

Preparation and Characterization of Solid Adsorbents for CO₂ Capture

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ABSTRAKT

Předložená diplomová práce je zaměřena na přípravu a charakterizaci oxidu hořečnatého (MgO). Oproti oxidu vápenatému, CaO, je schopen zachytu emisí CO₂ při nižších teplotách běžných v elektrárnách při spalování, nebo dokonce před ním, a následné regenerace při mnohem nižších nákladech. V teoretické části je diskutován koncept zachytu, ukládání a využívání uhlíku v kontextu narušení uhlíkového cyklu následkem lidských aktivit a souvisejícími klimatickými změnami. Podrobně jsou uvedeny pevné adsorbenty CO₂ a zejména pak MgO. Praktická část je zaměřena na přípravu MgO a jeho aktivaci pomocí tavných solí, respektive jejich eutektických směsí.

Klíčová slova: uhlíkový cyklus; emise CO₂; klimatická změna; zachyt CO₂; MgO; termogravimetrie;

ABSTRACT

The presented thesis focuses on the preparation and characterization of magnesium oxide (MgO). Compared to calcium oxide, CaO, it is capable of capturing CO₂ emissions at lower temperatures typical in power plants during combustion, or even before it, and subsequent regeneration at much lower costs. The theoretical section discusses the concept of carbon capture, storage, and utilization in the context of the disruption of the carbon cycle caused by human activities and related climate change. Solid CO₂ adsorbents, particularly MgO, are discussed in detail. The practical part focuses on the preparation of MgO and its activation using molten salts, specifically their eutectic mixtures.

Keywords: carbon cycle; antropogenic CO₂ emission; climate change; CO₂ capture; MgO; thermogravimetry

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INTRODUCTION

Currently, the world is facing serious environmental challenges, including excessive emissions of greenhouse gases, particularly carbon dioxide (CO₂). These emissions are the main contributors to global warming and climate change, which have far-reaching consequences for ecosystems, human health, and the economy.

Greenhouse gases like CO₂ trap heat in the atmosphere, causing the greenhouse effect, which gradually increases the Earth's average temperature. This phenomenon results in the melting of glaciers, rising sea levels, and extreme weather events such as hurricanes, floods, and droughts. These changes threaten biodiversity, cause the loss of natural habitats, and negatively impact agriculture, leading to food shortages and increased prices.

The health impacts of climate change are also severe. Rising temperatures can lead to an increase in the incidence of insect-borne diseases such as malaria and dengue and worsen air quality, negatively affecting respiratory health. Additionally, extreme temperatures can cause heat stress and deaths, especially among vulnerable populations such as the elderly and children.

The economic consequences of climate change are also significant. Natural disasters caused by extreme weather events can lead to enormous financial losses, destruction of infrastructure, and job losses. Agriculture, fisheries, and tourism, which depend on stable climate conditions, are particularly at risk. The costs of adapting to climate change and mitigating its impacts represent an additional financial burden for governments and societies worldwide.

Reducing the concentration of CO₂ in the atmosphere is, therefore, a key goal for sustainable development and environmental protection. One effective method for capturing CO₂ is the use of solid adsorbents. This thesis focuses on the preparation and characterization of solid adsorbents for CO₂ capture, with an emphasis on the use of magnesium oxide (MgO) in combination with molten salts. MgO is known for its excellent adsorption properties, such as high capacity and selectivity for CO₂, and molten salts can further enhance its efficiency in capturing CO₂ by reducing the energy requirements of the process and increasing the stability of the adsorbent.

This thesis aims not only to contribute to research in the field of green technologies but also to offer practical solutions for reducing CO₂ emissions. This study's results could significantly impact the development of new materials and technologies for capturing greenhouse gases, which is crucial for combating climate change. Thorough characterization of the prepared adsorbents includes analysis of their physical and chemical properties, such as surface area, porosity, and thermal stability, enabling a better understanding of their behavior in CO₂ adsorption.

This thesis also focuses on optimizing the preparation conditions of the adsorbents and testing them under real conditions, providing valuable information for their practical application. The results could contribute to developing efficient and economically viable technologies for CO₂ capture, which are essential for achieving sustainable development goals and climate protection.

I THEORETICAL PART

1 CARBON CYCLE

Carbon is the fundamental building block of life on Earth. It constitutes the molecular framework of all known biological macromolecules and plays a pivotal role in the structural and metabolic organization of living organisms. Humans are composed of carbon-based compounds, rely on carbon-rich food sources for energy, and have developed civilizations underpinned by carbon in various forms, ranging from construction materials to fossil fuel-derived energy systems. Carbon-based materials also form the basis of our technological and industrial infrastructure, underscoring carbon's centrality not only to life but also to the functioning of modern society. The carbon cycle, a crucial component of the broader biogeochemical cycles, encompasses the continuous exchange of carbon among Earth's major spheres: the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere. This interconnected system regulates the flow and transformation of carbon through both short-term biological pathways and long-term geological mechanisms. It enables carbon to be recycled and reused within and between living organisms and their environment, thereby sustaining life and influencing climate regulation over a variety of temporal and spatial scales. To better understand the behavior and balance of carbon in the environment, the carbon cycle is commonly divided into two distinct but interconnected components: the fast (biological) carbon cycle and the slow (geological or deep) carbon cycle. The fast carbon cycle primarily operates on timescales of days to decades and involves processes such as photosynthesis, respiration, decomposition, and ocean-atmosphere gas exchange. In contrast, the slow carbon cycle spans millions of years and includes the weathering of rocks, subduction of tectonic plates, volcanic outgassing, and the long-term burial of organic carbon in sediments and fossil fuels. The major reservoirs, or carbon pools, within the global carbon cycle include:

- (i) the atmosphere, which holds carbon primarily in the form of CO_2 and CH_4
- (ii) the terrestrial biosphere, comprising vegetation, soils, and microorganisms
- (iii) the ocean, which contains both dissolved carbon and organic carbon in marine organisms
- (iv) sediments and fossil fuels, where carbon is stored in the lithosphere and aquatic sediments over geological timescales
- (v) the Earth's interior, including the mantle and crust, which engage in carbon exchange via volcanic activity and plate tectonics.

A schematic illustration of fast and slow carbon cycle in terrestrial environment is provided in Figure 1.

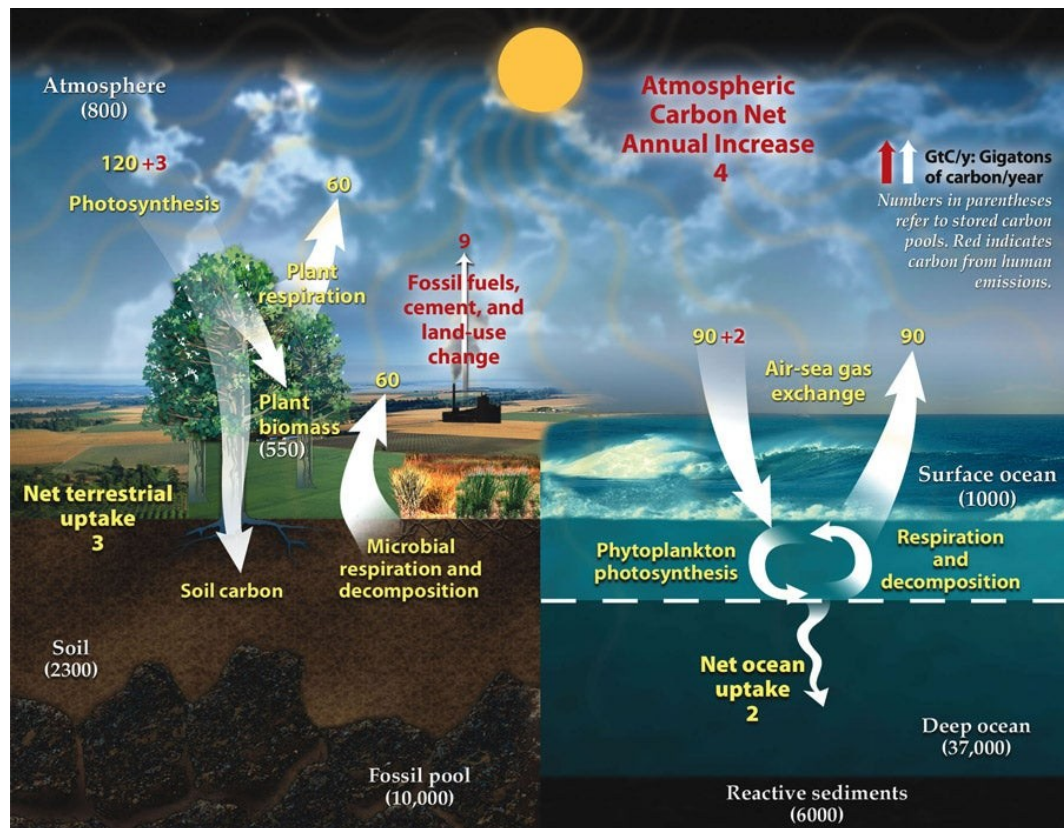


Figure 1. Fast and slow carbon cycle across different pathways. Carbon reservoirs are labelled in white text. Reproduced from Ref. [1].

Carbon fluxes between these reservoirs are mediated through a suite of chemical, physical, geological, and biological processes, and under natural conditions, these exchanges are relatively balanced, ensuring a quasi-steady-state carbon distribution. For example, the oceans act as a major carbon sink due to their large capacity to absorb and store CO_2 , while terrestrial ecosystems sequester carbon through plant growth and soil organic matter formation. However, since the onset of the industrial revolution, and most dramatically post-World War II, anthropogenic activities have significantly disrupted the natural carbon cycle. The large-scale combustion of fossil fuels, deforestation, cement production, and extensive land-use changes have resulted in the mobilization of vast quantities of carbon from long-term geospheric reservoirs into the atmosphere. These processes have not only elevated atmospheric CO_2 concentrations to levels unprecedented in the recent geological past but also altered the functioning of terrestrial and oceanic carbon sinks. Furthermore, the synthesis and release of anthropogenic carbon compounds, many of which are recalcitrant and toxic, have introduced novel forms of carbon into the environment. These compounds

persist across environmental media and can act as long-term pollutants in soils, water bodies, and the atmosphere. The carbon cycle is also susceptible to perturbations from natural disturbances, such as wildfires, droughts, insect outbreaks, and disease events. Importantly, the frequency and intensity of many of these disturbances are increasingly being modulated by human-induced climate change. For instance, rising global temperatures and altered precipitation regimes, driven by elevated greenhouse gas (GHG) emissions, are enhancing the vulnerability of ecosystems to fire and pest infestations, which in turn release more carbon into the atmosphere, creating feedback loops that exacerbate climate change. Over geological timescales, variations in Earth's orbital parameters have historically driven major shifts in the global carbon cycle, often associated with glacial-interglacial cycles. However, the current anthropogenic perturbations, both in magnitude and rate, appear to exceed those observed in the paleoclimate record. This has led to concerns about long-term impacts on Earth system stability, including ocean acidification, permafrost thawing, and the potential for tipping points in critical carbon sinks. In summary, the carbon cycle represents a complex and dynamic system that is essential for life and climate regulation on Earth. While it has historically maintained a delicate equilibrium, recent human activities have induced profound and potentially irreversible changes, with cascading effects on ecological integrity and planetary health. [2]

1.1 Perturbation to the Global Carbon Cycle

The carbon cycle is also susceptible to perturbations from natural disturbances, such as wildfires, droughts, insect outbreaks, and disease events. Importantly, the frequency and intensity of many of these disturbances are increasingly being modulated by human-induced climate change. For instance, rising global temperatures and altered precipitation regimes, driven by elevated greenhouse gas (GHG) emissions, are enhancing the vulnerability of ecosystems to fire and pest infestations, which in turn release more carbon into the atmosphere, creating feedback loops that exacerbate climate change. Over geological timescales, variations in Earth's orbital parameters have historically driven major shifts in the global carbon cycle, often associated with glacial-interglacial cycles. However, the current anthropogenic perturbations, both in magnitude and rate, appear to exceed those observed in the paleoclimate record. This has led to concerns about long-term impacts on Earth system stability, including ocean acidification, permafrost thawing, and the potential for tipping points in critical carbon sinks.

In summary, the carbon cycle represents a complex and dynamic system that is essential for life and climate regulation on Earth. While it has historically maintained a delicate equilibrium, recent human activities have induced profound and potentially irreversible changes, with cascading effects on ecological integrity and planetary health.[3]

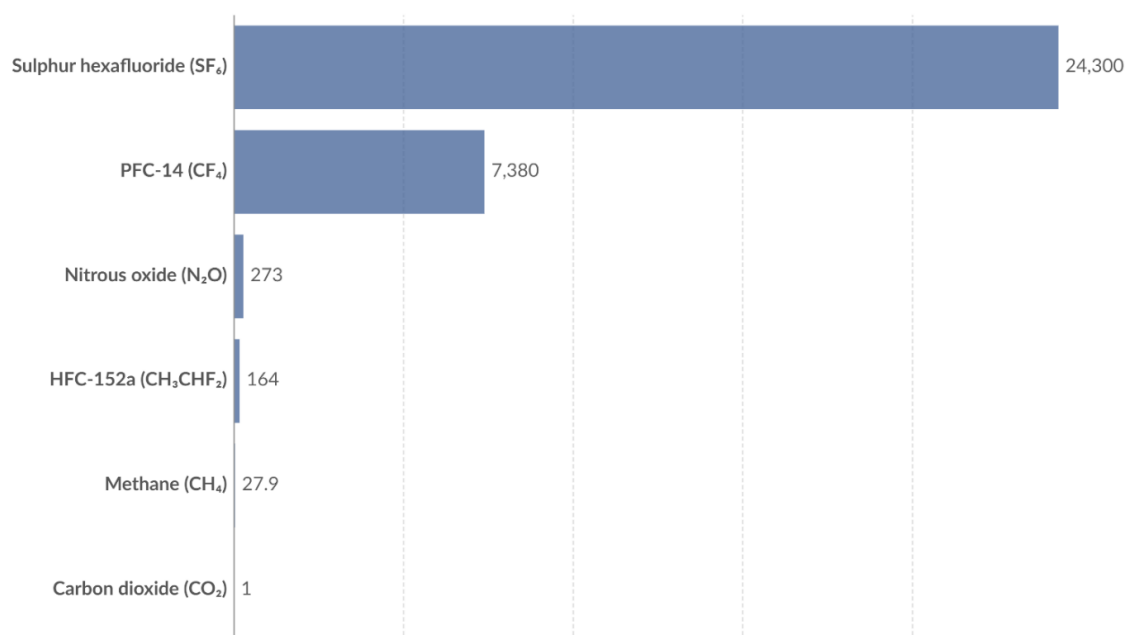
1.2 Greenhouse gases (GHGs)

The greenhouse effect is a natural process in the Earth's atmosphere due to solar radiation. The sun emits energy through visible light, ultraviolet rays, and infrared radiation. This energy penetrates the atmosphere, primarily composed of nitrogen, oxygen, water vapor, and various gases, including GHGs. The major GHGs include CO₂, primarily from fossil fuel combustion and deforestation; methane (CH₄), from agriculture and natural gas leaks; nitrous oxide (N₂O), from fertilizers and biomass burning; and synthetic fluorinated gases used in industrial applications. Water vapor also plays a role, but acts more as a feedback mechanism than a direct emission source. The interaction of these gases with infrared radiation is essential in creating the greenhouse effect. The greenhouse effect refers to the rise in the Earth's surface temperature caused by the warming of the lower layers of the atmosphere due to the accumulation of greenhouse gases. This results in higher air temperatures than would otherwise be expected, leading to irreversible consequences such as climate change and global warming. However, not all GHGs are equal in their respective impact on the environment.

Global Warming Potential (GWP) is a measure that compares the ability of different greenhouse gases to trap heat in the atmosphere over a period of 100 years, relative to CO₂, which is assigned a GWP of 1. GWP takes into account both how strongly a gas absorbs heat and how long it remains in the atmosphere. For instance, methane has a GWP of about 28-36, meaning it can trap 28 to 36 times more heat than CO₂ over a century, while N₂O has a GWP of around 265-298. Fluorinated gases, like sulfur hexafluoride (SF₆), have extremely high GWPs, often exceeding 23,000, despite being present in smaller quantities. These values highlight that even trace amounts of high-GWP gases can significantly contribute to global warming, emphasizing the need to control both the abundance and potency of emissions in climate mitigation strategies. [4]

Global warming potential of greenhouse gases relative to CO₂

Global warming potential¹ measures the relative warming impact of one unit mass of a greenhouse gas relative to carbon dioxide over a 100-year timescale.



Data source: IPCC (2021)

OurWorldInData.org/co2-and-greenhouse-gas-emissions | CC BY

Figure 2. Relative global warming potencies of GHGs measured on GWP scale.
Reproduced from [5]

1.3 Climate action plans and policies

To address the adverse environmental impact brought by the excessive level of GHG emissions, various governmental and regulatory bodies have put forward various plans to contain and lower the negative impact due to anthropogenic activities. A Climate Action Plan (CAP) is a strategic framework developed by governments, institutions, or organizations to systematically address climate change through the reduction of greenhouse gas emissions and the implementation of adaptation measures. It typically includes a baseline inventory of emissions, quantifiable reduction targets, and a set of sector-specific strategies covering areas such as energy, transportation, waste management, and land use. In addition to mitigation efforts, CAPs also incorporate adaptation strategies to enhance resilience against climate-related impacts such as extreme weather events and sea-level rise. Effective implementation involves clearly defined responsibilities, timelines, and monitoring mechanisms to ensure accountability and progress assessment. CAPs are often aligned with broader international commitments, such as the Paris Agreement, and serve as essential tools for guiding sustainable development and environmental policy. So far, various CAPs have been implemented and adopted by various countries at the regional and global levels. Some

prominent CAPs currently implemented and in practice are as following: The Intergovernmental Panel on Climate Change (IPCC) is a scientific body established in 1988 by the United Nations Environment Program (UNEP) and the World Meteorological Organization (WMO). Its primary purpose is to provide comprehensive assessments of current scientific knowledge on climate change, its impacts, and potential future risks, as well as to propose adaptation and mitigation strategies. The group is divided into three working groups: (i) the physical science basis, (ii) Impacts, adaption, and vulnerability, and (iii) mitigation of climate change. Various agreements have been approved under IPCC, in particular, Kyoto protocol (1997), Paris agreement (2015), and Conference of Parties, with each agreement establishing different climate and sustainable development related goals. The key objectives Kyoto protocols were to reduce emissions by an average of 5.2% below 1990 levels over the commitment period 2008–2012 in developed countries. Paris agreement which was ratified by over 190 parties set the objective to limit global warming to well below 2°C, preferably 1.5°C, compared to pre-industrial levels. Additionally, developed countries committed to providing financial support to developing countries to mitigate the adverse impact from the environment. Moreover, UN countries put forward an ambitious plan to achieve environmental sustainability by objectives set in United Nations Sustainable Development Goals (UN SDGs) which are set of 17 plans adopted in 2015 by all UN Member States as part of the 2030 Agenda for Sustainable Development. They provide a shared blueprint for peace, prosperity, and environmental sustainability for people and the planet. The 13th SDG, i.e., climate action provides a framework for urgent and coordinated action to combat climate change and its impacts. The goal recognizes that climate change is a global challenge with far-reaching and potentially irreversible consequences for the environment, human health, economic development, and social equity. SDG 13 also calls for the enhancement of education, awareness-raising, and institutional capacity on climate change mitigation, adaptation, and impact reduction and is aligned within UNFCCC and Paris Agreement. [6]

1.4 Anthropogenic Emissions

Human activities have significantly increased carbon dioxide emissions, rising from 24.9 to 41 billion tons annually between 1990 and 2022. Growing production volumes and the number of vehicles drive this increase. A slight decline in emissions occurred during 2018-2020 due to the development of electric cars, environmentally friendly energy sources,

and the COVID-19 pandemic. The primary sources of anthropogenic CO₂ emissions are fossil fuel combustion, agriculture, cement and concrete production, and deforestation. Nearly 4/5 of all anthropogenic emissions come from fossil fuel combustion, with the remaining quarter divided among agriculture, cement and concrete production, and deforestation. [7]

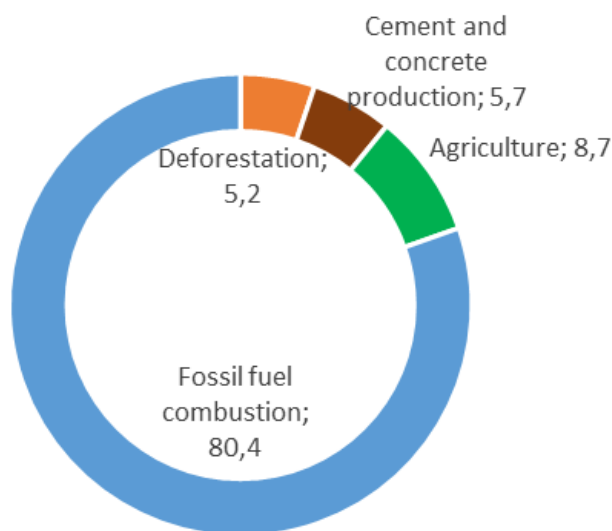


Figure 3: Ring graph of the primary anthropogenic carbon dioxide emissions sources in billion t/y CO₂. Data taken from [20]

1.5 Carbon Capture, Utilization, and Storage

Carbon Capture, Utilization, and Storage (CCUS) is an approach aimed at mitigating anthropogenic CO₂ emissions, particularly from large contributing sectors such as power generation, cement, steel, and chemical industries. As global climate policies described in the preceding sections increasingly emphasize deep decarbonization and net-zero targets, CCUS has emerged as an indispensable tool in the addressing the climate related adverse effects due to excessive carbon levels in the environment. CCUS plays a dual role in mitigation of carbon emissions: (i) it prevents new emissions from entering the atmosphere and (ii) it enables negative emissions when combined with bioenergy or direct air capture. According to the International Energy Agency (IEA), achieving net-zero emissions by mid-century will be nearly impossible without deploying CCUS at scale, especially in sectors where alternative low-carbon technologies are currently insufficient or economically unviable. CCUS technology relies on generated carbon capture, its utilization, and long-term storage. Carbon capture involves the separation of CO₂ from gas streams. Technologies include post-combustion (amine scrubbing), pre-combustion (gasification followed by CO₂ separation), and oxy-fuel combustion. Emerging techniques such as membrane-based

separations and solid sorbents have also been reported. In capturing CO₂, three technologies can be broadly classified, i.e., post-combustion, pre-combustion, and oxyfuel combustion. [8]

Post-combustion capture is the most widely applicable and commercially mature method for CO₂ capture, particularly suitable for retrofitting existing fossil-fuel power plants and industrial facilities. In this approach, carbon dioxide is separated from the flue gas produced after the combustion of fossil fuels such as coal or natural gas. The flue gas typically contains CO₂ in relatively low concentrations (about 10-15% for coal and 3-6% for natural gas) along with nitrogen, water vapor, and other pollutants. The gas is passed through a solvent, most commonly aqueous amines like monoethanolamine (MEA), which chemically binds with the CO₂. The CO₂-rich solvent is then sent to a regeneration unit, where heat is applied to release the CO₂ as a concentrated stream and regenerate the solvent for reuse. While this method is technologically well-established, it suffers from significant energy penalties due to the heating required during solvent regeneration and the handling of dilute gas streams, which can impact the overall efficiency and economics of the process.

