Kamran and Park, 2021). The impregnation metal oxides using natural clay mineral is effective in rectifying the issues that arise during the adsorption (Khoshraftar *et al*., 2021). Impregnation provides higher CO_2 adsorption capacity and more efficient capture performance. Expanding the production and development of adsorbents with abilities such as enhancing adsorption capacity, cost-effectiveness and high efficiency is one of the efficient solutions to meet the challenges of CO_2 capture (Adhikari *et al*., 2018; Taheri *et al*., 2019). The impregnation with supporting materials has been regarded as a constructive strategy that has garnered considerable attention due to its availability, reliability, low cost and high stability of the adsorbent.

1.2 Problem statement

Environmental pollution has become a serious issue due to the rapid development of urbanization and industrialization. Notably, this issue significantly contributes to rising atmospheric CO_2 levels. To address this problem, various CCS technologies have been developed, aiming to reduce CO_2 emissions and mitigate their

impact on climate change. There is a great need to develop a low-cost and effective solid adsorbent for the safety of environment.

Besides CaO and amine-based solids, ferrite–based oxides is one of the promising adsorbents owing to its low price, chemical stability, and tunable structural properties. However, despite its versatility, ferrite–based oxides exhibit relatively lower CO_2 adsorption capacity compared to advanced materials such as amine-functionalized adsorbents or metal–organic frameworks (MOFs) (Bagherinasab *et al*., 2020). This limitation is primarily linked to factors such as restricted surface area, suboptimal pore structures, and insufficient active site availability. To date, most single metal oxide adsorbents cannot meet the demands to capture high amounts of CO_2 from the atmosphere (Hakim *et al*., 2016). Therefore, these issues must be addressed for high adsorption performance and for practical application of ferrite–based oxides. A systematic approach is applied by comparing single ferrite–based oxides with different crystal structure (ternary and quaternary) to evaluate their structural influence on CO_2 adsorption. Despite all extensive studies, the application of ternary and quaternary ferrite–based oxides specifically for CO_2 adsorption remains largely unexplored.

Additionally, the application of ferrite–based oxides for CO_2 adsorption faces the inherent challenge of limited adsorption capacity, primarily due to their insufficient surface area and number of active sites. This limitation drives the need for structural modifications, such as doping or crystal structure adjustment, to enhance surface area, create additional active sites, and improve pore structure for more effective CO_2 capture. However, during doping or surface modification, the introduction of excessive active sites may lead to pore blockage, causing steric hindrance that limits the diffusion of CO_2 molecules into the adsorbent structure (Elvira *et al*., 2017). Thus, impregnation

of adsorbent onto a support is one of the alternatives to overcome this problem. This approach could minimize the percentage of adsorption capacity loss during reusability by enhancing structural stability, and maintaining accessible pore structures throughout multiple adsorption–desorption cycles, ultimately improving the long-term performance and economic viability of the CO_2 capture process.

While sol-gel methods have been widely employed for the synthesis of ferrite–based oxides due to their simplicity, cost-effectiveness, and ability to control particle size, crystallinity, and porosity, this approach presents challenges. The process relies on chelating agents such as citric acid (CA) or others to form stable metal–ligand complexes, ensuring homogeneous mixing and preventing unwanted precipitation. However, the method is highly sensitive to reagent ratios and pH control. An adequate amount of chelating agent is required to complete chelation, but excessive it can create an overly acidic environment that disrupts its own dissociation, complicating gel formation. Careful pH adjustment, often using ammonia is necessary to maintain the equilibrium for proper sol formation. However, even minor deviations in pH or reagent balance can result in unwanted precipitation rather than forming a stable sol, making the process less consistent and more difficult to scale for practical CO_2 adsorption applications. Therefore, the optimized condition needs to be established to ensures consistent and reproducible synthesis outcome by precisely controlling key parameters. This optimization not only minimizes issues but also makes the process more reliable and scalable for practical carbon capture applications.

1.3 Research objectives

The main aim of this research is to synthesis ferrite–based oxide adsorbents using a sol-gel method for CO_2 capture at low temperature. There are several objectives for this research as listed below.

1. To prepare, characterise, and compare the CO_2 adsorption performance of ferrite–based oxides adsorbents, $NiFe_2O_4$, $BaFe_{12}O_{19}$ and $BaNi_2Fe_{16}O_{27}$ prepared by sol gel method.
2. To prepare, characterise, and compare the CO_2 adsorption performance of Al–doped $BaNi_2Fe_{16-x}Al_xO_{27}$ ($0.3 \leq x \leq 1$) with the undoped at low temperatures under TGA analysis.
3. To prepare and characterize the impregnated halloysite nanotubes/aluminium doped barium nickel ferrite (HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$) composite adsorbents using various wt % of $BaNi_2Fe_{16-x}Al_xO_{27}$ (x=1.0).
4. To investigate the potential of HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ composite adsorbent towards the CO_2 adsorption capacity followed by the optimization of the reaction conditions and kinetics involved during the low temperature of adsorption activities.

1.4 Significance of study

This study highlights the development of ferrite–based oxides as sustainable and efficient adsorbents for CO_2 capture applications. The employment of the sol-gel method as the synthesis route offers simple, cheaper and controllable processing approach which helps to offers a reliable and efficient route. The use of ferrite–based oxides as CO_2 adsorbent with precise control and optimized on synthesis condition by regulating parameters such as chelating agent ratio, pH balance, and calcination

temperature in the preparation of ferrite–based oxide suggests a more feasible technique with regards to achieving enhanced surface area, and improved phase purity, while also ensuring better reproducibility, scalability, and energy efficiency in CO_2 capture. The improved method after the optimization eliminates the need for excessive amounts of chelating agents and removes the cumbersome requirement for real-time pH adjustment such as using ammonia water. The preparation process is greatly simplified minimizes issues like uncontrolled precipitation, and inconsistent phase formation.

Additionally, the introduction of metal dopants in ferrite–based oxides such as aluminium (Al) is beneficial as it is an effective strategy in enhancing the structure of ferrit-based oxides, addressing the limited CO_2 adsorption capacity typically observed on metal oxides. Al is easily available and abundant as a metal dopant is more practical and cost-effective to the adsorbent. Its small ionic radius and ability to integrate into the ferrite lattice contribute to improved structural stability, surface area, and porosity, making it ideal for enhancing CO_2 adsorption performance. Furthermore, the impregnation of porous and naturally supporting materials such as halloysite nanotubes (HNT) is favored and exceptionally advantageous as it possesses high reusability and a large specific surface area that gives benefits on adsorption application. Their unique tubular morphology and abundant surface functional groups provide additional active sites and facilitate better dispersion of the ferrite–based oxides, minimizing agglomeration. Additionally, the risk of pore blockage commonly encountered during surface modification such a doping can be alleviated, as the open tubular channels of HNT help maintain accessible pathways for CO_2 molecules, ensuring efficient diffusion and maximizing adsorption capacity. This combination contributes to improved adsorption capacity with long-term operational efficiency,

making HNT-impregnated ferrite composites a promising option for sustainable CO_2 capture applications.

1.5 Scope of study

This study focuses on the development of cost effective and efficient ferrite–based solid adsorbent using a sol-gel method. Several preparation parameters were varied including the citric acid to metal ions (CA:MI) molar ratio, calcination temperature and duration to optimize the synthesis of the adsorbents. Additionally, the study explores the doping of the ferrite–based oxide with aluminium (Al) to enhance the basicity and surface properties, which are important for CO_2 adsorption. Furthermore, the adsorbents were impregnated with HNTs to improve structural stability, increase surface area, and enhance the adsorption kinetics. These modifications aim to enhance the CO_2 capture performance of the adsorbent by increasing its active sites and maintaining structural properties during multiple adsorption-desorption cycles. The adsorbents were characterized using various techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), nitrogen adsorption-desorption (NAD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and temperature-programmed desorption (CO_2-TPD). The adsorption parameters (effect of adsorption temperature, adsorbent loading and gas flow rate), recyclability, kinetics and thermodynamic study were also presented.

1.6 Thesis layout

This thesis is structured into seven chapters. Chapter 1 (Introduction) describes the general overview of the work about climate change and CO_2 emission in atmosphere. The overview of the entire thesis including the problem statements, research objectives and scope of the study have been presented to summarize the content of the thesis. Chapter 2 (Literature Review) elaborates about different types of solid adsorbent for CO_2 capture and most importantly ferrite–based adsorbents that have been developed. Subsequently, an overview of the CO_2 capture technologies in the atmosphere that available these days have been explained. Chapter 3 (Experimental) presents the research methodology, which includes the materials and chemicals. The characterization techniques used to analyze the adsorbents have also been described in this chapter. Experimental design for CO_2 adsorption study also presented in this section. Chapter 4 (Results and Discussions) discusses the synthesis and optimization of synthesis parameters of ferrite–based oxides. Characterization analyses and CO_2 adsorption performance are also presented. In Chapter 5, the characterization of structural, morphological as well as the findings on the CO_2 adsorption for Al–doped $BaNi_2Fe_{16}O_{27}$ ($0.3 \leq x \leq 1$) at low temperatures are compared and discussed. Chapter 6 outlines the characterization of the impregnated HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ adsorbent at various wt %. The findings on the CO_2 adsorption capacity of HNT/$BaNi_2Fe_{16-x}Al_xO_{27}$ are discussed and compared. Finally, Chapter 7 (Conclusion and Recommendation) concludes the major findings of the study and some recommendations for future works are also presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Impact of industrialization on CO_2 emission and climate change