Pre-combustion capture involves removing CO₂ before the fuel is combusted, making it fundamentally different from post-combustion systems. This method is primarily applied in integrated gasification combined cycle (IGCC) power plants or hydrogen production units. In pre-combustion processes, fossil fuels such as coal, oil, or natural gas are first converted into a synthetic gas (syngas) composed mainly of hydrogen and carbon monoxide. This is achieved through a process like gasification or reforming. The carbon monoxide in the syngas is then reacted with steam in a water-gas shift reactor to produce additional hydrogen and CO₂. The resulting CO₂-rich gas mixture, which contains CO₂ at much higher concentrations and pressures than in post-combustion flue gas, allows for more efficient CO₂ separation using physical solvents or membranes. The remaining hydrogen can be used as a clean fuel for electricity generation or industrial applications. While pre-combustion capture is more efficient and cost-effective in separating CO₂ compared to post-combustion methods, it is a cost-intensive process, limiting its widespread adoption. However, current concerted research efforts related to mitigation have also enabled high-performing CO₂ adsorbent materials, thoroughly discussed in the next section, and operate via physisorption (weak van der Waals interactions) or chemisorption (strong chemical bonding), with the latter providing higher selectivity and capacity. A wide variety of materials have been investigated, including activated carbons, zeolites, metal-organic frameworks (MOFs),

porous silica, and alkaline earth metal oxides like MgO and CaO. [9, 10] MgO has attracted significant attention due to its high CO₂ uptake at moderate temperatures and potential for cyclic stability through reversible formation of MgCO₃. To further make this technology competitive in comparison to other alternatives, current research focuses on enhancing the surface area, pore structure, and CO₂ affinity of these materials, as well as developing hybrid or functionalized adsorbents to improve capture efficiency.

Oxy-fuel combustion involves burning fossil fuels in pure oxygen instead of air, resulting in a flue gas that consists primarily of CO₂ and water vapor, with minimal nitrogen dilution. [11] After combustion, the water vapor is easily removed through condensation, leaving a concentrated stream of CO₂ that can be readily captured and compressed for storage or utilization. This approach eliminates the need for complex gas separation steps required in post-combustion capture, as the CO₂ concentration in the flue gas is significantly higher. However, generating pure oxygen through air separation units is energy-intensive and costly, which poses a major economic challenge.

In the utilization aspect, captured CO₂ is usually converted into value-added products such as fuels, chemicals (e.g., urea, methanol), polymers, or mineral carbonates. CO₂-enhanced oil recovery (CO₂-EOR) remains the primary utilization pathway to date, though it is not considered highly suitable due to its fossil-fuel association. The storage path is the long-term sequestration involving injecting CO₂ into geological formations such as depleted oil and gas reservoirs, deep saline aquifers, or unmineable coal seams. This enables CO₂ storage without adversely impacting the environment on long-term basis.

2 SOLID SORBENTS FOR CO₂ CAPTURE

Solid sorbents for CO₂ capture have attracted considerable interest as promising alternatives to conventional amine-based liquid absorbents, particularly due to their enhanced thermal stability, reduced corrosion, and lower regeneration energy requirements. Among the key parameters that dictate the performance of a solid adsorbent, such as adsorption/desorption kinetics, regeneration, stability, and adsorption capacity, the binding energy (BE) between the sorbent surface and CO₂ molecules plays a crucial role. [12] This parameter determines both the strength of interaction and the ease of regeneration, thereby influencing the cyclic stability and overall capture efficiency. The binding energy of CO₂ with a sorbent should ideally fall within a moderate range to ensure a balance between sufficient interaction for capture and facile desorption during regeneration. The binding energy is also closely related to the operating temperature of adsorbent materials, as shown in

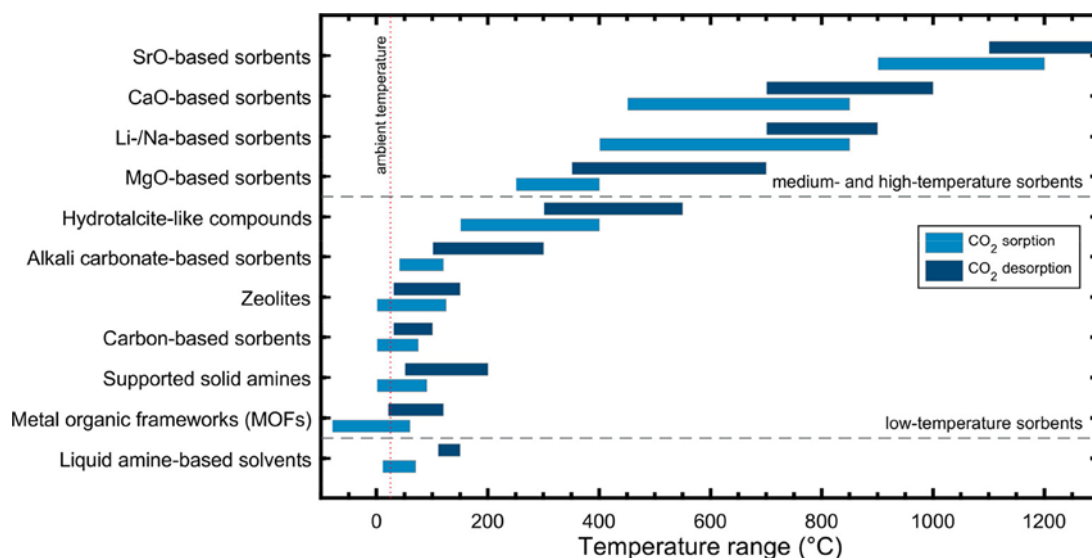


Figure 4. Materials with very low binding energies, such as some carbon-based materials, typically adsorb CO₂ via physisorption, which is reversible but may result in poor adsorption capacity at ambient conditions. Conversely, strong chemisorption, often observed in alkali metal oxides or amine-functionalized solids, usually presents higher BEs, which could hinder desorption and increase energy costs during regeneration. Among metal oxides, MgO has emerged as a unique candidate for CO₂ adsorption due to its high thermal stability, low cost, and the moderate basicity of surface O²⁻ sites. [13] However, the interaction of CO₂ with pristine MgO is typically weak, often insufficient for practical applications unless structural or surface modifications are introduced. This relatively weak interaction is attributed to the low polarizability and minimal surface defects in bulk MgO, which limit

the activation of CO₂ molecules. [14] To address this, recent studies have explored defect engineering, nanostructuring, and hybridization strategies to enhance the reactivity of MgO surfaces., [15, 16] Furthermore, doping MgO with alkali or transition metals (e.g., Li, Na, or Fe) has been shown to increase surface basicity and facilitate stronger CO₂ adsorption. [17] In addition, combining MgO with high-surface-area supports such as silica or carbon can improve dispersion and provide synergistic effects that raise the overall adsorption capacity while tuning the binding energy to fall within a desirable operational window. [18, 19]

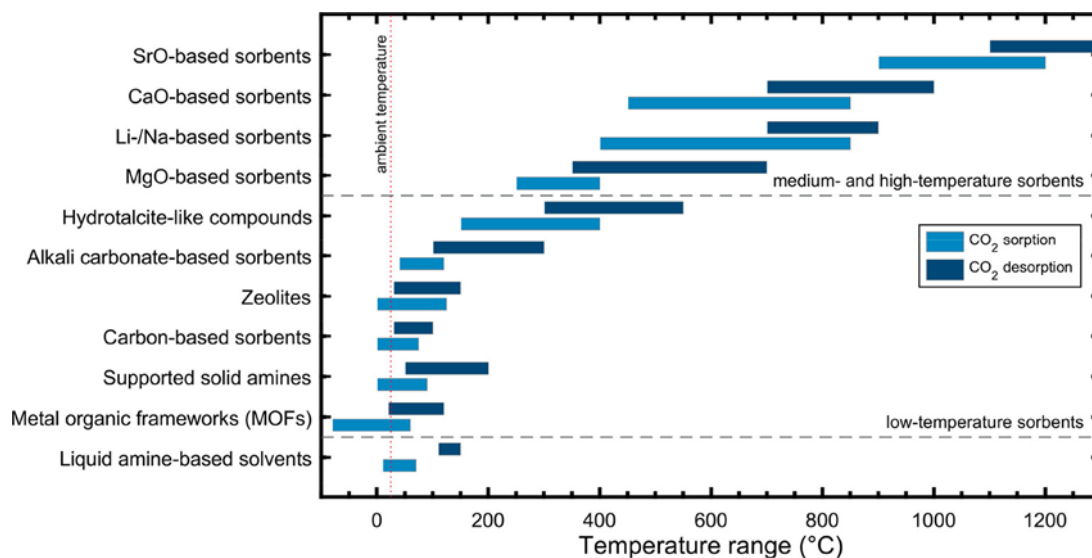


Figure 4: Overview of solid sorbents for CO₂ capture with their typical application temperature ranges. Reprinted with permission from [20]. Copyright 2021, American Chemical Society.

2.1 Alkali/Alkaline Metal Oxides CO₂ adsorbents

Metal oxides capable of reversible CO₂ uptake typically involve binary oxides of alkali metal/alkaline earth metal

The following equation can generalize the reversible capture of CO₂ by the metal oxide sorbents;



Alkaline earth metals and alkaline metals in Earth's (continental) crust are abundant; Ca 4.15 %, Na 2.36 %, Mg 2.33 %, K 2.09 %, (Ca+Na+Mg +K contribute for almost 11%) Ba 0.0425 %, Sr 0.037 %, Rb 0.009 %, Li 0.002 %, Cs 0.0003 %, Ra 9 x 10⁻¹¹ %, Be 0.00028 %, Fr trace

Based on the equilibrium temperatures required for reversible CO₂ capture and regeneration, metal oxide solid sorbents can be classified into three categories: (i) CaO, which reversibly

captures CO₂ at high temperatures; (ii) MgO, which does so at near-intermediate temperatures; and (iii) other oxides such as Li₂O, Na₂O, K₂O, SrO, and BaO, which are very strong bases whose corresponding carbonates require impractically high decomposition temperatures, often exceeding the melting point of the carbonate itself. Oxides of elements that are rare or expensive (e.g., Rb₂O and Cs₂O) or radioactive (e.g., Fr₂O and RaO) are not considered. Operating temperature regimes of various commonly encountered solid CO₂ adsorbents are graphically presented in Figure 5, with respect to temperature. Among metal oxides, MgO has emerged as a unique candidate for CO₂ adsorption due to its high thermal stability, low cost, and the moderate basicity of surface O²⁻ sites. [21] However, the interaction of CO₂ with pristine MgO is typically weak, often insufficient for practical applications unless structural or surface modifications are introduced. This relatively weak interaction is attributed to the low polarizability and minimal surface defects in bulk MgO, which limit the activation of CO₂ molecules. [22] To address this, recent studies have explored defect engineering, nanostructuring, and hybridization strategies to enhance the reactivity of MgO surfaces. Furthermore, doping MgO with alkali or transition metals (e.g., Li, Na, or Fe) has been shown to increase surface basicity and facilitate stronger CO₂ adsorption [23]. In addition, combining MgO with high-surface-area supports such as silica or carbon can improve dispersion and provide synergistic effects that raise the overall adsorption capacity while tuning the binding energy to fall within a desirable operational window. [24, 25] The general physico-chemical properties of the selected metal carbonates are accessible and are clearly organized in a tabulated format, see Table 1.

However, the alkali/alkaline metal oxide adsorbent exhibits poor working stability under cyclic loading. Microscopically, adsorbent particles undergo significant structural changes as they cyclically take up and release CO₂. The reason for the steep decrease in CO₂ uptake performance during the initial few cycles is due to the large difference in the molar volume of the metal oxide/carbonate pair and high operating temperatures, causing deactivation due to sintering. Due to these limitations, there are considerable gaps between the sorbents' stoichiometric CO₂ uptake capacities and those that are practically accessible after multiple carbon capture cycles. To address these two major challenges and improve the performance of MgO sorbents, various approaches have been proposed:

- **Modification with Alkaline Metal Carbonates/Nitrates:** Enhancing the formation of [Mg²⁺ O²⁻] ionic pairs and facilitating the formation of MgCO₃.

- **Dispersing MgO on Porous Supports:** Increasing the surface area and improving CO₂ diffusion.
- **Synthesizing Mesoporous MgO:** Creating high surface area materials to enhance CO₂ uptake.
- **Preparing MgO-Based Mixed Oxides:** Combining MgO with other oxides to improve performance.
- **Microstructural Modification:** Altering the microstructure to enhance CO₂ capture efficiency.

Chemistry:

- **Reaction Mechanism:** The main role of promoters is to dissolve MgO and enhance the formation of $[\text{Mg}^{2+} \cdot \text{O}^{2-}]$ ionic pairs. Gaseous CO₂ is adsorbed on the MgO surface and migrates to the triple phase boundary to form $[\text{Mg}^{2+} \cdot \text{CO}_3^{2-}]$ ionic pairs that precipitate as solid MgCO₃ upon reaching saturation.
- **Promoter Roles:** Promoters reduce the surface area covered by a CO₂-impermeable unidentate layer and dissolve CO₂, which can react with oxide ions (O²⁻) present in the alkali metal nitrate to form carbonate ions (CO₃²⁻). [26]

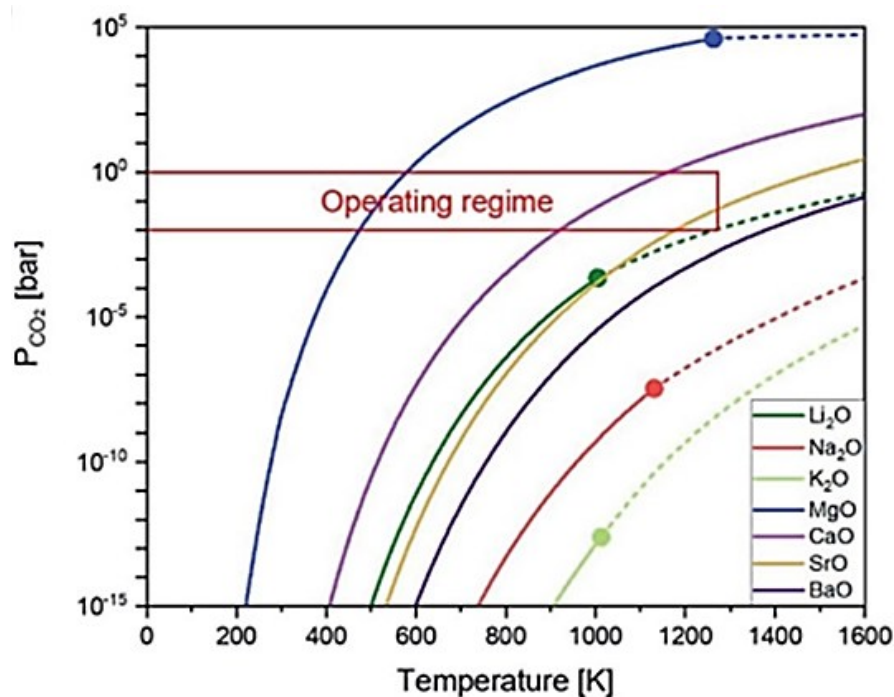


Figure 5: Metal oxides classification according to equilibrium temperatures. Reproduced from Ref. [27] with permission from the Royal Society of Chemistry.

Table 1: Overview of physico-chemical properties of alkali/alkaline earth metals

Metal oxide/ carbonate	Molecular weight (g mol ⁻¹)	CO ₂ uptake capacity (g _{CO2} g _{MgO} ⁻¹)	Gibbs free energy* (carbonation) (kJ mol ⁻¹)	Enthalpy of reaction* (carbonation) (kJ mol ⁻¹)	Specific heat capacity* (J K ⁻¹ mol ⁻¹)	Equilibrium temperature p _{CO2} = 0,15/1,00 bar (°C)	Melting point (°C)	Molar volume (cm ³ mol ⁻¹)	True density (kg m ⁻³)	Carbonation reaction
MgO	40,304	1,094	-48,55	-100,89	37,24	(255/340) /	2825	11,29	3570	MgO + CO ₂ → MgCO ₃
MgCO ₃	84,314				76,11	(305/395)	990	28,01	3010	
CaO	56,077	0,786	-130,44	-178,17	42,05	770/885	2900	16,74	3350	CaO + CO ₂ → CaCO ₃
CaCO ₃	100,087				83,47		1330	36,93	2710	
SrO	103,619	0,426	-190,18	-241,49	45,25	1070/1225	2530	20,68	5010	SrO + CO ₂ → SrCO ₃
SrCO ₃	147,629				82,42		1495	38,45	3840	
BaO	153,326	0,288	-220,73	-272,49	4702	1335/1560	1973	25,26	6070	BaO + CO ₂ → BaCO ₃
BaCO ₃	197,336				85,98		1555	45,79	4310	
Li ₂ O	29,881	1,476	-174,65	-222,71	54,1	1150/1395	1455	16,24	1840	Li ₂ O + CO ₂ → Li ₂ CO ₃
Li ₂ CO ₃	73,891				98,32		730	35,70	2070	
Na ₂ O	61,979	0,712	-270,60	-321,11	69,12	>1500	1130	28,43	2180	Na ₂ O + CO ₂ → Na ₂ CO ₃
Na ₂ CO ₃	105,989				112,30		860	41,56	2550	
K ₂ O	94,196	0,468	-350,31	-396,29	72,00	>1500	740	40,08	2350	K ₂ O + CO ₂ → K ₂ CO ₃
K ₂ CO ₃	138,206				114,43		900	61,73	2239	
Rb ₂ O	186,935	0,236	-357,17	-401,09	74,00	>1500	505	46,39	4030	Rb ₂ O + CO ₂ → Rb ₂ CO ₃
Rb ₂ CO ₃	230,945				117,60		875	70,63	3270	
Cs ₂ O	281,810	0,156	-348,44	-394,99	76,00	>1500	495	59,71	4720	Cs ₂ O + CO ₂ → Cs ₂ CO ₃
Cs ₂ CO ₃					123,88					

3 MgO-BASED SOLID ADSORBENTS FOR CO₂ CAPTURE (MgO-MgCO₃ SYSTEM)

The MgO-MgCO₃ system offers a promising route for CO₂ capture at medium to high temperatures. MgO, an alkaline earth metal oxide, can capture CO₂ effectively at relatively lower temperatures (25–400 °C) compared to metal oxides such as CaO, while endowing high regeneration capability at 450–500 °C under a N₂ atmosphere. This lower regeneration temperature makes MgO an attractive alternative to CaO, potentially reducing the overall energy consumption of the CO₂ capture process. The equilibrium reaction thermodynamics of the Mg-MgCO₃ system can be described by the following equation:



However, despite the relatively high performance of MgO as a CO₂ adsorbent, the practical CO₂ uptake of commercially available MgO is typically limited to only 2–4 wt.%. This reduced performance is primarily due to the formation of a dense, impermeable MgCO₃ layer on the surface of MgO particles. This passivation layer acts as a barrier, hindering CO₂ diffusion to the unreacted MgO core and thus significantly slowing down the overall carbonation reaction. A 27-year study of MgO as a solid absorbent has shown the formation of a reactive layer measuring between 1.3 and 1.7 μm, composed of hydrated magnesium carbonates, magnesium hydroxide, and possibly amorphous magnesium carbonates, as shown in Figure 6 [28].