Environmental issues due to the emission of pollutants have increased due to heavy pollution from industrial facilities since the beginning of the industrial revolution. Most of the pollution is the result of burning fossil fuel (coal, crude oil and natural gas) (Olajire *et al*., 2010; Koirala *et al*., 2011; Lee *et al*., 2021; Donaghy *et al*., 2023). Today, one of the most challenging and urgent environmental issues that needs to be addressed is the increase of CO_2 concentration in the atmosphere which is widely reported to be the main anthropogenic greenhouse gas (GHG) that leads to global warming and climate changes (Mar *et al*., 2022; Yusuf *et al*., 2023). The amount of CO_2 is increasing by two ppm per year in the atmosphere which suggests that more than a third of the CO_2 emitted remains in the atmosphere. In 2020, the average annual level of CO_2 in the atmosphere was approximately 50 % higher than in the 60's and has attained the greatest value recorded in history of 412.55 ppm (IEA, 2021).

Unfortunately, the rapid development of the world's economy, accelerating industrialization as well as, soaring world population will continuously cause a gradual growth of CO_2 emissions and will affect global warming in the next 30 years at the current state (Sinehbaghizadeh *et al*., 2022; Dziejarski *et al*., 2023; Guo *et al*., 2023). According to the Intergovernmental Panel on Climate Change (IPCC) report in 2022, climate change mitigation efforts should be executed immediately to prevent this scenario. IPCC estimation indicates that the peak of GHG emissions must take place in 2025 at the latest and by 2030 a 43 % reduction of it will possibly be achieved.

Otherwise, by the end of 2100 the average temperature on Earth and atmospheric concentration of CO_2 will increase by 3.2 ℃ and 570 ppm, respectively (Shukla *et al*., 2022). Hence, in order to prevent this occurrence, specific energy management should be adopted. In particular, innovative transformation should be done by industries which are responsible for 25 % of CO_2 emissions (IEA, 2019).

In view of this, for the last several decades there have been initiatives to create new systems for carbon capture aiming to reduce CO_2 emission from entering the atmosphere. These systems are known as carbon capture, utilization and storage (CCUS) which can be divided into carbon capture and storage (CCS), carbon capture and utilization (CCU) and bioenergy with carbon capture and storage (BECCS). In these systems both liquid and solid adsorbents play a crucial role in the capture of CO_2.

2.2 Current materials for CO_2 capture

Solid and liquid adsorbents are two approaches used to capture CO_2 from the atmosphere. Liquid adsorbents require high temperatures of 300–900 °C to capture CO_2. Adsorbents such as aqueous amino acids, aqueous monoethanolamine (MEA), ionic liquids (ILs) and aqueous solution of hydroxides, are commonly used to capture CO_2 in industries (Xiao *et al*., 2021). The advantage of liquid adsorbents is that they are effective in capturing CO_2. However, the corrosive effect of liquid adsorbents affects the service life of the equipment. Another drawback is that liquid adsorbents can react chemically with other acid gases resulting in less active CO_2 being adsorbed. In contrast to liquid adsorbents, solid adsorbents can capture CO_2 at ambient pressure with temperatures range starting from room temperature. Furthermore, solid adsorbents are less corrosive and does not require the treatment of large volumes of aqueous phase.

Several important definitions that should be used in the CO_2 adsorption process. Adsorbent is defined as a solid or liquid on which gas molecules are adsorbed and adsorbate is a gas that is adsorbed on the surface of the adsorbent (Santamaria *et al*., 2023). There are two main types of gas molecule adsorption on the surface of a solid. If the accumulation of the adsorbate on the surface of the solid occurs due to weak intermolecular van der Waals interaction, then adsorption is termed physisorption or physical adsorption (Ghaedi, 2021). Meanwhile, when gas molecules accumulate on the surface of the adsorbent by chemical bond, the phenomenon occurring is called chemical adsorption or chemisorption (Tatarchuk *et al*., 2023).

2.3 Liquid adsorbents

2.3.1 Aqueous amino acids

Aqueous amino acids have been investigated for CO_2 capture as liquid adsorbent as it is relatively non-volatile, environmentally friendly and can be regenerated using mild heating (≈ 100 °C). For instance, Custelcean and co-workers (2019) reported using amino acid-based adsorbents with a capacity of 0.7 mol of CO_2 mol^{-1} of aqueous solution in ambient air conditions. The CO_2 capture reaction of this adsorbent is shown in Figure 2.1. In this study, the CO_2-saturated species in the solution were then crystallized using 2,6-pyridine-bis(iminonoguanidine) to form a solid hydrated carbonate in an aqueous solution. Three consecutive adsorption and regeneration cycles were conducted with observed low cyclic capacities of 0.12–0.20 CO_2 mol^{-1} and a measured regeneration energy demand of 360 kJ mol^{-1}. The adsorbent system offers a notable advantage due to its substantially lower generation temperatures (60–120 °C) compared to $CaCO_3$ (900 °C). However, the energy demand surpasses the corresponding energy for the $CaCO_3$ direct air capture (DAC) benchmark

(278 kJ mol^{-1}) hence becomes energetically less efficient. Higher regeneration energy demand indicates more energy required to restore the adsorbent after the adsorption process, making it less economically viable. Recker *et al*. (2022) also reported that amino acids as adsorbents usually present low cyclic capacities which are typically in the range of 0.12–0.40 mol CO_2 mol^{-1} adsorbent. However, amino acids with basic functional group are desirable liquid adsorbent for CO_2 capture (Ramezani *et al*., 2022).

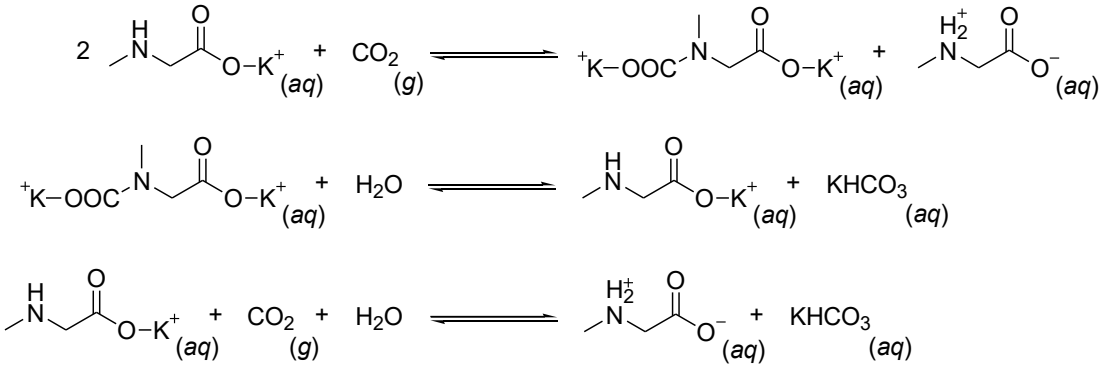

Figure 2.1 CO_2 capture reaction with aqueous amino acids (Custelcean *et al*., 2019).

2.3.2 Aqueous monoethanolamine (MEA)

MEA is one of the most researched liquid adsorbents for CO_2 capture from atmosphere. However, MEA suffers from a series of inherent problems including corrosive nature of the amines and the need for high regeneration energy. MEA was reported to be inefficient in capturing CO_2 at concentrations of 400 ppm (Lee *et al*., 2023). Meanwhile, this adsorbent was reported to have lower adsorption rate compared to other alkaline liquid adsorbents such as potassium carbonate (K_2CO_3) and piperazine (secondary amine). It degrades when exposed to oxygen and is environmentally unfriendly (Abdullatif *et al*., 2023). A recent study of different MEA under 0.044 % of CO_2 in air was conducted (Barzagli *et al*., 2020). In this screening

study, several MEA particularly those already known for their utilization in CCS were tested. The percentage of CO_2 adsorption was evaluated in 24 hours capture experiments and the species formed were identified and quantified using NMR spectroscopy. The correlation between chemical structures of the different amines and the species formed in solution showed that a high yield production of amine carbamate is the decisive factor for an effective CO_2 capture (Barzagli *et al*., 2020). Despite their effectiveness in capturing CO_2, the use of this adsorbent potentially may pose environmental hazards. The common environmental concerns include toxicity and potential persistence in the environment. It is crucial to carefully manage the environmental impact of any adsorbent to ensure that the benefits of CO_2 capture are not outweighed by negative environmental consequences.

2.3.3 Ionic liquids (ILs)

Other adsorbents that have potential for CO_2 capture from atmosphere are ionic liquids (ILs). This is due to their low melting point and the ability to tailor their properties by structural manipulations. Several research activities have been reported to investigate ILs as substitutes for MEA as adsorbents for CO_2 capture (Perumal *et al*., 2021; Zhang *et al*., 2022; Bisht *et al*., 2023). This is mainly due to their relatively lower regeneration energy and low volatility (Ma *et al*., 2021).