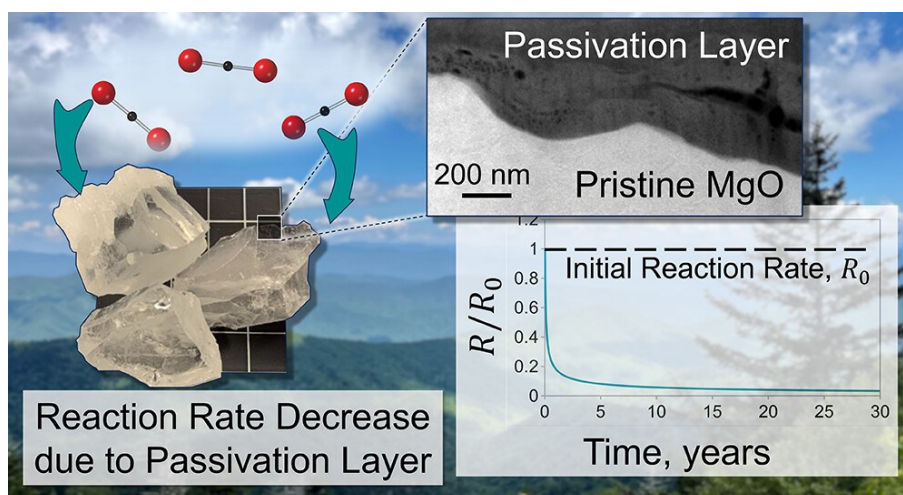


Figure 6. CO₂ adsorption on MgO in a 27-year period. Reproduced with permission from [28]. Copyright 2023, American Chemical Society.

In contrast, short-term experiments (83 days) showed that new carbonate phases tend to form along step features on the MgO surface, highlighting the role of reactive site density in

initiating carbonation. Modeling indicates that the majority of carbonation occurs within the first few years, with limited additional carbonation over longer periods. The study suggested that strategies such as reducing particle size to the sub-micrometer range, optimizing microstructure, or altering surface morphology are essential for enhancing reactivity and scalability.

3.1 Mechanism of MgO Promotion by Alkali Molten Salts

The carbonation of MgO promoted by molten salt involves two proposed mechanisms as shown in Figure 7:

1. Dissolution and Ionic Pair Formation:

- The promoter dissolves MgO and enhances the formation of $[\text{Mg}^{2+} \cdot \text{O}^{2-}]$ ionic pairs.
- Gaseous CO_2 is adsorbed on the MgO surface and migrates to the triple phase boundary.
- At the triple phase boundary, $[\text{Mg}^{2+} \cdot \text{CO}_3^{2-}]$ ionic pairs are formed, which precipitate as solid MgCO_3 upon reaching saturation.

2. Surface Area Reduction and CO_2 Dissolution:

- The promoter reduces the surface area of MgO covered by a CO_2 -impermeable unidentate layer.
- It dissolves CO_2 , which can react with oxide ions (O^{2-}) present in the alkali metal nitrate ($\text{NO}_3^- \leftrightarrow \text{NO}_2^+ + \text{O}^{2-}$) to form carbonate ions (CO_3^{2-}).
- These carbonate ions then participate in the formation of MgCO_3 .

Key Points:

- The promoter plays a crucial role in enhancing the carbonation process by facilitating the formation of ionic pairs and dissolving CO_2 .
- The interaction between CO_2 and MgO is influenced by the surface facets of MgO, with the MgO (111) facet showing more favorable reactions due to alternating layers of O and Mg atoms.
- The use of molten salts as promoters can significantly impact the electrostatic interactions with the MgO surface, affecting the overall CO_2 uptake rate.

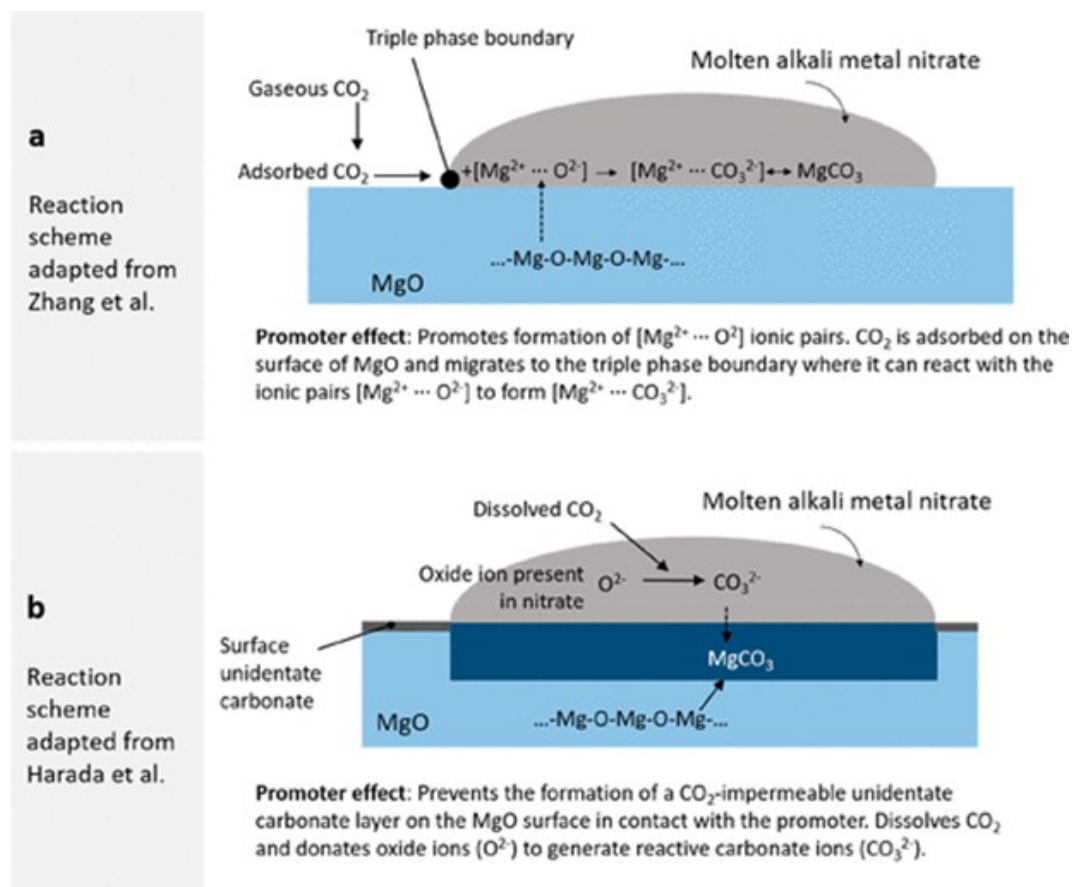


Figure 7: Mechanism of adsorption by promoted MgO. Reprinted with permission from [20]. Copyright 2021, American Chemical Society.

4 MOLTEN SALTS

Molten salts were first used by Oak Ridge National Laboratory (ORNL) in 1950 for a nuclear-powered aircraft engine. By 1954, ORNL focused on nuclear reactors due to their thermal stability. The U.S. Atomic Energy Commission (AEC) developed a successful molten salt test breeding reactor in the 1960s, but funding was denied in favor of the Liquid Metal Fast Breeding Reactor (LMFBR), ending molten salt reactor research in 1976. The first molten salt reactor operated at 882 °C and used molten fluorides like uranium and thorium fluoride. By 1959, AEC focused on breeding reactors, leading to the Molten-Salt Reactor Experiment (MSRE) proposal. Despite addressing concerns, the MSRE struggled for funding against the LMFBR project. In 1993, Solar Two, the first solar power plant using molten salts for energy storage, was developed in California. It stored 10 MW of electricity for one hour using heliostats to concentrate sunlight. Reports documented the project's findings, aiding the development of molten salt energy storage systems globally. [29]

4.1 Physical and Thermodynamic Properties of Molten Salts

Molten salts are ionic liquids and form a broad category of fluids named after their anion. These salts are typically blends of two or more salts designed to achieve desirable thermophysical properties for their respective applications. Therefore, molten salts are often used in their eutectic composition. The eutectic point of a salt mixture provides transitions from a solid to a liquid phase at a unique temperature that is lower than the melting points of any of the individual components or any other combination of those components. Consequently, larger operational temperature ranges can be achieved, which make molten salts attractive fluids for high-temperature sensible heat storage and transfer. Molten salts exhibit a high specific heat capacity associated with high density values, consequently, a large amount of energy can be stored and carried per unit of volume. Moreover, molten salts are considered efficient heat transfer fluids due to their suitably high thermal conductivity. Another significant advantage of these salts is their low vapor pressure, which allows operation at higher temperatures without pressure build-up, which offers advantages when compared to thermal oil and steam. This characteristic also enables the use of thin walls, reduces the wall temperature gradient, and temperature-induced mechanical stress. Furthermore, molten salts present low viscosity values, which result in reduced pressure drops and associated pumping power, thereby lowering the overall operational cost.

Consequently, molten salts can contribute to simpler and more compact systems when compared to currently available alternatives, requiring fewer heat exchangers and simpler piping schemes, thereby reducing equipment costs as well. However, one of the primary drawbacks of utilizing molten salts is associated with their high melting points, posing the risk of solidification within pipes. This necessitates the use of trace heating to prevent such solidification. After the salt is fully melted, it remains thermally stable until it reaches its maximum operational temperature, which is commonly limited by the salt's thermal decomposition, but can also be influenced by its vapor pressure at high temperatures. Lastly, corrosion in containers, pipes, valves, and pumps limits the application of molten salts in many areas and increases the capital cost. Therefore, the molten salt's temperature must be monitored and controlled at all times. [30]

4.2 Nitrates Molten Salts

Nitrate molten salts are mixtures of nitrate salts used as heat transfer and storage media in concentrated solar power (CSP) plants and industrial applications. These salts enable the transfer and storage of heat, which is helpful during periods of low solar radiation or at night. For example, Solar Salt has a melting range from 223 °C to 240 °C, while lithium nitrates have high thermal stability up to 550–600 °C.

Nitrate molten salts are used in CSP plants for heat storage and increased energy production. In industrial applications, they are used to produce chemical compounds such as phthalic anhydride, maleic anhydride, methyl methacrylate, acrylic acid, and acrolein. Reactors using nitrate molten salts can achieve high operating temperatures up to 550 °C.

Nitrates are classified as "Class I oxidizers," meaning they slightly increase the burning rate of combustible materials but do not cause spontaneous ignition. It is important to handle them as oxidizing hot liquids to avoid the risk of deflagration.

Nitrate molten salts can cause corrosion to ferro-alloys at high temperatures. Stainless steels such as 304, 316L, 321H, and 347H are used for contact with the salts due to their good corrosion resistance, thanks to high contents of chromium, nickel, titanium, niobium, and molybdenum. [30]

Table 2. Overview of commercial nitrates molten salts composition. Redrawn from [30] Solar Salt and NaKLiNO₃, as typical representatives of double and triple AMS, respectively, were selected for MgO promotion in the experimental part.

Name	NaNO ₃	NaNO ₂	KNO ₃	KNO ₂	Ca(NO ₃) ₂	LiNO ₃	T _m / °C	T _d / °C
Solar Salt	60		40				240	601
Hitec	7	40	53				140	500
Hitec XL	7		45		48		140	525
NaKLiNO ₃	18		52			30	120	550
CaLiNO ₃ NaKNO ₂		16,8		45	13,6	24,6	72	400
Sandia Mix	13		66		14	7	90	500

5 AIMS & OBJECTIVES OF WORK

The aim of this master's thesis is to investigate the impact of alkali metal salts promotion on the CO₂ capture performance of MgO solid adsorbent at intermediate temperature.

In order to achieve this aim, a set of objectives has been developed as follows;

- To synthesize MgO with well-defined morphology
- To select alkali metal salts and their eutectic mixtures for MgO promotion
- To prepare promoted MgO samples at various alkali metal salt ratios
- To evaluate the CO₂ uptake performance of promoted MgO samples by thermogravimetry
- To evaluate the working stability of the best-performing samples by cycling loading

II PRACTICAL PART

6 SUBSTANCES AND APPARATUS

6.1 Chemicals

- Magnesium acetate tetrahydrate, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O}$ (CAS:16674-78-5; Sigma Aldrich, 99.5 -102%)
- Urea, $\text{CO}(\text{NH}_2)_2$ (CAS: 57-13-6; Sigma Aldrich, $\geq 99.5\%$)
- Lithium nitrate, LiNO_3 (CAS: 7790-69-4; ThermoScientific, 98%+)
- Sodium nitrate for analysis, NaNO_3 (CAS: 7631-99-4; ACS, ISO, Reag. Ph Eur)
- Potassium nitrate for analysis, KNO_3 (CAS: 7757-79-1; PENTA, ISO, Reag. Ph Eur)
- ultra-pure water (UPW)

6.2 Tools and Equipment

- Microwave-focused field reactor Magnum II ERTEC V 2
- Centrifuge THERMO Multifuge X3R
- Muffle furnace LAC-LMH 07/12
- Laboratory oven MEMMEERT VO 400
- Analytical balance Kern ABT 120-4M
- Hotplate with magnetic stirrer Heidolph MR Hei-Standart

Common laboratory supplies, such as glass rod, spoons, spatula, beakers, tweezers, mortar and pestle, ceramic crucibles with lids, nitrile examination and protective gloves,

6.3 Characterization techniques

- Scanning electron microscope Nova Nano SEM450 (SEM)

Micrographs were captured at accelerating voltage 5 kV, using TLD detector. keeping magnification at 10 kX for better comparison.

- X-ray diffractometer Rigaku MiniFlex 600 (XRD)

XRD patterns were recorded in the diffraction angle ranging from 10° to 90° 2θ with step 0.02° and scanning rate $8^\circ/\text{min}$ at voltage and current of 40 kV and 15 mA, respectively, by using $\text{CoK}\alpha$ radiation.

- Volumetric sorption analyzer BELSORP-mini II

Specific surface area and pore size distribution of the samples were evaluated via Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis of N₂ adsorption/desorption isotherms recorded at 77 K.

- Thermogravimetric analyzer TA Q500 (TG)

Thermogravimetry was used for the evaluation of CO₂ uptake performance, as specified in detail in paragraph 8.

7 MATERIAL PREPARATION

7.1 Synthesis of MgO rods

MgO rods were prepared by thermal decomposition of a precursor material synthesized via microwave-assisted synthesis, following the procedure reported in [31], with slight modification as follows.

Briefly, 3.22 g of the magnesium acetate tetrahydrate and 0.65 g of the urea were dissolved in 45 mL and 15 mL of ultra-pure water, respectively. After that, solutions were mixed together and transferred into a Teflon vessel with a volume of 108 mL and enclosed in a pressure vessel made of steel. The reaction was performed by the high temperature (up to 300 °C) and pressure (up to 5 MPa) controlled microwave reactor Magnum II (Ertec, Poland, energy density of about 5 W/mL at the bottom of the reaction vessel, permitting to raise the temperature at a rate of approximately 1 K/s) at the 180 °C for 30 minutes at microwave power 75 %. A record of Temperature/pressure as a function of time for a typical microwave synthesis procedure is shown in Appendix P I.

After cooling to room temperature, the obtained product was thoroughly washed with ethanol and centrifuged twice for 10 minutes at 8,000 rpm using a centrifuge. Finally, the product was left to dry overnight in a laboratory oven (Laboratory oven MEMMEERT VO 400) at 65 °C. MgO rods were obtained by thermal decomposition of precursor material in a Muffle furnace at 500°C for one hour at a heating rate of 10 °C/min. Calcining temperature was chosen based on the TG analysis of the precursor material Figure 12

7.2 Promotion of MgO Nanorods by Alkali Metal Salts

In the next step, as-prepared MgO nanorods were promoted by alkali metal salt following a literature survey in the theoretical part (see Table 2. Overview of commercial nitrates molten salts composition. Redrawn from [30] Solar Salt and NaKLiNO₃, as typical representatives of double and triple AMS, respectively, were selected for MgO promotion in the experimental part. MgO samples were promoted by NaNO₃ and LiNO₃ single metal salts at molar ratios of 10, 20, and 30 % (relative to Mg). Furthermore, MgO samples promoted by NaNO₃/KNO₃ double alkali metal salts with molar fraction corresponding to their eutectic mixture (Na_{0.54}K_{0.46})NO₃ (see appendix P II) and LiNO₃/NaNO₃/KNO₃ triple alkali metal salts with molar fraction corresponding to their eutectic mixture (Li_{0.38}Na_{0.18}K_{0.44})NO₃ (see appendix P III). Similar to single AMS promoted MgO samples, also double and triple AMS

promoted MgO samples were prepared at molar ratio 10, 20 and 30 % (relative to Mg). Generally, samples were promoted by wet incipient method, as follows; Calculated amount of AMS (either single, double, or triple) weighted using analytical balance directly into a PP cup with volume of 5 mL were dissolved in 1 mL of UPW added. All AMS used for MgO promotion were dried overnight in a laboratory oven at 120 °C overnight in an open glass vial to minimize impact of moisture on sample composition. Then, 0.2 g of as prepared MgO was added into AMS solution and dried at 60 °C in a laboratory oven. Both UPW volume and MgO weight were optimized prior to a sample preparation to obtain sample with consistency of paste. This should prevent sample inhomogeneity and ensure uniform deposition of AMS onto MgO surface. Finally, dried sample were transferred into ceramic crucible covered by a lid and thermally treated in a Muffle furnace at 450 °C for three hours with a heating rate of 2 °C/min, which is necessary for AMS fusion. After cooling down naturally, samples were collected in a vial flask and kept in a desiccator prior their characterization by relevant methods of instrumental analysis and evaluation of CO₂ uptake performance.

Table 3. Summary of the composition of the AMS and their mixture of as-promoted MgO samples. Amount of AMS and their mixture were calculated relative to 0.2 g of MgO

Sample	Molar ratio of AMS relative to MgO (%)	LiNO ₃ (mg)	NaNO ₃ (mg)	KNO ₃ (mg)
Na1	10		42.18	
Na2	20		84.36	
Na3	30		126.54	
Li1	10	34.22		
Li2	20	68.44		
Li3	30	102.66		
NaK1	10		22.78	23.08
NaK2	20		45.55	46.16
NaK3	30		68.33	69.25
LiNaK1	10	13.00	7.59	22.08
LiNaK2	20	26.01	15.18	44.16
LiNaK3	30	39.01	22.78	66.24

8 EVALUATION OF CO₂ UPTAKE PERFORMANCE

The CO₂ uptake performance of prepared samples was characterized by using a thermogravimetric analyzer TGA Q500 (TA Instruments, USA). Non-isothermal, step-by-step incremental carbonation and cyclic experiments (methods) were designed to investigate the specific features of CO₂ uptake performance. The temperature procedure for each of them is specified below. For each experiment, the sample weight of around 11 ± 0.5 mg was uniformly distributed in a platinum sample pan. At the beginning of each method, the measured sample was subjected to a pre-treatment procedure including the heating of the samples from initial temperature to 450 °C at a constant heating rate of 10 °C.min⁻¹ and holding this temperature for 1 hour under purging the samples by a nitrogen (N₂) carrier gas (purity 5.0, SIAD, Czech Republic) at a flow rate of 100 mL.min⁻¹. This drying step was implemented in each method to remove any pre-adsorbed species (e.g., atmospheric CO₂, water, etc.) from the sample before examining the CO₂ uptake itself. The concentration of CO₂ (FOOD 2 grade, SIAD Czech Republic) used throughout experiments for carbonation was kept at 70 %, which was obtained by mixing the flow rates of pure CO₂ and N₂ in a ratio of 70/30 mL.min⁻¹.

8.1 Non-isothermal experiment

All prepared samples were initially investigated by the non-isothermal method. The goal of these experiments was to quickly evaluate the CO₂ adsorption capacity and determine the optimum amount of AMS (loading) for each set of samples. A scheme of the temperature procedure for the non-isothermal experiment is shown in Figure 8.

The temperature procedure consist of sequence of consecutive steps as follows; (i) heating from 30 °C to 450 °C at the heating rate of 10 °C/min under N₂ atmosphere (100 mL.min⁻¹); (ii) 60 minutes isotherms at 450 °C; (iii) cooling down to 30 °C at the heating rate 10 °C/min; (iv) holding the defined temprerature (30 °C) for 10 minutes; (v) switching gas from pure N₂ to CO₂ and setting the required CO₂ concentration to 70 % by adjusting CO₂/N₂ flow rates to 70/30 mL.min⁻¹, and heating the sample to 450 °C at the heating rate of 5 °C/min followed by cooling down (cooling step is not shown).

Based on the performed experiment, the best performing sample (i.e, with the highest CO₂ maximum uptake value) with optimum molar ratio of AMS was selected from each set of sample series for further evaluation by step-by-step incremental carbonation and cyclic test experiments.

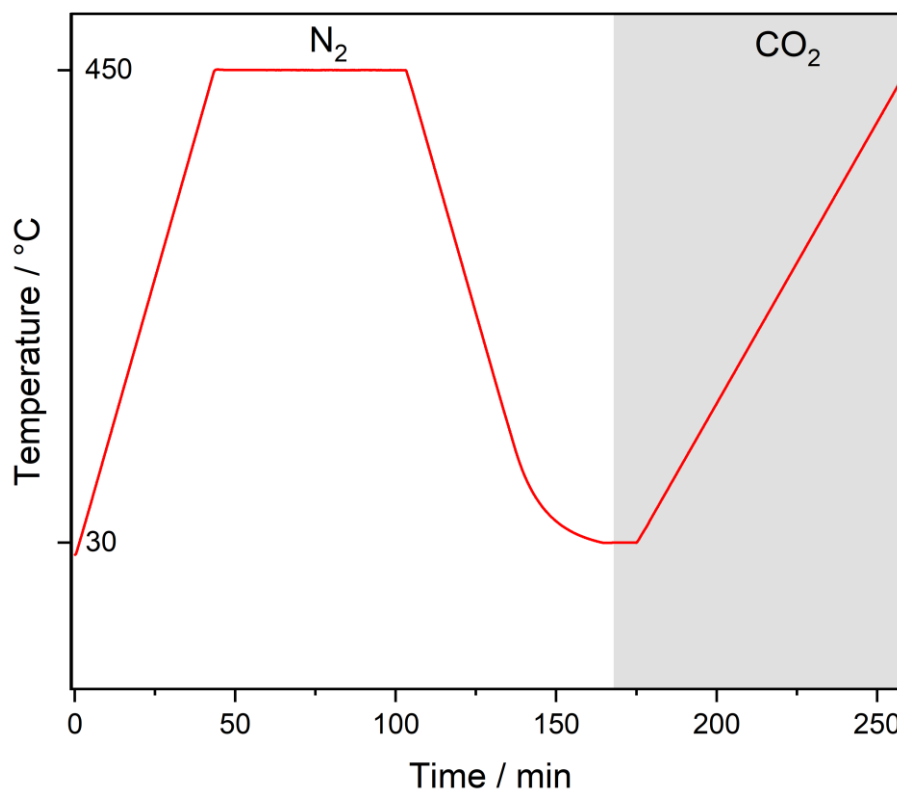


Figure 8. Scheme of the temperature procedure for the non-isothermal experiment.

8.2 Step-by-step (Stepwise) incremental carbonation experiments

A step-by-step incremental carbonation experiment was performed to gain insight into the adsorbent's uptake intensities at different temperatures. The first step was the same as in the non-isothermal method, including drying the sample at 450 °C for one hour, followed by cooling down to 30 °C at the heating rate of 10 °C.min⁻¹ under nitrogen atmosphere. In contrast to the non-isothermal method, the set temperature (30 °C) was held for one hour. Then, the N₂ atmosphere was switched to CO₂, and the concentration of CO₂ was adjusted to the required 70 % while increasing the temperature to 50 °C and holding this temperature for 60 min. The temperature increases in a stepwise manner with an increment of 25 °C and isothermal heating for 60 minutes at each step. The temperatures increased sequentially as follows: 50 °C, 75 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, 275 °C, 300 °C, and finally 325 °C. The CO₂ flow rate remained constant throughout the experiment. An experimental design allowed the evaluation of the carbonation onset temperature as well as the contribution of an adsorbent's uptake at each temperature increment, providing valuable insights into its performance across various thermal conditions.

In contrast to non-isothermal and cyclic experiments, samples were not calcined at the end of the experiment, providing a partially carbonized sample for analysis. The procedure for the step-by-step incremental carbonation experiment is shown in Figure 9.

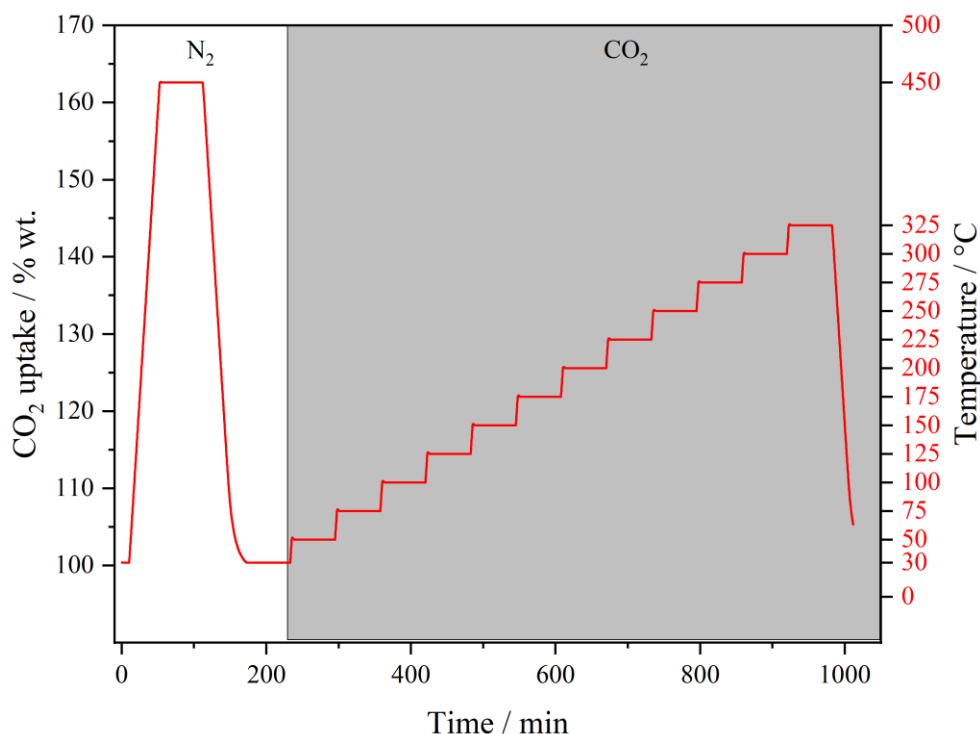


Figure 9. Scheme of temperature procedure for step-by-step incremental carbonation experiment.

8.3 Cyclic experiments

A cyclic experiment was performed to evaluate the working stability of adsorbents under cyclic conditions. The initial drying step was performed as previously described to ensure the sample was free from moisture and contaminants. In contrast to previous methods, the set temperature (30 °C) was held for 10 min. The first cycle starts with CO₂ adsorption, which was gained by switching the atmosphere from nitrogen to CO₂ and setting the desired concentration of CO₂ (70 %). Then, the temperature increases gradually from 30 °C to 325 °C at the heating rate of 10 °C/min. The set temperature was then kept for 30 minutes under isothermal conditions. For desorption, the temperature was further increased to 375 °C at the same heating rate of 10 °C/min and held for 20 minutes. Of course, the carrier gas was switched back from CO₂ to nitrogen during the desorption process. Finally, the temperature was cooled down to 30 °C, completing the first cycle. This process was repeated for 10 cycles, excluding the initial drying step for subsequent cycles. This cyclic experiment

allowed the quantification of the adsorbent's uptake capacity over multiple cycles, providing valuable insights into long-term performance and stability. The scheme of the temperature procedure for the cycling experiment is shown in Figure 10.

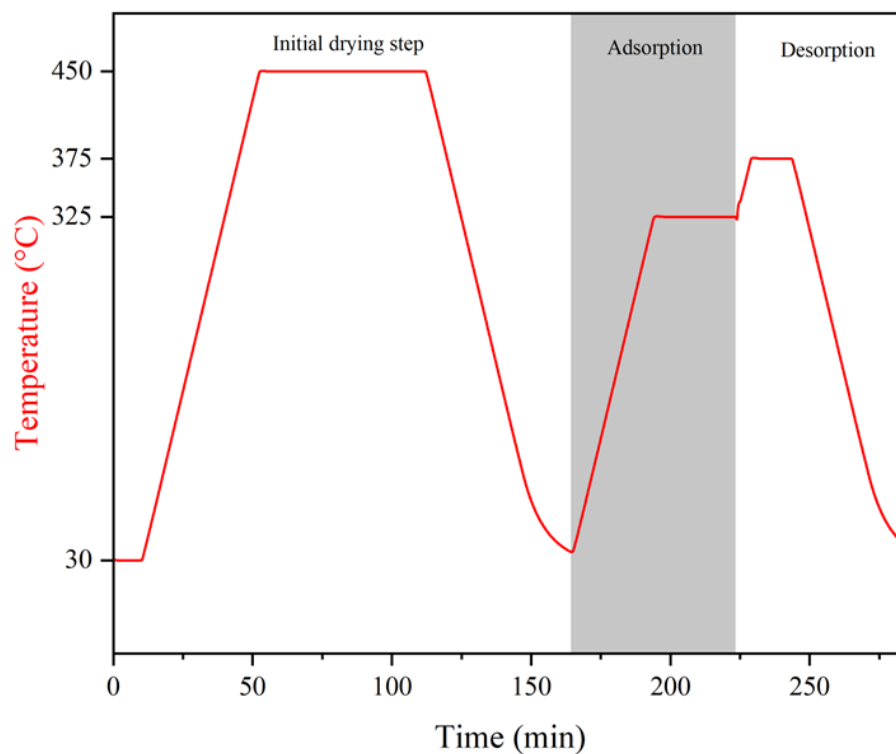


Figure 10. Scheme of temperature procedure for the cyclic experiment. Displayed as one cycle out of ten cycles.

9 RESULTS AND DISCUSSION

9.1 MgO synthesis

The morphology of product obtained by microwave-assisted synthesis is shown in the left panel in Figure 11. As can be seen, it exhibits rod-like structure with dimension at micron scale.

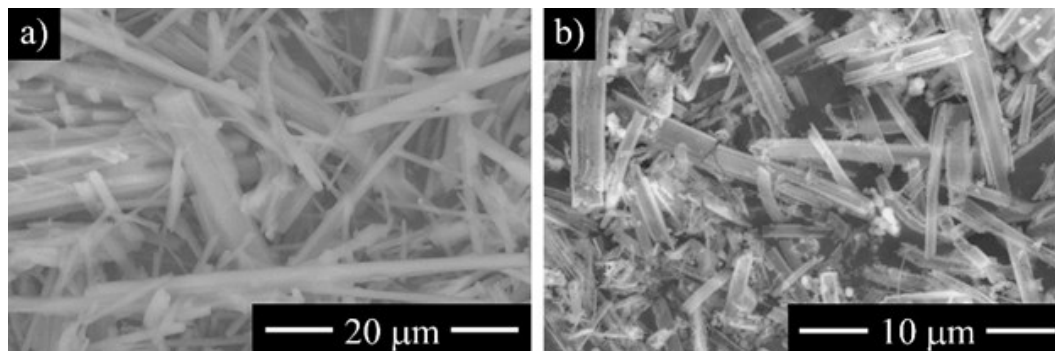


Figure 11. Morphologies of precursor material before (left panel) and after calcining (right panel)

Diffraction pattern of synthesis product exhibits typical features of layered material with phase structure corresponding to Giorgiosite mineral (PDF Card No.: 00-029-0858) with idealized composition $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (Figure 13). To determine calcining temperature required for conversion of the precursor to MgO, TG analysis was performed in the temperature range from 30 to 700 °C at a heating rate 10 °/min under air atmosphere. As can be seen in Figure 13, precursor material decomposed in three well separated consecutive steps with overall mass loss 67.18 wt. % which agrees with values reported elsewhere. [32] Following results from TG analysis, calcining temperature at 500 °C was identified to be sufficient for thermal decomposition of the precursor.

Morphology of sample obtained by calcining of synthesized precursor material resemble morphology of precursor material yet with porous structure due to the evolution of gaseous components during calcining. Inevitably, micro-rods dimensions has been significantly reduced (See right panel in Figure 11). Diffraction peaks observed in diffraction pattern of calcined sample in Figure 13 b) can be attributed to the cubic MgO phase structure corresponding to Periclase mineral (PDF Card No.: 00-045-0946)

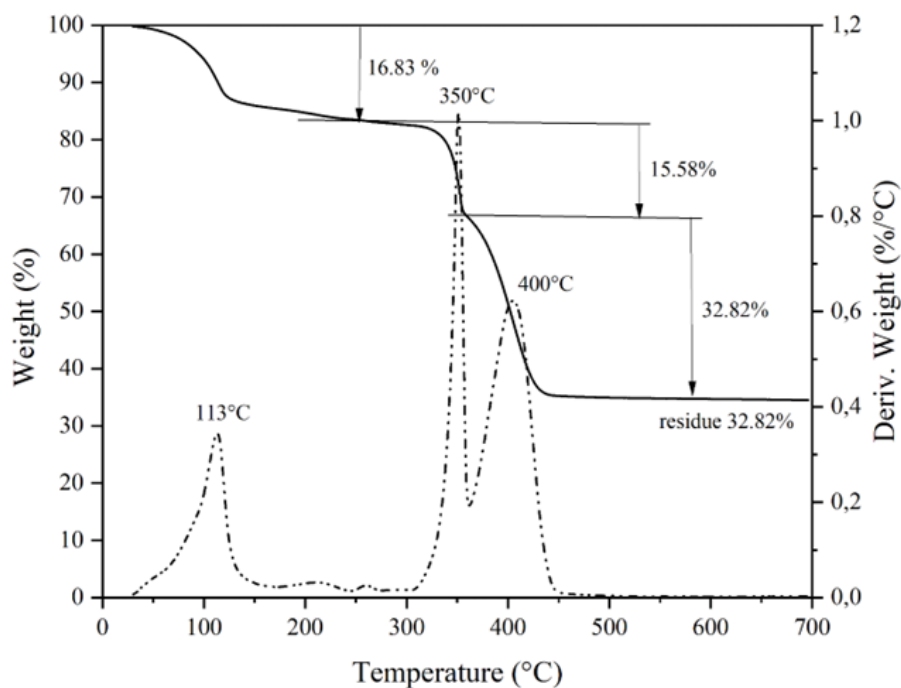


Figure 12. TG curve and its derivative recorded for thermal decomposition of MgO precursor material obtained by microwave synthesis.

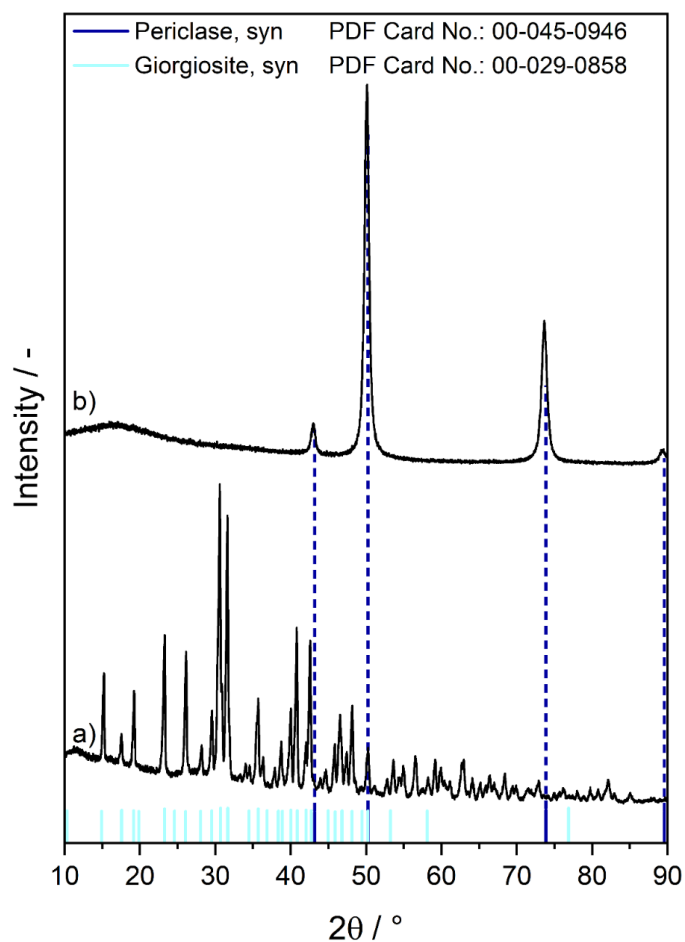


Figure 13. Diffraction patterns of MgO precursor material (a) and calcined product (b)

9.2 Analysis of CO₂ uptake for non-isothermal experiment

The non-isothermal experiment is described in detail in section 11.1. enables the rapid initial assessment of CO₂ uptake performance in terms of maximum uptake capacity and to determine the optimum molar ratio of alkali metal salt promoter. This experiment is characterized by turning temperature.

$$T_{turn} = \frac{\Delta_r H^\circ(T_{turn})}{\Delta_r S^\circ(T_{turn})} \approx \frac{\Delta_r H_{298}^\circ}{\Delta_r S_{298}^\circ} \quad 3$$

at which $\Delta_r G^\circ_{298} = 0$ is commonly used to determine suitable operation conditions. (with respect to Mg)

9.2.1 Analysis of CO₂ uptake of MgO samples promoted by NaNO₃

In order to determine optimum molar ratio of alkali metal salt promoter (with respect to Mg) TG curves were recorded following temperature program described in a detail in the section 11.1. Non-isothermal experiment

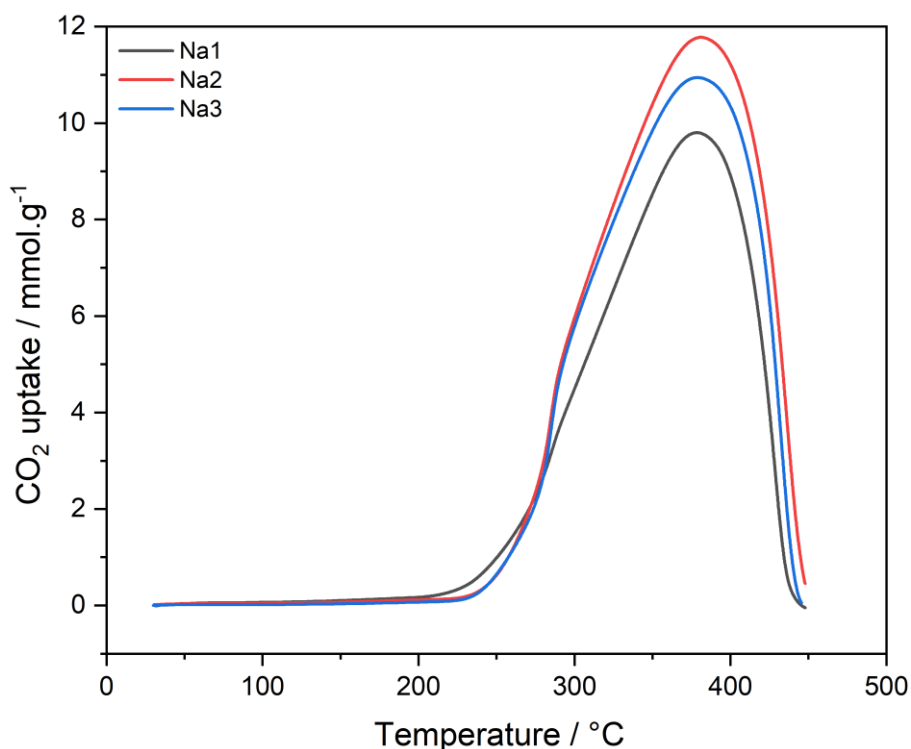


Figure 14. CO₂ uptake of MgO samples promoted by 10 mol % (Na1), 20 mol % (Na2) and 30 mol % (Na3) of NaNO₃.