Chen and co-workers (2017) reported the adsorbent for CO_2 capture from atmosphere involving ionic liquid [P4444][p-2-O] and pyrene-based conjugated polymer (IL-CP). The adsorbent was reported to be capable of efficiently adsorbing CO_2 under ambient conditions. The stability and reusability of the IL-CP were examined and it could be regenerated and reused to adsorb CO_2 from atmosphere for

at least five times. The results indicate that the IL-CP was stable and reusable. However, the process involved is difficult to scale up and very costly.

To date, numerous studies have also demonstrated remarkable CO_2 adsorption using ILs such as imidazolium, pyridinium and pyrrolidinium based cations as well as fluoroalkyl based anions (Perumal *et al*., 2021; Ab Rahim *et al*., 2023). Most commonly fluorinated anions possess excellent features owing to their low reactivity and high chemical stability. However, fluorinated anions are expensive, have low thermal stability and release toxic compounds which is a major environmental concern (Han *et al*., 2021).

2.3.4 Aqueous solution of hydroxides

The latest liquid adsorbents for CO_2 capture involve the use of aqueous solutions such as sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) and potassium hydroxide (KOH) (Keith *et al*., 2018; Leonzio *et al*., 2022; Abanades *et al*., 2023). The usage of NaOH for CO_2 adsorption has been studied intensively and has an excellent CO_2 adsorption capacity. Ghaffari *et al*., (2023) investigated the CO_2 capture efficiency of NaOH at varying wt %. In this study, a NaOH system with a concentration between 3 to 10 wt % was used to capture a gas mixture with diluted CO_2 (0.0153–1.2 vol %). The obtained results show the maximum amount of adsorption capacity at 6 wt % NaOH. It was deduced that the CO_2 capture efficiency in a NaOH system is highly dependent on the concentration of the solvent. However, aqueous NaOH adsorbent cannot be easily regenerated due to the formation of $NaHCO_3$ when reacted with CO_2. Besides, $NaHCO_3$ has high solubility in an aqueous solution. Its decomposed product, Na_2CO_3 is a thermally stable compound that can be

decomposed to Na_2O at a temperature of over 800 °C. The overall CO_2 adsorption reaction with NaOH is as follows:

$$NaOH\ (aq) + CO_2\ (g) \longrightarrow NaHCO_3\ (aq) \quad (2.1)$$

$Ca(OH)_2$ aqueous solution has the potential to be an effective adsorbent for CO_2 capture due to relatively low in cost. These materials are inexpensive and non-hazardous to the environment. The experiment conducted by Pinto *et al*., (2019) on CO_2 capture by pure $Ca(OH)_2$ shows the adsorption capacity of 0.786 CO_2 g^{-1}. This study then modified the $Ca(OH)_2$ based materials with magnesium oxide and ammonium phosphate. The result showed an increment of 50 wt % of CO_2 adsorption capacity. However, this adsorbent has not received much interest as the regeneration process of $Ca(OH)_2$, is energy-intensive. To regenerate $Ca(OH)_2$, $CaCO_3$ needs to undergo a calcination process at a high temperature (650–765 °C) to obtain CaO which is a direct source of $Ca(OH)_2$.

Additionally, KOH has also been included as an aqueous hydroxide adsorbent (Smith *et al*., 2019). However, the research on KOH is only limited to its CO_2 performance data. A detailed description of its CO_2 capture mechanism is still not available (Ngu *et al*., 2019; Chai *et al*., 2022). This necessitates further exploration of alternative adsorbents to enhance efficiency in the CO_2 capture process.

2.4 Criteria for selecting solid CO_2 capture materials

Several criteria are significant in selecting suitable solids for CO_2 capture (Figure 2.2). Among these, crystallinity plays an important role in the selection of materials for CO_2 capture. The organized crystalline structure contributes to the formation of well-defined pores which enhance the ability to capture CO_2 because of

its high surface area. Meanwhile, amorphous materials lack long-range order in their atomic or molecular arrangement. The structure is more random with no distinct repeating pattern, resulting in a lower surface area. This may limit the number of active sites available for CO_2 capture. Ultimately, the choice between crystalline and amorphous materials hinges on the specific demands of CO_2 capture applications and desired performance. Joutsuka and Tada, (2023) studied the adsorption behavior of CO_2 on amorphous and crystalline zirconia. The XRD analysis and CO_2-TPD experiment indicates that adsorption of CO_2 on amorphous zirconia is weaker than that on a crystalline zirconia surface. In 2023, Ma and co-workers (2023) studied the CO_2 adsorption capacity of crystalline SiO_2 and amorphous SiO_2. The adsorption capacity test revealed that crystalline SiO_2 adsorbed about 23 % more CO_2 than amorphous SiO_2.