Figure 14 shows the adsorption of MgO promoted by NaNO₃ at different concentrations. Adsorption for the Na1 sample starts at 200°C, while the other two samples begin adsorbing

at 230°C. The highest adsorption is exhibited by the Na2 (11,8 mmol.g⁻¹), followed by the Na3 (10,9 mmol.g⁻¹), and the lowest adsorption is shown by the Na1 (9,8 mmol.g⁻¹).

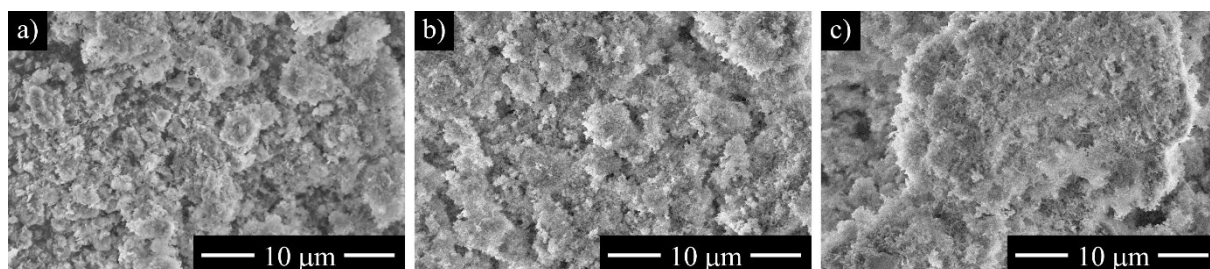


Figure 15. SEM images of *fresh* MgO samples promoted by NaNO₃ at various molar ratios: a) Na1, b) Na2, and c) Na3.

Figure 15 shows the surface morphology of MgO promoted by NaNO₃. The morphology of the Na1 and Na2 samples does not differ significantly, whereas the surface of the Na3 sample has spread more horizontally rather than forming crystals.

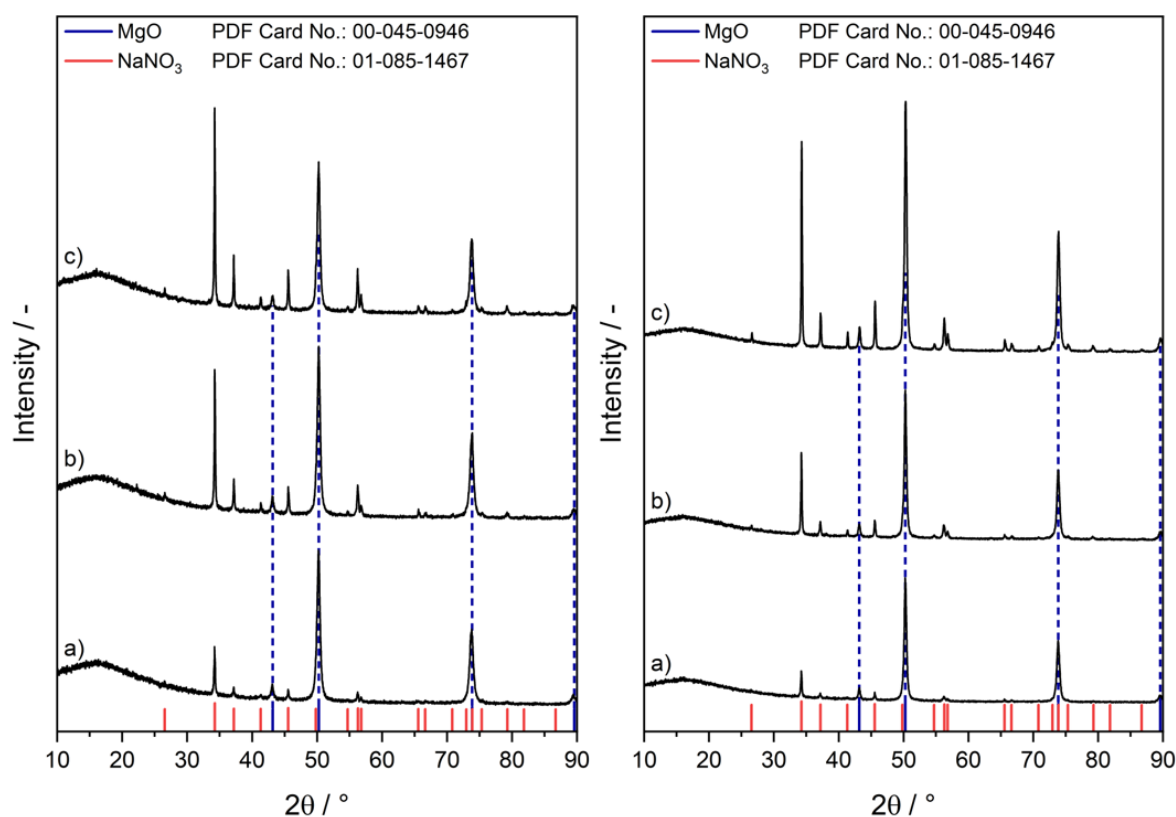


Figure 16. Diffraction patterns recorded for *fresh* MgO samples promoted by NaNO₃ at various molar ratios: a) Na1, b) Na2, and c) Na3 (left panel) and *after* non-isothermal experiment (right panel).

Figure 16 shows the diffraction patterns of MgO promoted by NaNO₃ before and after the non-isothermal experiment. In both cases, it can be observed that as the salt concentration increases, the intensity of their peaks also increases.

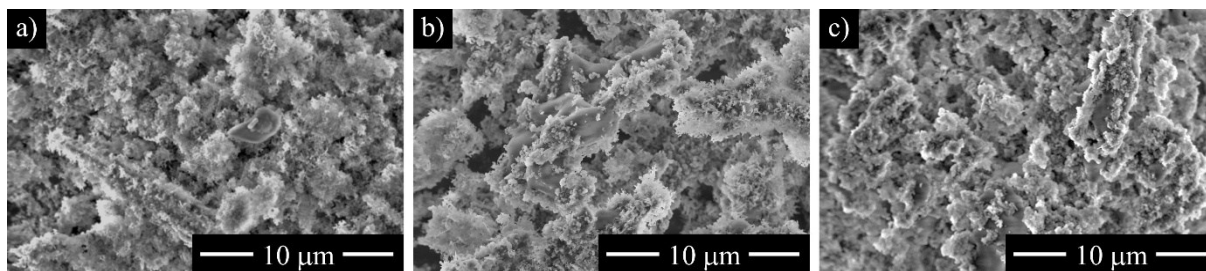


Figure 17. SEM images of MgO samples promoted by NaNO_3 at various molar ratios captured *after* non-isothermal experiment: a) Na1, b) Na2, and c) Na3.

Figure 17 shows the surface morphology of MgO promoted by NaNO_3 at different concentrations. In the Na1 sample, a subtle indication of MgO nanowires can be observed. Surface segregation is visible in all samples, most prominently in the Na2 sample.

Table 4. Summary of maximum CO_2 uptake values and textural characteristics for MgO samples promoted by NaNO_3 at various molar ratios. Textural properties were evaluated for both *fresh* samples, i.e., prior to the experiment, and samples collected *after* the non-isothermal TG experiment.

Sample	CO_2 uptake (mmol. $\text{g}_{\text{sorbent}}^{-1}$)	*BET ($\text{m}^2 \cdot \text{g}^{-1}$)		** V_T ($\text{cm}^3 \cdot \text{g}^{-1}$) *** d_P (nm)		****Dc (nm)*	
		fresh	after	fresh	after	fresh	after
Na1	9.8	31.63	16.07	0.471 / 59.55	0.158 / 39.43	19.3 ± 4.3	26.1 ± 3.3
Na2	11.8	16.67	7.63	0.183 / 43.93	0.069 / 36.16	19.5 ± 4.5	27.1 ± 2.1
Na3	10.9	10.28	4.68	0.109 / 42.27	0.038 / 32.73	22.9 ± 9.4	35.7 ± 7.3

*Specific surface area estimated based upon Brunauer-Emmet-Teller analysis

**total pore volume

***mean pore diameter

****average crystalline domain size estimated by Halder-Wagner method

In Table 4, the comparison of individual concentrations before and after the non-isothermal experiment can be observed. The highest adsorption is exhibited by sample Na2, while the lowest is shown by sample Na1. The specific surface area decreases with increasing concentration, and after the non-isothermal experiment, the specific surface area was reduced to approximately half. The total pore volume follows a similar trend to the specific surface area, with the largest pore volume found in sample Na1 and the smallest in sample Na3. Regarding crystallinity, samples Na1 and Na2 have similar crystallinity, whereas sample Na3 has slightly higher crystallinity. After the non-isothermal experiment, crystallinity increases in all samples, with sample Na3 exhibiting the highest crystallinity.

9.2.2 Analysis of CO₂ uptake of MgO samples promoted by LiNO₃

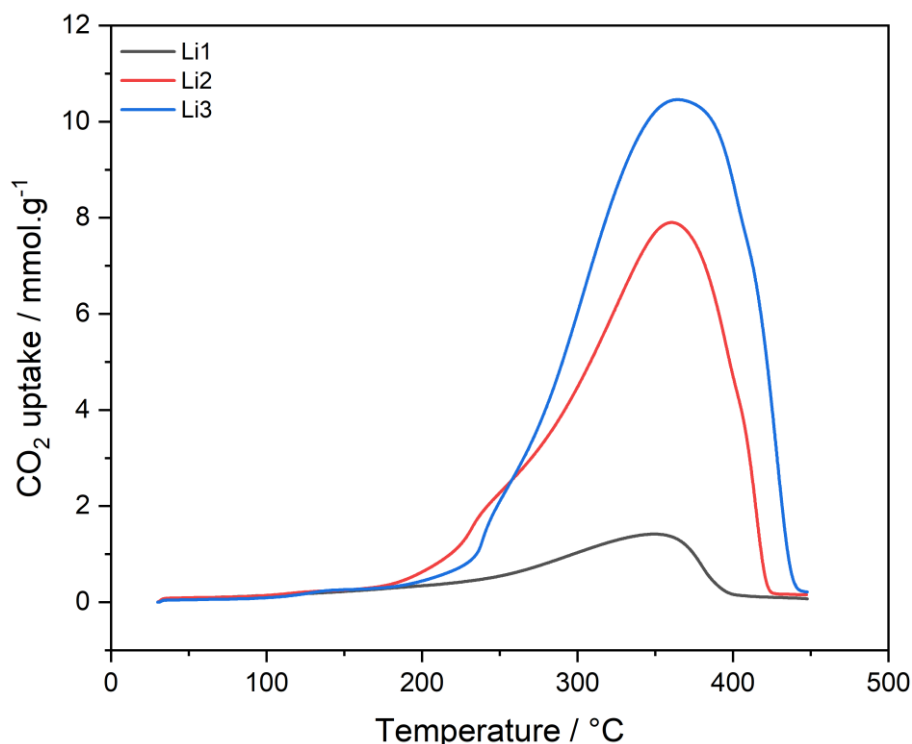


Figure 18. CO₂ uptake of MgO samples promoted by 10 mol % (Li1), 20 mol % (Li2) and 30 mol % (Li3) of LiNO₃.

In Figure 18, we can see that the uptake by MgO samples is promoted by LiNO₃ in different concentrations. All three samples have approximately the same initial temperature (170°C) for starting the adsorption. But Li3 exhibits the highest uptake (10,4 mmol.g⁻¹), and as the concentration decreases, this adsorption diminishes, with Li1 being significantly lower (1,4 mmol.g⁻¹) than the other two.

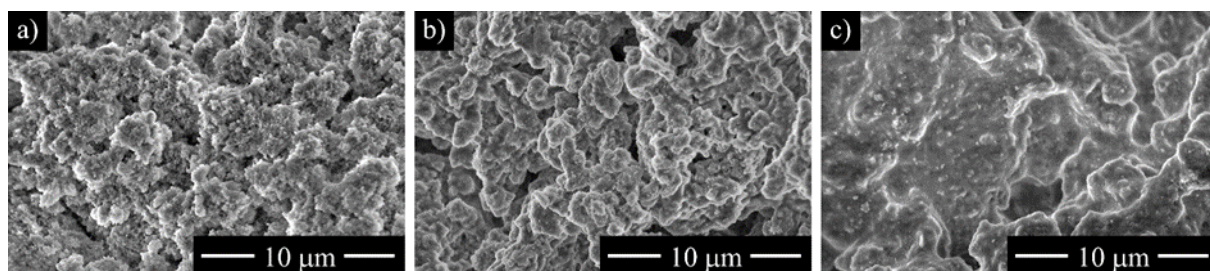


Figure 19 SEM images of fresh MgO samples promoted by LiNO₃ at various molar ratios: a) Li1, b) Li2, and c) Li3.

In Figure 19, we can observe how the surface of the sample varies with different concentrations. For the Li1, sharply defined crystals can be seen, whereas in the subsequent concentrations, this sharpness decreases. The surface of Li3 appears most blurred due to the high concentration of LiNO₃.

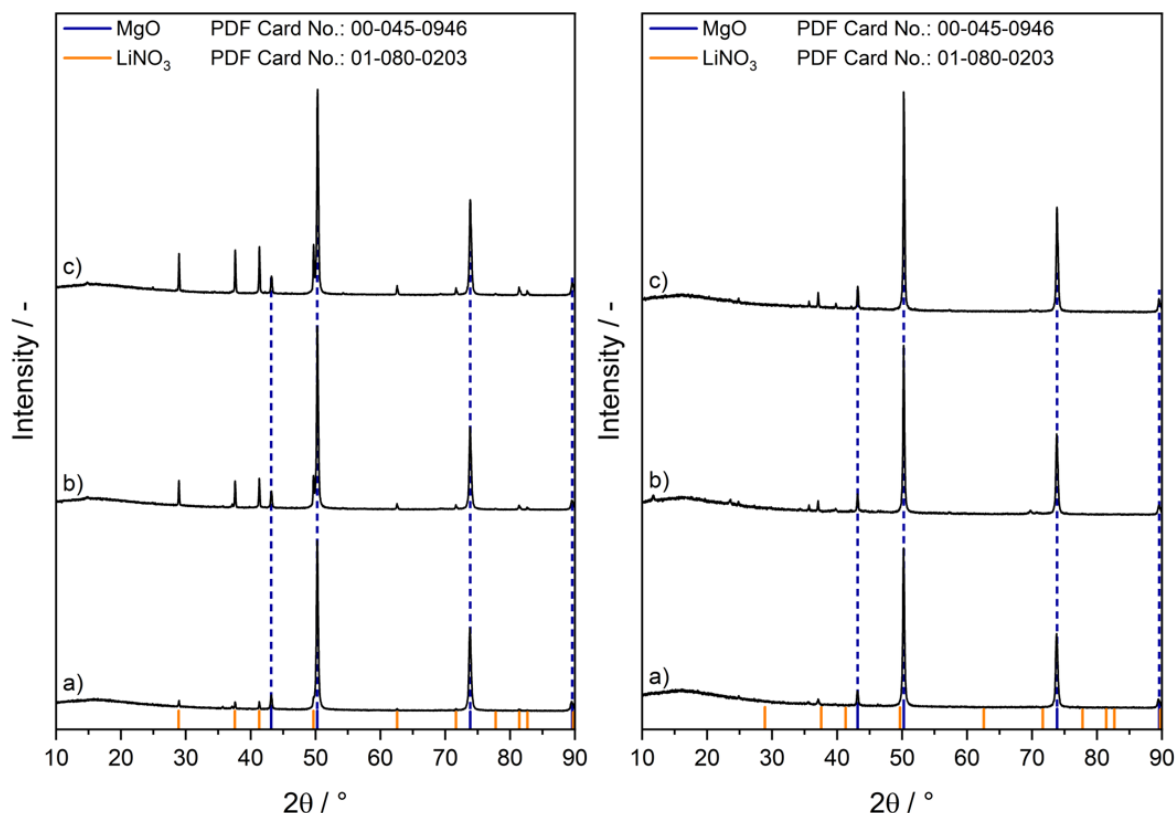


Figure 20. Diffractograms recorded for *fresh* MgO samples promoted by LiNO₃ at various molar ratios: a) Li1, b) Li2, and c) Li3 (left panel) and *after* non-isothermal experiment (right panel).

In Figure 20, we can observe the diffractograms of fresh samples and samples after a non-isothermal experiment at various concentrations. As the concentration of LiNO₃ increases, the intensity of its peaks also increases. In the non-isothermal experiment, the intensity of the LiNO₃ peaks slightly decreased compared to the original sample.

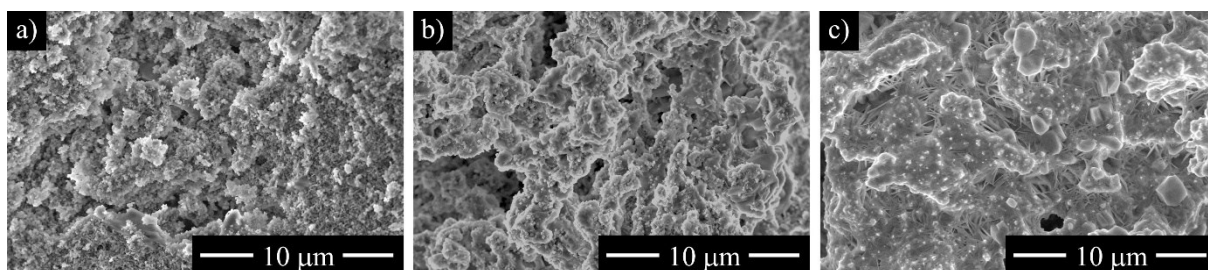


Figure 21. SEM images of MgO samples promoted by LiNO₃ at various molar ratio captured *after* non-isothermal experiment: a) Li1, b) Li2, and c) Li3.

In Figure 21, we can see how the surface of the sample changes with varying concentrations. For the sample, Li1, sharply defined crystals are visible. As the concentration increases, this sharpness diminishes. The surface of Li3 appears most blurred due to the high concentration of LiNO₃.

Table 5. Summary of maximum CO₂ uptake values and textural characteristics for MgO samples promoted by LiNO₃ at various molar ratios. Textural properties were evaluated for both *fresh* samples and samples collected *after* a non-isothermal TG experiment.

Sample	CO ₂ uptake (mmol. g _{sorbent} ⁻¹)	*BET (m ² . g ⁻¹)		**V _T (cm ³ . g ⁻¹) ***d _p (nm)		****Dc (nm)*	
		fresh	after	fresh	after	fresh	after
Li1	1.4	14.01	14.72	0.178 / 50.88	0.168 / 45.75	45.2 ± 3.9	54.8 ± 8.2
Li2	7.9	7.27	10.47	0.067 / 36.83	0.064 / 24.42	57.7 ± 9.8	64.9 ± 7.6
Li3	10.4	4.66	7.43	0.046 / 39.96	0.070 / 37.69	62.9 ± 8.9	114.9 ± 43.3

*specific surface area estimated based upon Brunauer-Emmet-Teller analysis

**total pore volume

***mean pore diameter

****average crystalline domain size estimated by Halder-Wagner method

In Table 5, we can see a comparison of various concentrations. The sample Li3 exhibits the highest adsorption, whereas the Li1 sample shows the lowest. Regarding specific surface area, it approximately halves as the concentration increases. Interestingly, after the non-isothermal experiment, the specific surface area increases, and for the Li3 sample, this change is roughly double. The total pore size decreases with increasing concentration and slightly decreases after the non-isothermal experiment, except for the Li3 sample, which shows twice the value. The crystallinity trend is reversed, with the highest value for the Li3 sample and the lowest for Li1. After the isothermal experiment, crystallinity slightly increased for the Li1 and Li2 samples. For the Li3 sample, this change was the most intense, approximately doubling. Based on these measured parameters, the Li3 sample was chosen for further work due to its highest adsorption and roughly double increase in other parameters after the non-isothermal experiment.