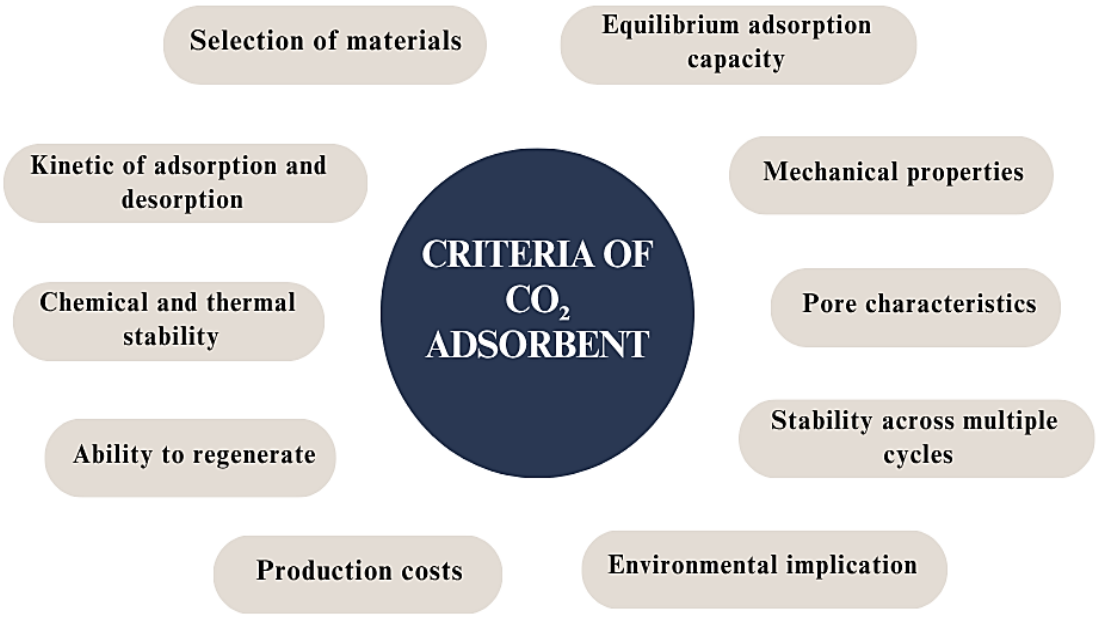

Figure 2.2 The important properties and criteria for selecting CO_2 capture materials.

The adsorption capacity is also related to pore size and surface interaction of the adsorbent. The pore size of an adsorbent is crucial as it determines the accessibility and accommodation of CO_2 molecules in the adsorbent. Yao *et al*. (2023) investigated the effectiveness of CO_2 capture using $CuCl_2$-activated sustainable microporous carbon. Based on the analysis, high amounts of well-developed microporosity are effective in capturing CO_2. Optimizing the pore size and surface chemistry of the adsorbent is a key strategy to enhance adsorption capacity of CO_2.

Kinetics of adsorption and desorption is another important factor, so that adsorption and desorption can occur in a short span of time and the number of cycles can be increased. However, this is influenced by several factors including the porosity of the adsorbent, the concentration of adsorbate and the type of chemical bonding formed during the process. Martin *et al*. (2016) investigated an economic and simple method to manufacture low cost but effective adsorbents for CO_2 capture through impregnating diethylenetriamine (DETA) into a porous silica gel. Although the capacities were unremarkable, the authors were able to demonstrate fast kinetics and relatively stable cyclic performance. This is desirable as a short time is required to attain the equilibrium state between the adsorbate-adsorbent.

The adsorbent should also be mechanically strong and resistant to abrasion and crushing during adsorption. The adsorption process often involves dynamic conditions experiencing forces due to the flow of the adsorbate molecules. If the adsorbent lacks mechanical strength, it could break down or undergo structural changes compromising its efficiency and performance. Plaza *et al*. (2015) reported that the wood-based activated carbon (AC) exhibited potential as an industrial-level CO_2 adsorbent as it has high economical and adsorption efficiency with excellent mechanical resistance.

Mechanically strong adsorbent contributes to the reliability and longevity of the adsorption process. It ensures the adsorbent remains intact and effective over multiple cycles of adsorption and desorption.

Pore characteristics are an important feature for this application. There is a correlation between the type of pore and the gas molecules. Reddy *et al*., (2021) developed a new adsorbent with bigger pores to enable fast transport and gas/surface interactions to capture CO_2. The modification or addition of specific functional groups to the porous adsorbent is aimed at enhancing the performance of adsorbents in terms of the ability to capture CO_2 effectively. Essentially, the specific pore structure of the adsorbent is a key determinant of its performance in adsorbing and transporting gases in this application.

Chemical and thermal stability are also important characteristics of an adsorbent especially when used at elevated temperatures. It is to ensure that it can be used for its proper lifetime with consistently high equilibrium adsorption capacity. Wang *et al*., (2020) studied the thermal stability and CO_2 adsorption of ZIF-8 and its modification by using parallel flow-drop solvothermal method. Different amounts of -NH_2 (0, 6, 12 and 18 % NH_2-ZIF-8) was successfully introduced into the surface of ZIF-8 by modification with polyaniline. It was found that the decomposition temperature of 12 % doped content of polyaniline in NH_2-ZIF-8 slightly increased to 632.71 ℃, suggesting their higher thermal stability compared to 0, 6 and 18 % doped content. The improvement of thermal stability after modification shows the increase in CO_2 adsorption of the adsorbent. The introduction of -NH_2 functional group into ZIF-8 can effectively change the electrostatic force between ZIF-8 and CO_2, thus improving the CO_2 adsorption property of ZIF-8.

Adsorbents usually undergo a regeneration process after the adsorption capacity is exhausted. The process of regeneration involves removal of the adsorbed CO_2 molecules from the pores and the surface by desorption. This will allow restoration of the adsorption capabilities of the adsorbent. The regeneration capability of a material is an important factor in determining the suitability of a material for CO_2 adsorption. The regeneration process is largely affected by temperature and pressure. The selection of optimal temperature and pressure parameters is crucial to ensure the successful release of adsorbed CO_2 from the adsorbent. The desorption process typically requires elevated temperatures to break the bonds between CO_2 molecules and the adsorbent surface. Higher temperatures can enhance the kinetics of desorption allowing for the efficient release of CO_2 and regeneration of the adsorbent for subsequent cycles. However, the choice of temperature needs to balance the need for effective desorption with energy considerations and adsorbent stability. Pressure also plays a role in the regeneration process, influencing the thermodynamics of desorption. Changes in pressure can impact the equilibrium between adsorbed and desorbed CO_2 affecting the efficiency of the desorption step. Optimal pressure conditions need to be determined to achieve effective and controlled release of CO_2 during regeneration. In summary, both are critical parameters in the regeneration process for CO_2 adsorption systems. Finding the right combination of these conditions is essential for maximizing the performance, energy efficiency and overall effectiveness of CO_2 capture technology.

The stability in adsorption and desorption cycles also play a crucial role in the adsorption process. High surface area of carbon adsorbents was prepared by KOH activation of carbonized PAN which exhibits CO_2 adsorption capacities in the range of 1.7–2.5 mmol g^{-1} by Singh *et al*., (2019). Based on analysis, the adsorbent exhibits

stable adsorption capacity (2.5 mmol g^{-1}) over five cycles of adsorption/desorption with no loss in efficiency. The cost is another crucial criterion that needs to be considered. The economic viability of the adsorbents is defined as the cost per unit mass of the raw materials used in the synthesis process (Sarafraz *et al*., 2019). The cost of adsorbent preparation can be determined based on the cost of raw materials or industrial-grade precursors and the chemical used to process them (Kani *et al*., 2020). Operational costs are also included as the cost factors in this application. Table 2.1 show the cost effectiveness and features of adsorbents for CO_2 capture.

Table 2.1 Cost effectiveness and features of adsorbents for CO_2 capture.

Adsorbent	Features	Price (USD $/kg)
Activated Carbon	-Widely available -Thermally stable -Ease of regeneration -Require high operating pressure	~35.1 (Merck, 2023; Kumar *et al*., 2020)
Metal organic frameworks (MOFs)	-Tunable pore structure -Large surface area -Ease of regeneration	~527.3 (Mubarak *et al*., 2022; Cui *et al*., 2023; Wang *et al*., 2023)
Zeolite	-Universal availability -Thermally stable -High surface area -Low adsorption capacity	~3.5 (Chemxin, 2023; Bai *et al*., 2022)
Silica	-Thermally and mechanically stable -Tunable pore structure -Improper reusability -Difficulty in large scale production	~12.2 (Zaed *et al*., 2023; Pang *et al*., 2023)
Metal oxide	-Widely available -Low toxicity	~32.5 (CaO, Bernd Kraft, 2023; Musa *et al*., 2023)