9.2.3 Analysis of CO₂ uptake of MgO samples promoted by (Na_{0.54}K_{0.46})NO₃ alkali metal salt mixture

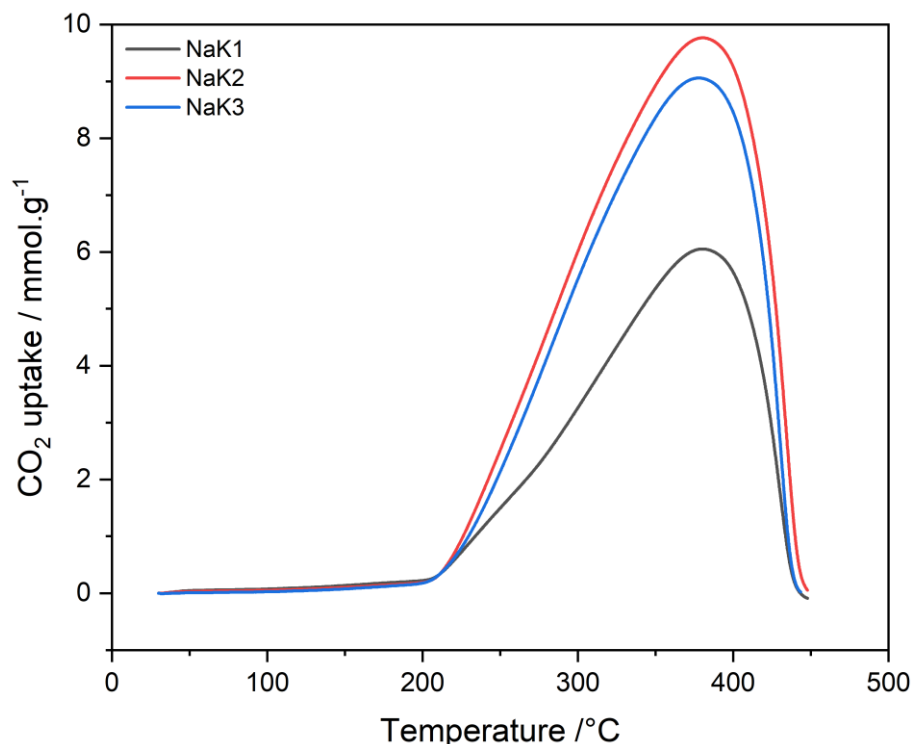


Figure 22. CO₂ uptake of MgO samples promoted by 10 mol % (NaK1), 20 mol % (NaK2) and 30 mol % (NaK3) of (Na_{0.54}K_{0.46})NO₃ alkali metal salt mixture

In Figure 22, we can observe uptake of MgO samples enhanced with (Na_{0.54}K_{0.46}) NO₃ at different concentrations. All three samples start the adsorption process at the same initial temperature of 205°C. However, the NaK2 sample demonstrates the highest uptake, reaching 9.8 mmol.g⁻¹. Following NaK3, the NaK1 sample shows a lower adsorption, and the NaK1 sample exhibits the lowest adsorption.

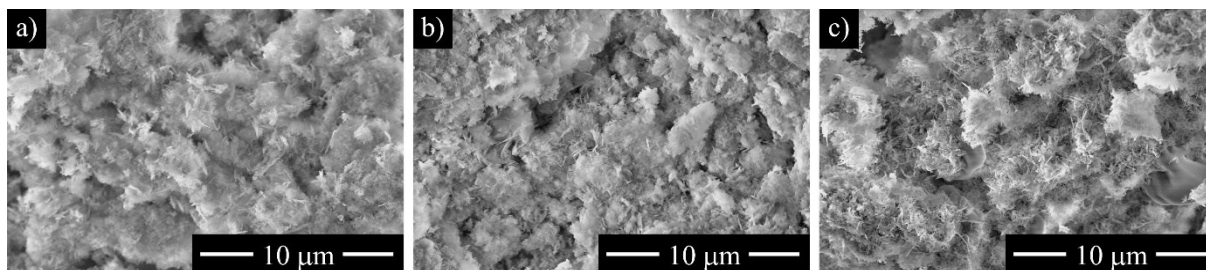


Figure 23. SEM images of *fresh* MgO samples promoted by (Na_{0.54}K_{0.46})NO₃ alkali metal salt mixture at various molar ratio: a) NaK1, b) NaK2, and c) NaK3.

In Figure 23, we can see a comparison of morphology at different concentrations. In the NaK3 sample, the presence of MgO nanowires is more clearly visible than in the other two samples.

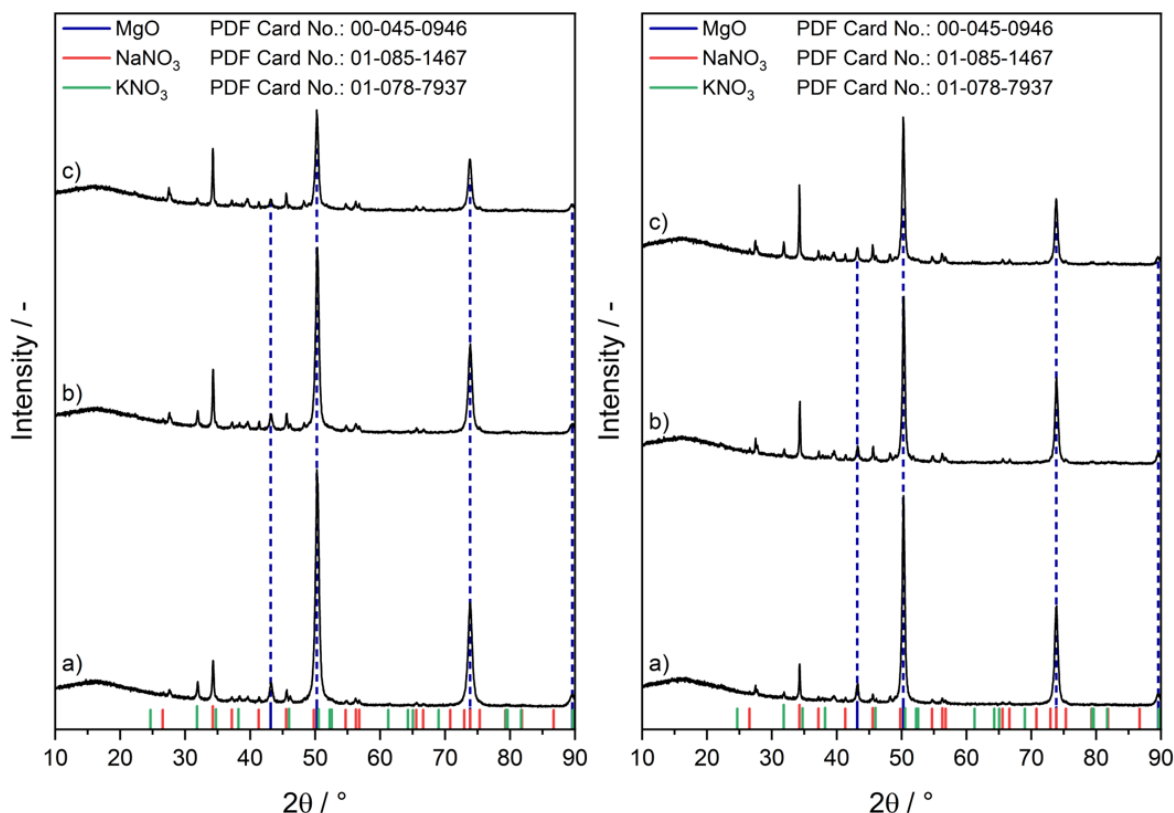


Figure 24. Diffractograms recorded for *fresh* MgO samples promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at various molar ratio: a) NaK1, b) NaK2, and c) NaK3 (left panel) and *after* non-isothermal experiment (right panel).

In Figure 24, we can observe the diffractograms of MgO samples promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at various molar ratios before and after the isothermal experiment. It can be seen that with increasing salt concentration, the peak intensity slightly increases. In the case of the non-isothermal experiment, the peak intensities do not change significantly.

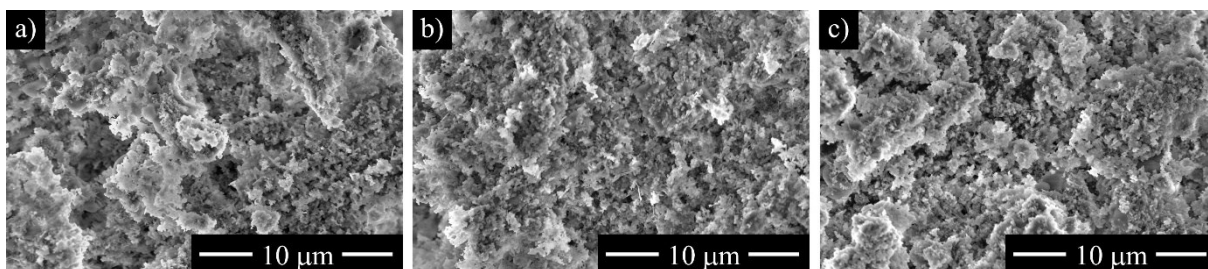


Figure 25. SEM images of MgO samples promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at various molar ratio captured *after* non-isothermal experiment: a) NaK1, b) NaK2, and c) NaK3.

In Figure 25, we can observe the morphology of samples after the non-isothermal experiment. Compared to the fresh sample, MgO nanowires are no longer present, and all samples appear quite similar.

Table 6. Summary of maximum CO₂ uptake values and textural characteristics for MgO samples promoted by (Na_{0.54}K_{0.46})NO₃ alkali metal salt mixture at various molar ratios. The textural properties were evaluated for both *fresh* samples and samples collected *after* a non-isothermal TG experiment.

Sample	CO ₂ uptake (mmol. g _{sorbent} ⁻¹)	*BET (m ² . g ⁻¹)		**V _T (cm ³ . g ⁻¹) ***d _p (nm)		****Dc (nm)*	
		fresh	after	fresh	after	fresh	after
NaK1	6.1	35.02	18.21	0.509 / 58.15	0.177 / 38.85	18.9 ± 5.0	22.8 ± 2.8
NaK2	9.8	24.57	9.02	0.292 / 47.60	0.091 / 40.46	20.5 ± 7.9	22.6 ± 0.8
NaK3	9.1	11.86	5.93	0.139 / 46.95	0.059 / 39.52	19.4 ± 6.5	28.2 ± 4.3

*Specific surface area estimated based upon Brunauer-Emmet-Teller analysis

**total pore volume

***mean pore diameter

****average crystalline domain size estimated by Halder-Wagner method

In Table 6, we can see a comparison of various concentrations before and after the non-isothermal experiment. The NaK2 sample exhibits the highest adsorption, while the NaK1 sample shows the lowest. Regarding specific surface area, the NaK1 sample has the highest value, and the NaK3 sample has the lowest. This trend remains consistent after the non-isothermal experiment, with the samples showing approximately half the value compared to before the experiment. The total pore volume decreases with increasing salt concentration, and this trend continues after the non-isothermal experiment. A more significant change occurs in the crystallinity of the samples, where the samples have similar crystallinity before the experiment. After the non-isothermal experiment, the crystallinity slightly increased for the NaK1 and NaK2 samples, while it increased more significantly for the NaK3 sample.

9.2.4 Analysis of CO₂ uptake of MgO samples promoted by (Li_{0.38} Na_{0.18} K_{0.44})NO₃ alkali metal salt mixture

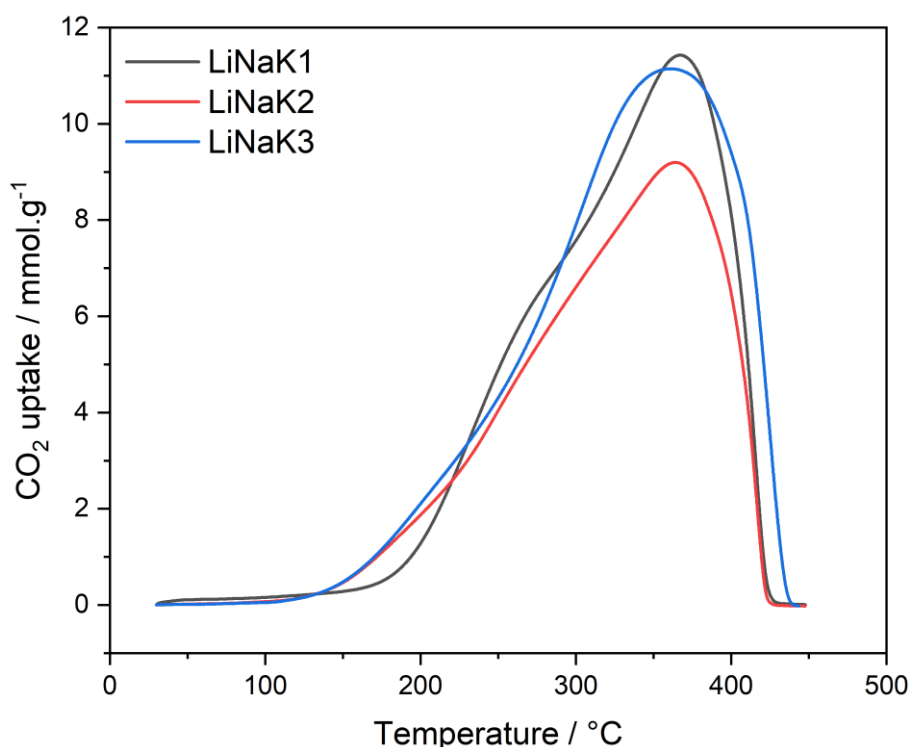


Figure 26. CO₂ uptake of MgO samples promoted by 10 mol % (LiNaK1), 20 mol % (LiNaK2) and 30 mol % (LiNaK3) of (Li_{0.38} Na_{0.18} K_{0.44})NO₃ alkali metal salt mixture.

Figure 26 shows the adsorption of MgO with the addition of (Li_{0.38} Na_{0.18} K_{0.44}) NO₃ at different concentrations. The LiNaK2 and LiNaK3 samples exhibit the same adsorption onset temperature (120°C), whereas the LiNaK1 sample starts adsorbing at a higher temperature (170°C). The highest adsorption is observed in the LiNaK1 sample (11.4 mmol.g⁻¹), slightly lower in the LiNaK3 sample (11.1 mmol.g⁻¹), and the lowest adsorption is exhibited by the LiNaK2 sample.

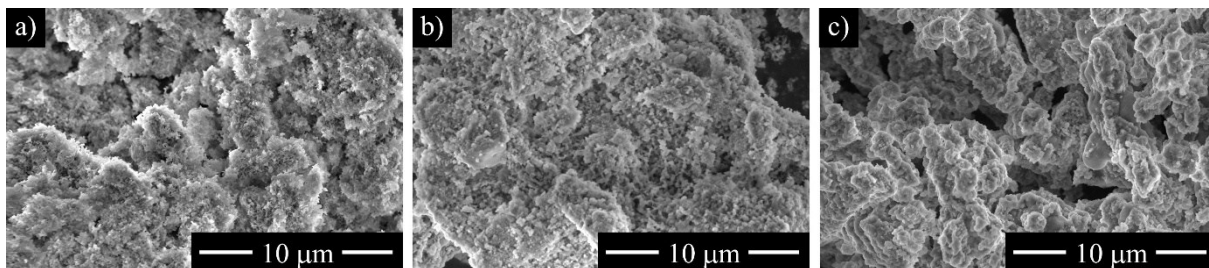


Figure 27. SEM images of *fresh* MgO samples promoted by (Li_{0.38} Na_{0.18} K_{0.44})NO₃ alkali metal salt mixture at various molar ratio: a) LiNaK1, b) LiNaK2, and c) LiNaK3.

Figure 27 shows the morphology of fresh samples promoted by (Li_{0.38} Na_{0.18} K_{0.44})NO₃. The LiNaK1 and LiNaK2 samples do not differ significantly, except that LiNaK2 is more spread out. In contrast, the LiNaK3 sample forms granular crystals.

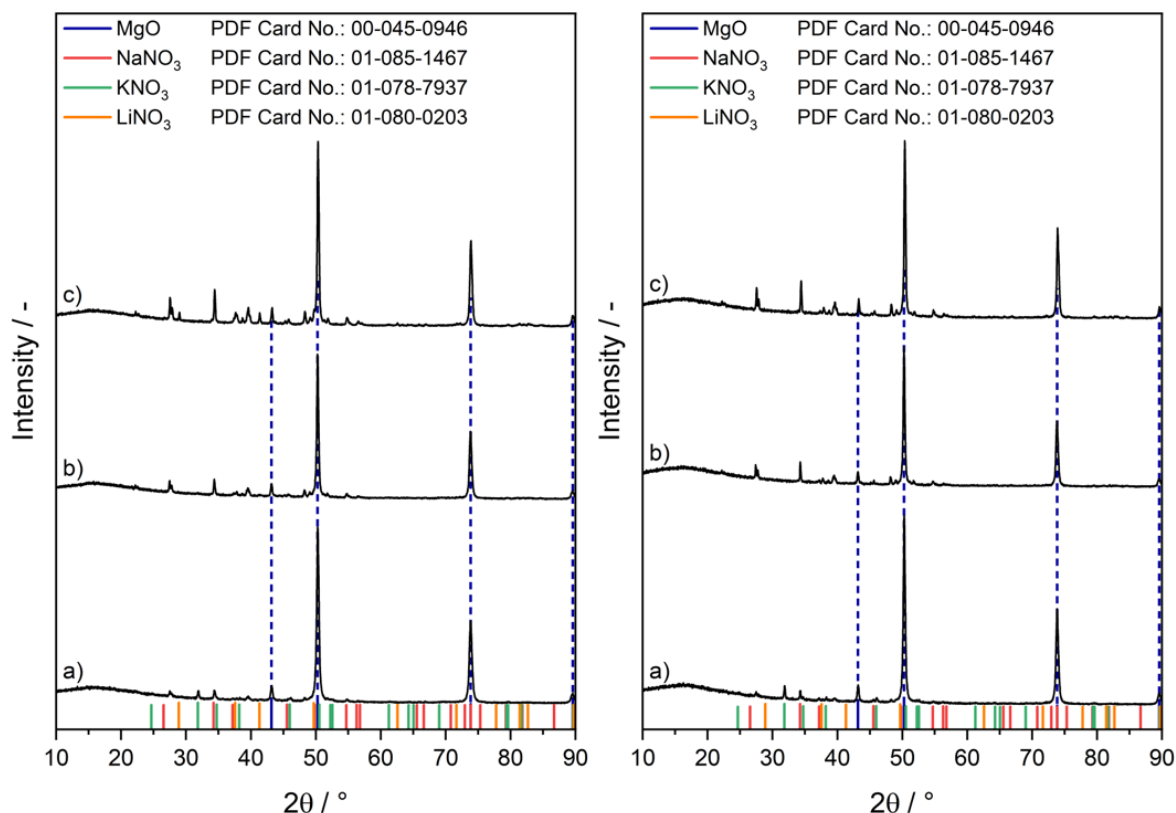


Figure 28. Diffractograms recorded for *fresh* MgO samples promoted by $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ alkali metal salt mixture at various molar ratios: a) LiNaK1, b) LiNaK2, and c) LiNaK3 (left panel) and *after* non-isothermal experiment (right panel).

Figure 28 shows the diffractograms of MgO promoted by $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$, fresh and after the non-isothermal experiment. As the salt concentration increases, the peak intensity also increases. After the non-isothermal experiment, the peak heights remain unchanged, and the trend stays consistent

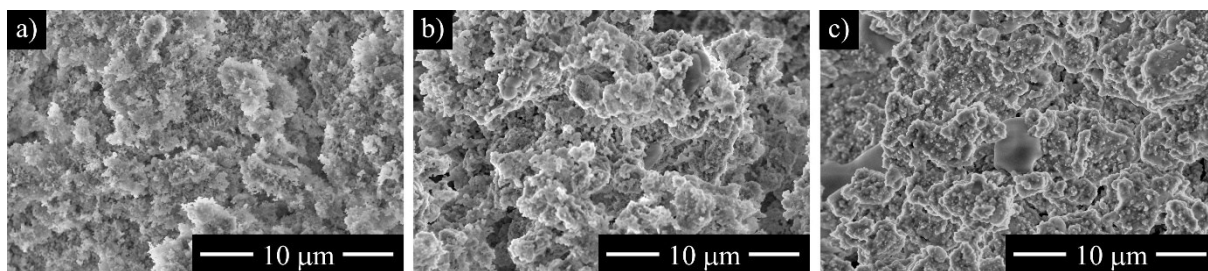


Figure 29. SEM images of MgO samples promoted by $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ alkali metal salt mixture at various molar ratios captured *after* non-isothermal experiment: a) LiNaK1, b) LiNaK2, and c) LiNaK3.

Figure 29 shows the morphology of sample surfaces after the non-isothermal experiment, where LiNaK3 forms sharper crystal interfaces compared to the other two samples. Conversely, LiNaK3 segregates, resulting in observable surface inhomogeneity.

Table 7. Summary of maximum CO₂ uptake and textural characteristics for MgO samples promoted by (Li_{0.38}Na_{0.18}K_{0.44})NO₃ alkali metal salt mixture at various molar ratio. Textural properties were evaluated for both *fresh* samples and samples collected *after a non-isothermal TG experiment*

Sample	CO ₂ uptake (mmol. g _{sorbent} ⁻¹)	*BET (m ² . g ⁻¹)		**V _T (cm ³ . g ⁻¹) ***d _p (nm)		****Dc (nm)*	
		fresh	after	fresh	after	fresh	after
LiNaK1	11.4	16.55	13.89	0.318 / 76.80	0.131 / 37.72	28.2 ± 2.9	36.3 ± 5.2
LiNaK2	9.2	5.66	4.33	0.057 / 40.43	0.025 / 23.31	41.0 ± 6.6	53.2 ± 16.7
LiNaK3	11.1	2.42	2.75	0.025 / 41.21	0.017 / 24.60	50.2 ± 15.0	55.4 ± 8.4

*specific surface area estimated based upon Brunauer-Emmet-Teller analysis

**total pore volume

***mean pore diameter

****average crystalline domain size estimated by Halder-Wagner method

In Table 7, we can see a comparison of various concentrations before and after the non-isothermal experiment. The LiNaK1 sample exhibits the highest adsorption, while the LiNaK2 sample shows the lowest. Regarding specific surface area, LiNaK1 has the highest value, and the other two samples have significantly lower specific surface areas. Comparing the fresh samples to those after the non-isothermal experiment, the specific surface area of LiNaK1 and LiNaK2 decreases, whereas LiNaK3 shows a slight increase. The total pore volume decreases as the salt concentration increases. After the non-isothermal experiment, the total pore volume of LiNaK1 and LiNaK2 is reduced by approximately half, while LiNaK3 shows only a slight reduction. Crystallinity increases with increasing concentration, and after the non-isothermal experiment, crystallinity further increases.

Table 8. Overview of selected samples and their properties

Sample	CO ₂ uptake (mmol. g _{sorbent} ⁻¹)	*BET (m ² . g ⁻¹)		**V _T (cm ³ . g ⁻¹) ***d _p (nm)		****Dc (nm)*	
		fresh	after	fresh	after	fresh	after
Na2	11.8	16.67	7.63	0.183 / 43.93	0.069 / 36.16	19.5 ± 4.5	27.1 ± 2.1
Li3	10.4	4.66	7.43	0.046 / 39.96	0.070 / 37.69	62.9 ± 8.9	114.9 ± 43.3
NaK2	9.8	24.57	9.02	0.292 / 47.60	0.091 / 40.46	20.5 ± 7.9	22.6 ± 0.8
LiNaK3	11.1	2.42	2.75	0.025 / 41.21	0.017 / 24.60	50.2 ± 15.0	55.4 ± 8.4

*specific surface area estimated based upon Brunauer-Emmet-Teller analysis

**total pore volume

***mean pore diameter

****average crystalline domain size estimated by Halder-Wagner method

The subsequent samples were selected: Na2, Li3, NaK2, and LiNaK3. These samples exhibited the most favorable results during the comparison of fresh samples with those acquired after a non-isothermal experiment. A cyclic experiment was conducted on these samples to evaluate changes in morphology, composition, and the depletion of adsorbed quantities throughout individual cycles.

9.3 Analysis of CO₂ uptake performance for step-by-step incremental carbonation experiment

9.3.1 Analysis of CO₂ uptake of MgO promoted by 20 mol. % of NaNO₃

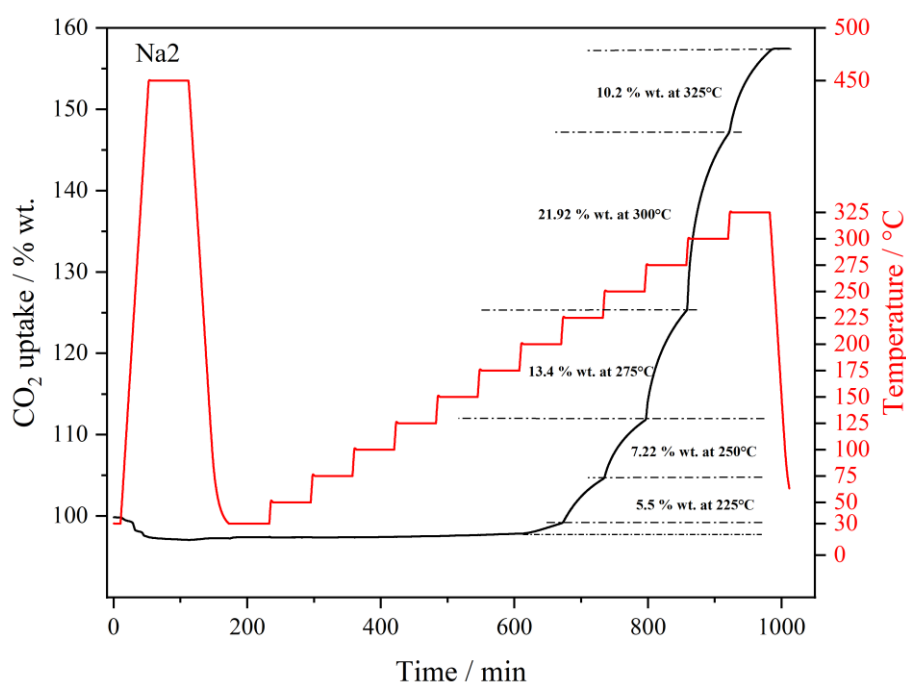


Figure 30. CO₂ uptake by MgO samples promoted by NaNO₃ at molar ratio 20 mol % (Na2) in the course of step-by-step incremental carbonation experiment.

Figure 30 illustrates the amount of CO₂ adsorbed at specific temperatures by MgO promoted by NaNO₃ at molar ratio 20 mol%. Adsorption begins at a temperature of 200°C, with 1.43 wt% being adsorbed. The adsorbed amount gradually increases, reaching its peak at 300°C with 21.92 wt% adsorbed, and then decreases to 10.2 wt% at the final temperature. This indicates that the optimal adsorption temperature for MgO promoted with NaNO₃ at a concentration of 20 wt% is 300°C.

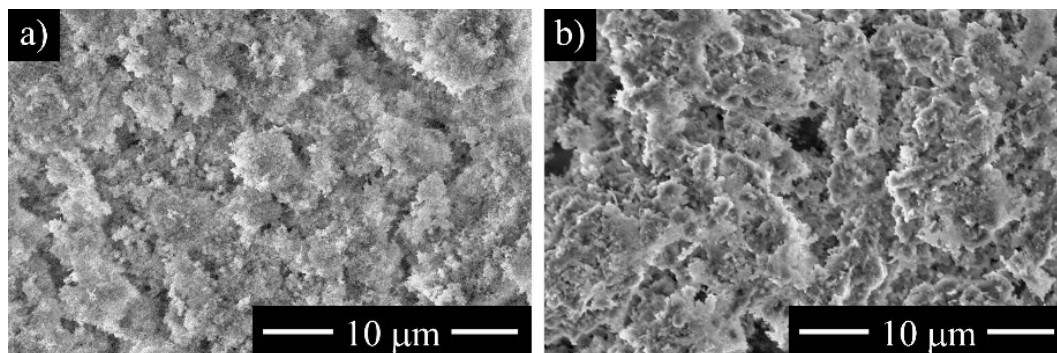


Figure 31. SEM images of MgO samples promoted by NaNO_3 at molar ratio 20 mol % (Na_2) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment

In Figure 31, a comparison between the fresh adsorbent and the adsorbent after carbonation can be seen. In the first case, the crystal structure appears blurred compared to the sample after carbonation, where slight surface segregation is visible.

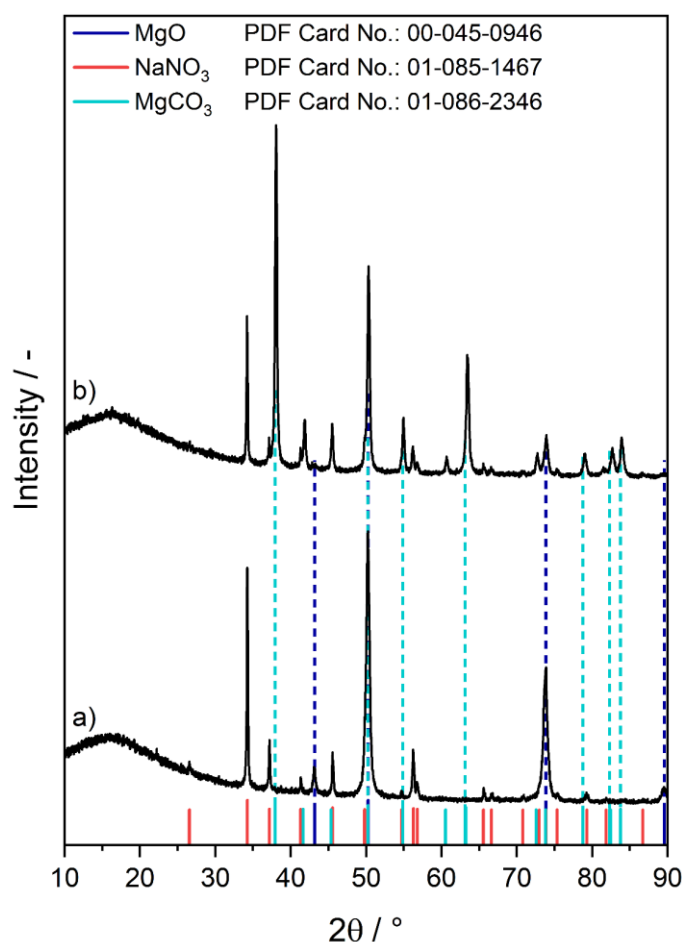


Figure 32. Diffractograms recorded for MgO samples promoted by NaNO_3 at molar ratio 20 mol % (Na_2) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment.

Figure 32 illustrates the diffractogram of the MgO sample promoted with NaNO_3 at a molar concentration of 20 mol% before and after carbonation. It can be observed that in the sample

after carbonation, MgO has transformed into MgCO_3 , resulting in a decrease in the intensity of MgO peaks and the formation of MgCO_3 peaks. A noticeable decrease in the intensity of NaNO_3 is also evident.

9.3.2 Analysis of CO_2 uptake of MgO promoted by 30 mol. % of LiNO_3

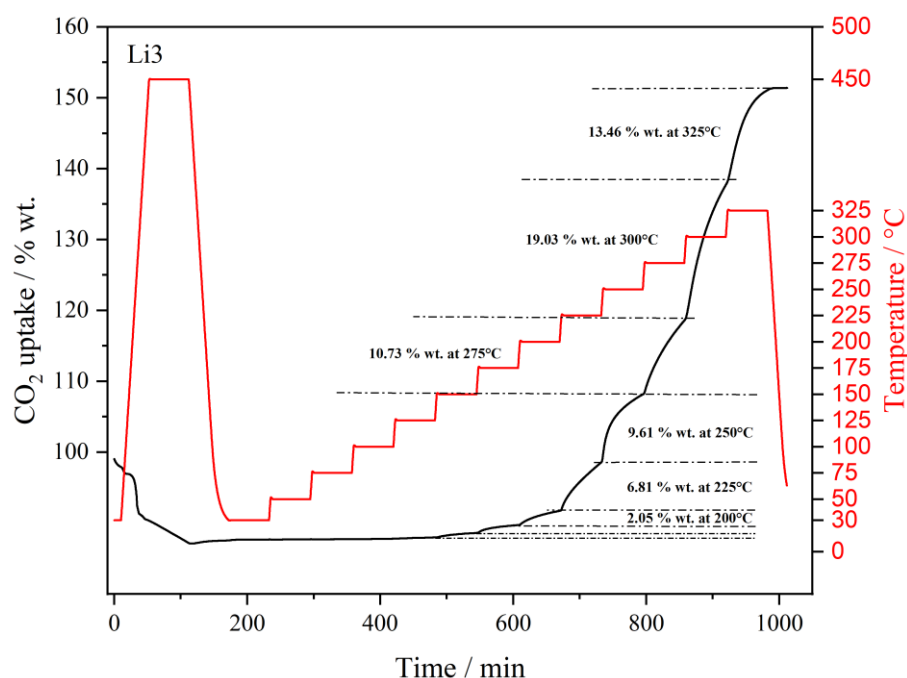


Figure 33. CO_2 uptake by MgO samples promoted by LiNO_3 at a molar ratio 30 mol % (Li3) in the course of step-by-step incremental carbonation experiment.

Figure 33 shows the adsorption of CO_2 using MgO promoted with LiNO_3 at a concentration of 30 mol%. Adsorption begins at 150°C , with 0.64 wt% being adsorbed. The adsorbed amount gradually increases until it reaches its peak at 300°C , with 19.03 wt% of CO_2 adsorbed. After this temperature, the adsorbed amount decreases. This indicates that the optimal adsorption temperature for MgO promoted with LiNO_3 at a concentration of 30 mol% is 300°C .

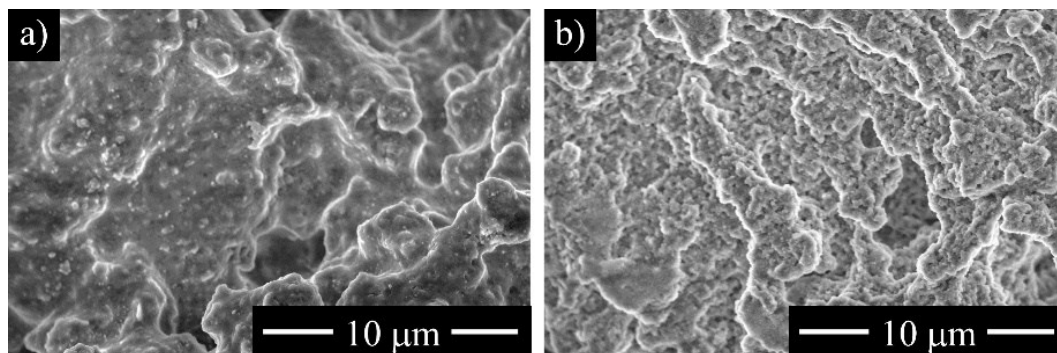


Figure 34. SEM images of MgO samples promoted by LiNO_3 at molar ratio 30 mol % (Li_3) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment.

Figure 34 shows the morphology of the MgO sample promoted with LiNO_3 at a concentration of 30 mol% before and after carbonation. In the case of the sample before carbonation, larger crystals can be seen. In the case of the sample after carbonation, a change in surface structure is visible, which may be due to the formation of a layer of lithium and magnesium carbonates.

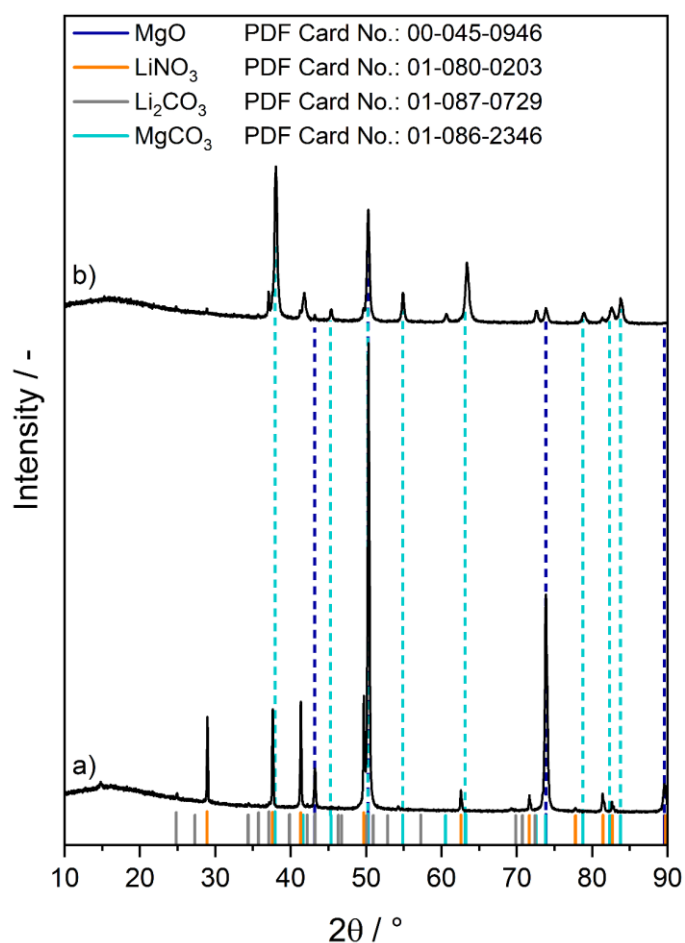


Figure 35. Diffractograms recorded for MgO samples promoted by LiNO_3 at molar ratio 30 mol % (Li_3) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment.

Figure 35 shows the diffractogram of the MgO sample promoted with LiNO_3 at a concentration of 30 mol% before and after carbonation. Before carbonation, peaks from MgO are visible, which diminish after carbonation, and MgCO_3 peaks are created. Additionally, a peak from LiNO_3 can be seen, which then transforms into LiCO_3 .

9.3.3 Analysis of CO_2 uptake of MgO samples promoted by 20 mol. % of $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$

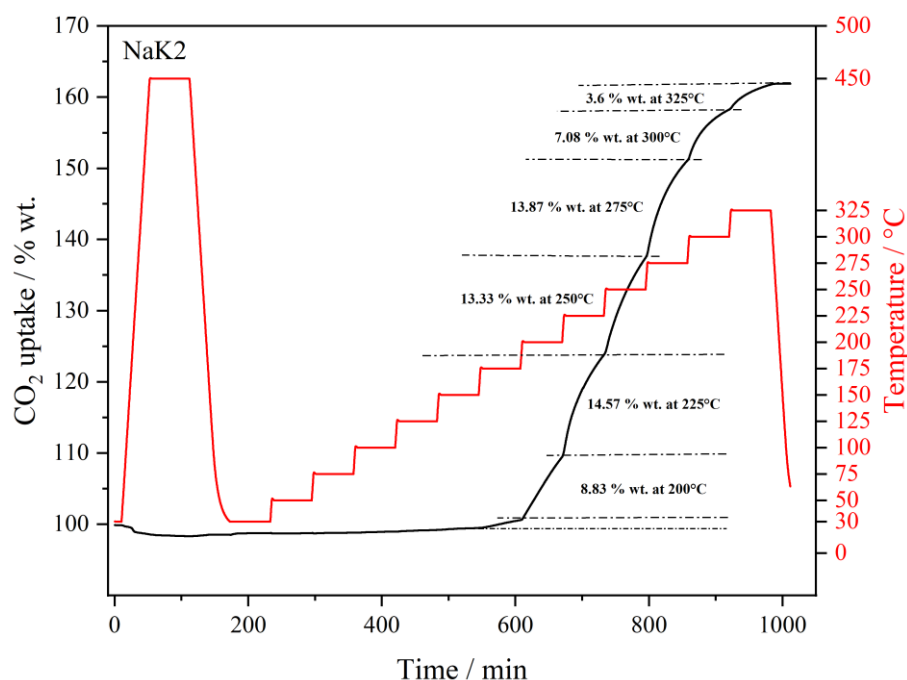


Figure 36. CO_2 uptake of MgO sample promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at a molar ratio of 20 mol% % (NaK2) in the course of a step-by-step incremental carbonation experiment.

Figure 36 shows the adsorption of CO_2 using MgO promoted with $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ at a concentration of 20 mol%. Adsorption begins at 175°C, with 1.2 wt% being adsorbed. The maximum adsorbed amount occurs at 225°C, with the highest amount of 14.57 wt% adsorbed. This is followed by a slight decrease until 275°C, where 13.87 wt% is adsorbed. After this temperature, the adsorbed amount of CO_2 significantly decreases. This indicates that the optimal adsorption temperature for MgO promoted with $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ at a concentration of 20 mol% is in the range of 225 to 275°C.