The choice of adsorbent materials for CO_2 capture hinges on a balance between performance characteristics and cost-effectiveness. As shown in Table 2.1, activated carbon is widely used due to its high availability, thermal stability, and ease of regeneration. However, it typically requires high operating pressure for effective CO_2

capture, which can increase energy costs. With a moderate price of ~$35.1/kg, it remains a cost-effective option for many industrial applications. Additionally, metal–organic frameworks (MOFs) are known for their exceptionally high surface area, tunable pore structures, and ease of regeneration, making them one of the most promising materials for CO_2 capture. However, their extremely high cost (~$527.3/kg) and challenges in large-scale synthesis currently hinder widespread practical use. Zeolites, on the other hand, are among the cheapest options (~$3.5/kg) and offer good thermal stability and high surface area, though they generally suffer from lower CO_2 adsorption capacities. Silica-based materials offer favorable characteristics such as high surface area, tunable pore structures, and thermal and mechanical stability. However, they also require high energy for regeneration, and are moderately priced at ~$12.2/kg. Meanwhile, metal oxides are commonly used due to their low toxicity and widespread availability. This adsorbent has potential in economic feasibility due to its relatively affordable cost of ~$32.5/kg. Overall, the ideal material depends on the specific application, operational conditions, and economic constraints.

2.5 Solid adsorbents

The application of solid adsorbent materials is regarded as one of the most promising research directions and has garnered a high amount of attention for carbon capture in CCUS (Dziejarski *et al*., 2023). Solid adsorbents such as carbonaceous materials (Kamran and Park, 2021), metal-organic framework (MOFs) (Bertina *et al*., 2022), zeolites (Kumar *et al*., 2020), hydrotalcites (HTlcs) and metal oxides have gained popularity over liquid adsorbents due to benefits such as considerably high CO_2 uptake efficiency, easy regeneration, simple handling, material stability and low cost

(Paradakhti *et al*., 2019). Figure 2.3 is the number of publications since 2013 that have concerned solid materials for CO_2 capture.

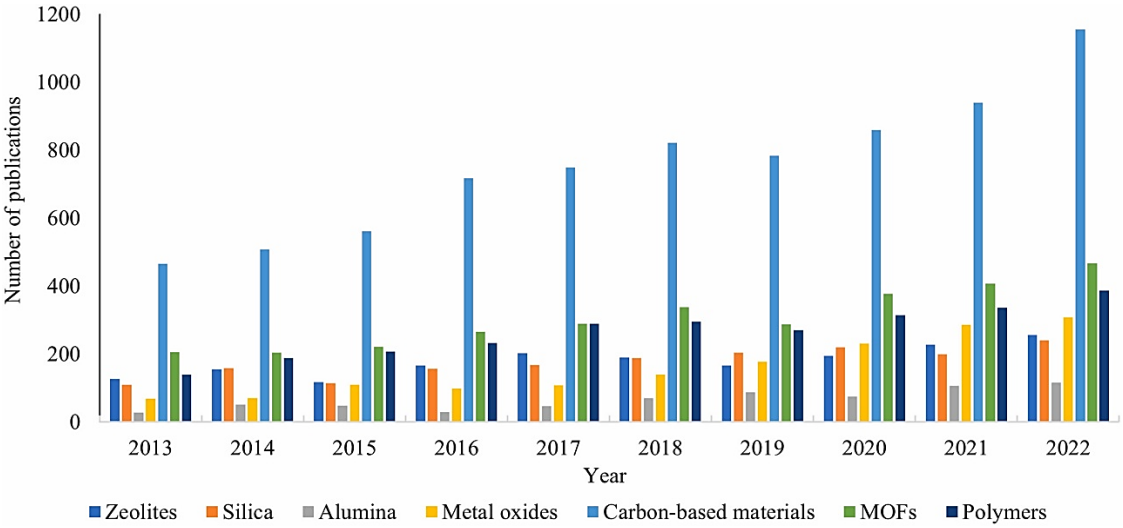

Figure 2.3 Number of publications on CO_2 capture with various solid adsorbents since 2013, based on Scopus with keywords "CO_2 adsorption" or "CO_2 capture" (Dziejarski *et al*., 2023).

2.5.1 Carbonaceous materials

Owing to their low-cost, high surface area, high amenability to pore structure modification and surface functionalization, carbon-based materials are considered to be one of the most promising adsorbents for capturing CO_2. However, the CO_2 adsorption on carbon materials is physical and weak which makes these adsorbents sensitive to temperature and pressure with relatively poor selectivity. Thus, current research efforts are focused on how to enhance the adsorbate-adsorbent interaction and the selectivity for CO_2. One approach is to increase the surface area and tune the pore structure of carbon adsorbent either by using different precursors or forming different structures. Jin *et al*., (2022) studied the adsorption of CO_2 from sawdust waste in ambient conditions. This study was undertaken to prepare low-cost sawdust wastes with different preparation parameters including sawdust type, activating agent,