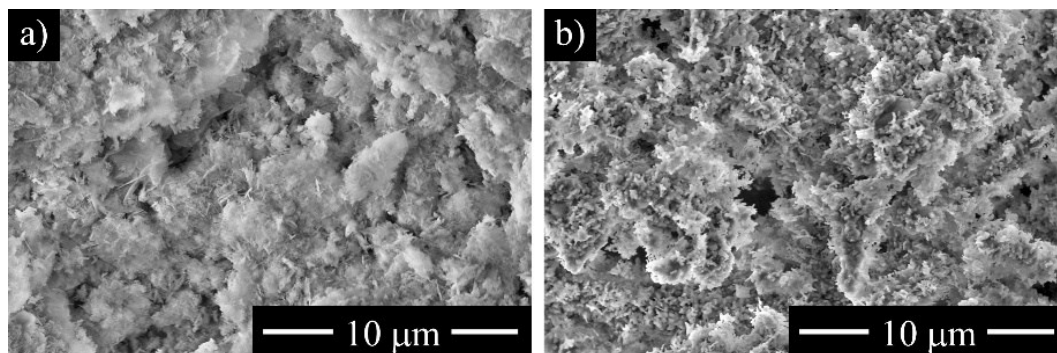


Figure 37. SEM images of of MgO sample promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at molar ratio 20 mol % (NaK2) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment.

Figure 37 shows the change in surface morphology of MgO promoted with $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ at a concentration of 20 mol% before and after carbonation. In the case of the fresh sample, the presence of MgO nanowires can be observed, which disappear after carbonation. A change in the surface can also be seen. This may be due to the formation of carbonates.

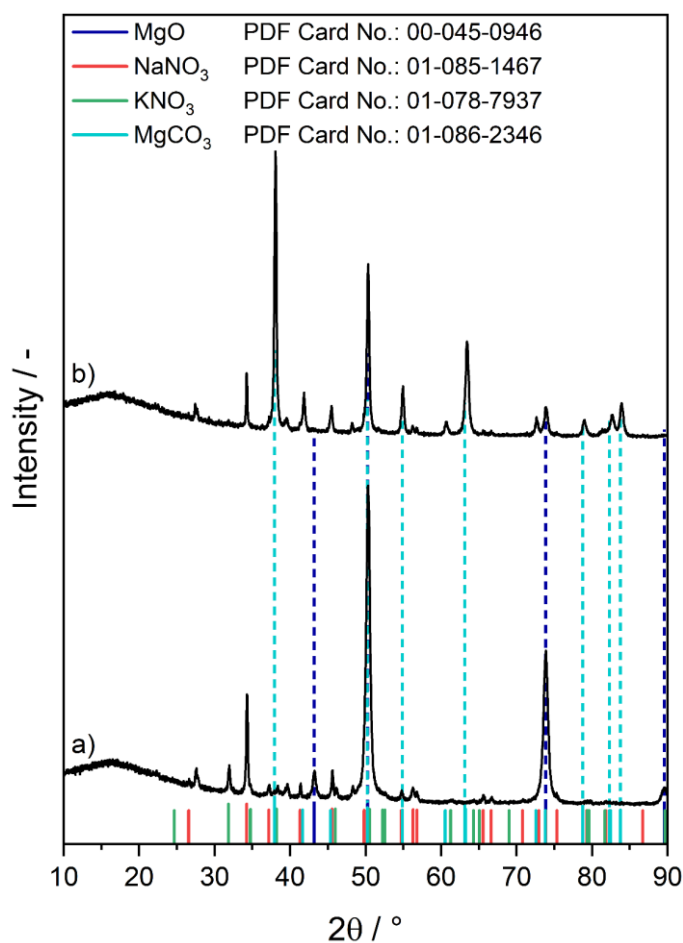


Figure 38. Diffractograms recorded for MgO samples promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at molar ratio 20 mol % (NaK2) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment.

Figure 38 displays the diffractograms before and after carbonation of the MgO sample promoted with $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ at a concentration of 20 mol%. In the case of the fresh sample, peaks from MgO can be seen, which subsequently diminish after carbonation due to the transformation into MgCO_3 .

9.3.4 Analysis of CO_2 uptake of MgO samples promoted by 30 mol. % of $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$

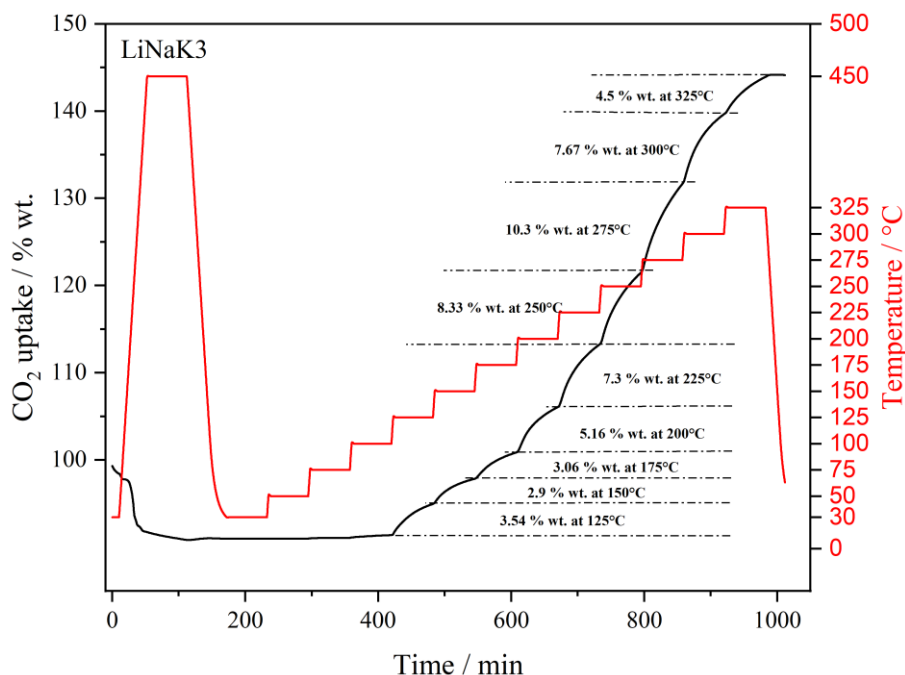


Figure 39. CO_2 uptake of MgO sample promoted by $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ alkali metal salt mixture at 30 mol % (LiNaK3) in the course of step-by-step incremental carbonation experiment.

Figure 39 shows the adsorption of CO_2 using MgO promoted with $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ at a concentration of 30 mol%. Adsorption begins at 125°C , with 3.54 wt% being adsorbed. The adsorbed amount then gradually increases until it reaches its peak at 275°C , with 10.3 wt% of CO_2 adsorbed. This is followed by a slight decrease until 300°C , where 7.67 wt% is adsorbed. After this temperature, the adsorbed amount of CO_2 significantly decreases. This indicates that the optimal adsorption temperature for MgO promoted with $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ at a concentration of 30 mol% is 275°C .

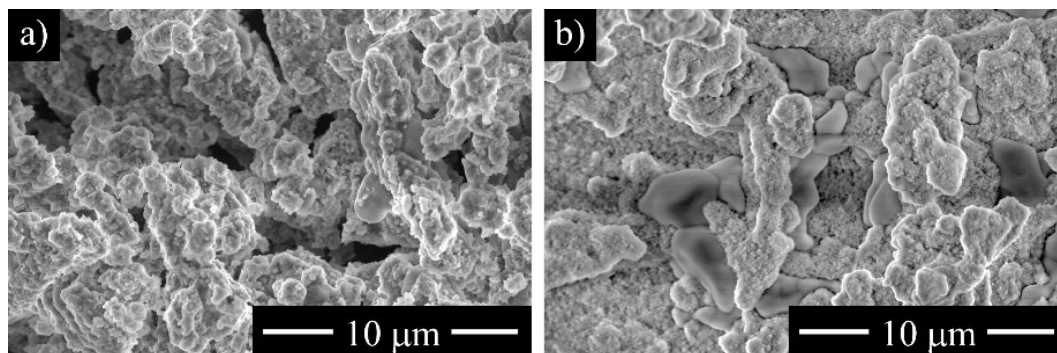


Figure 40. SEM images of of MgO sample promoted by $(\text{Li}_{0.38} \text{Na}_{0.18} \text{K}_{0.44})\text{NO}_3$ alkali metal salt mixture at molar ratio 30 mol % (LiNaK3) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment.

Figure 40 shows the change in morphology of the MgO sample promoted with $(\text{Li}_{0.38} \text{Na}_{0.18} \text{K}_{0.44})\text{NO}_3$ at a concentration of 30 mol% before and after carbonation. In the case of the fresh sample, the surface is more crystalline, although slight surface segregation can also be observed. In the case of the sample after carbonation, surface segregation is more pronounced.

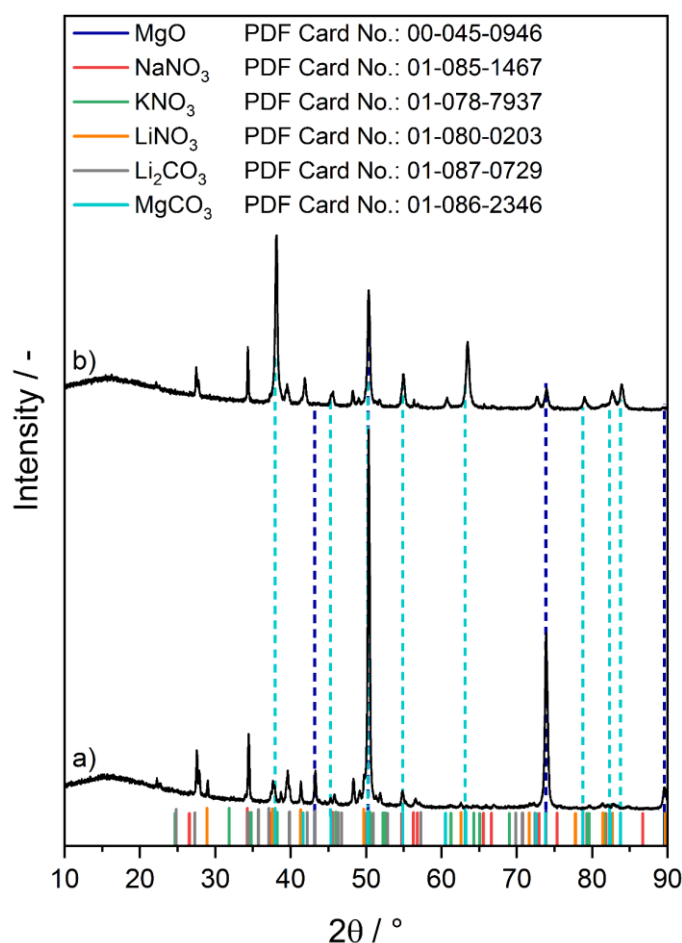


Figure 41. Diffractograms recorded for MgO samples promoted by $(\text{Li}_{0.38} \text{Na}_{0.18} \text{K}_{0.44})\text{NO}_3$ alkali metal salt mixture at molar ratio 30 mol % (LiNaK3) for a) *fresh* and b) *carbonated* sample collected after completed step-by-step incremental carbonation experiment.

Figure 41 shows the diffractograms of the MgO sample promoted with $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ at a concentration of 30 mol% before and after carbonation. In the fresh sample, peaks from MgO and salts are evident, which then transform into their carbonates after carbonation. This is reflected in the reduction of the original peaks and the emergence of carbonate peaks.

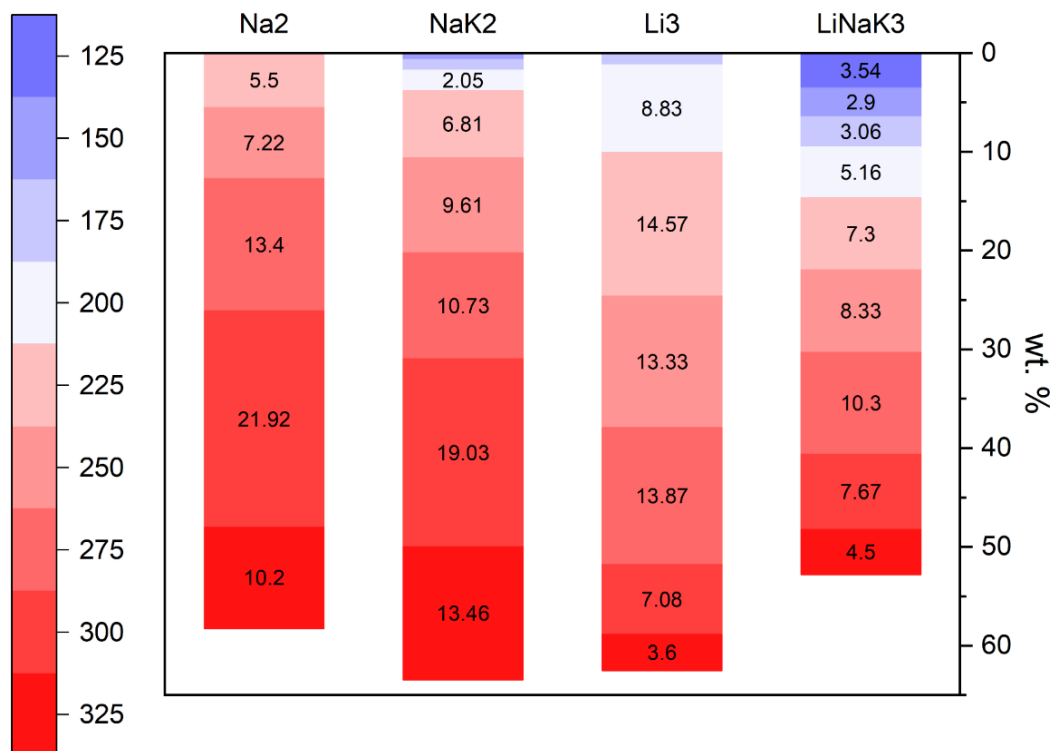


Figure 42. The amount of adsorbed CO_2 as a function of temperature during a step-by-step experiment by MgO samples promoted by: NaNO_3 at molar ratio 20 mol% (Na2), $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at molar ratio 20 mol% (NaK2), LiNO_3 at molar ratio 30 mol% (Li3) and $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ alkali metal salt mixture at molar ratio 30 mol % (LiNaK3)

Figure 42 shows the amount of adsorbed CO_2 for individual samples and temperatures. The highest amount of adsorbed CO_2 was observed for the Na2 sample at a temperature of 300°C. Interestingly, in the case of the LiNaK3 sample, adsorption began at 125°C, which is the lowest temperature among all samples. The graph indicates that the optimal adsorption temperature for the samples is 275°C.

9.4 Analysis of CO₂ uptake performance for cyclic experiment

9.4.1 Analysis of cyclic stability of MgO promoted by 20 mol % of NaNO₃

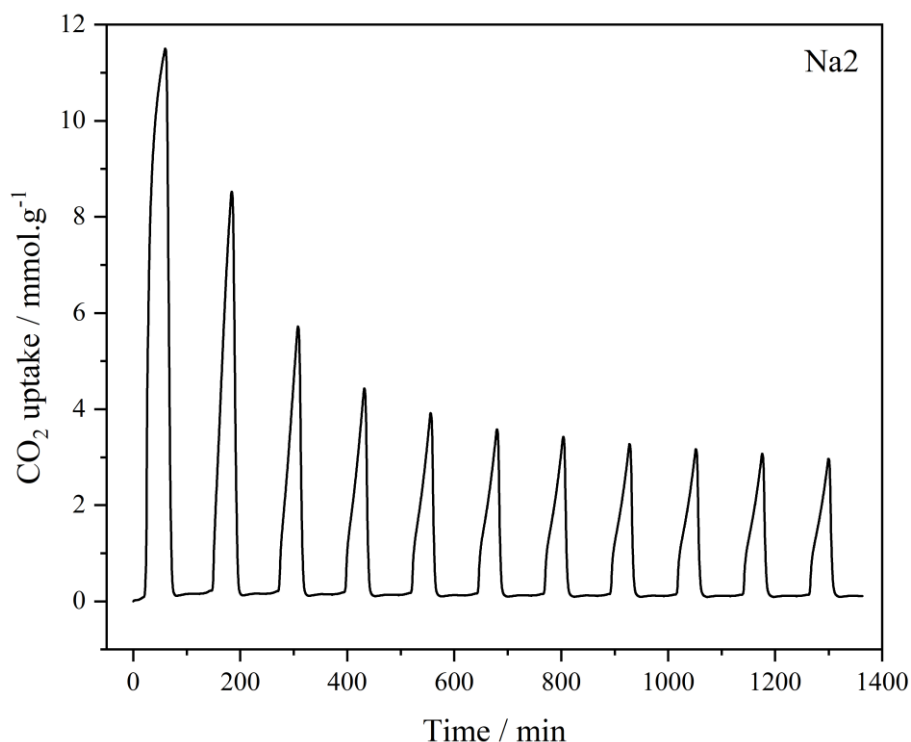


Figure 43. CO₂ uptake by MgO samples promoted by NaNO₃ at molar ratio 20 mol % (Na2) in the course of cyclic experiment.

Figure 43 illustrates the amount of adsorption in individual cycles for the MgO sample promoted with NaNO₃ at a concentration of 20 mol%. In the first cycle, 11.5 mmol.g⁻¹ of CO₂ was adsorbed. After five more cycles, the adsorption decreased, and after the sixth cycle, the decrease was negligible. The efficiency after 10 cycles of this sample is only 26%.

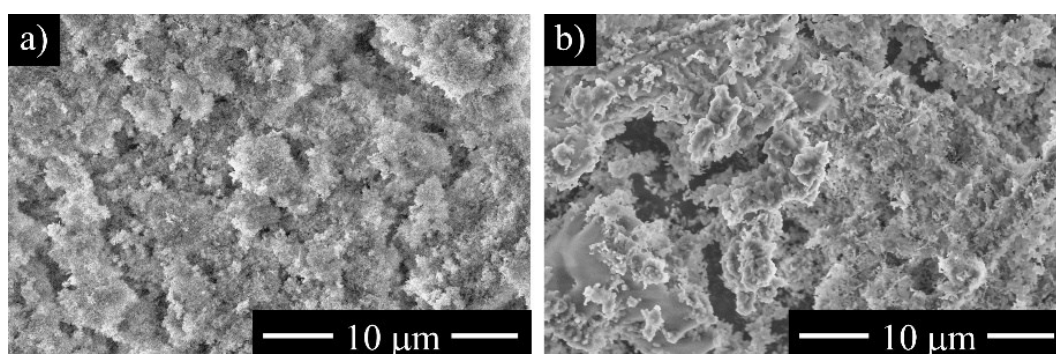


Figure 44. SEM images of MgO samples promoted by NaNO₃ at molar ratio 20 mol % (Na2) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 44 illustrates the change in morphology of the MgO sample promoted with NaNO₃ at a concentration of 20 mol% before and after 10 cycles. In the fresh sample, no segregations

are present, and sharp crystals are clearly visible. In contrast, the surface of the sample after 10 cycles has been segregated.

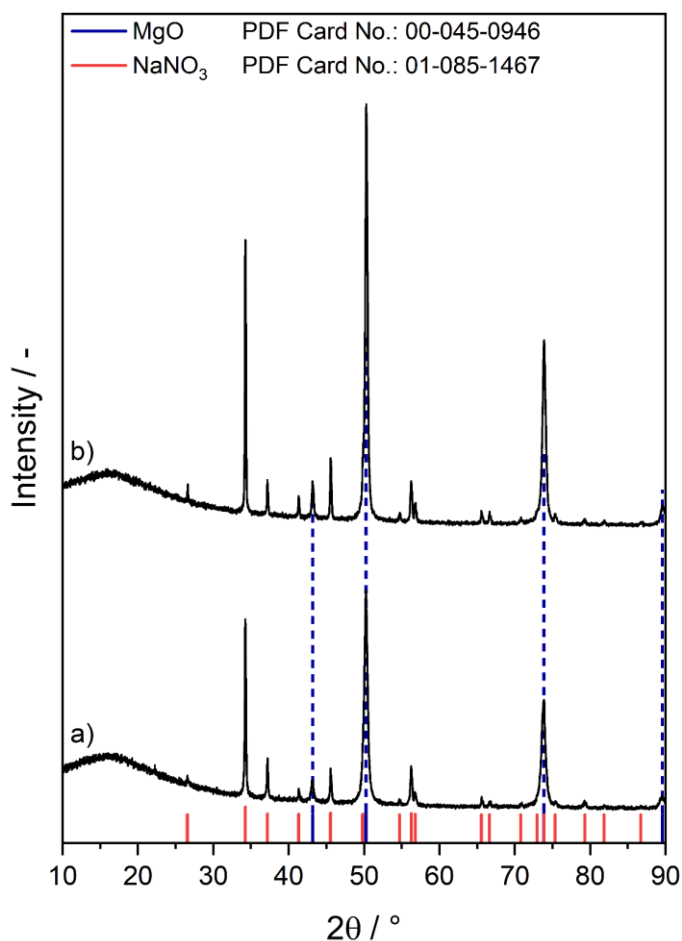


Figure 45. Diffractograms recorded for MgO samples promoted by NaNO₃ at molar ratio 20 mol % (Na₂) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 45 illustrates the diffractograms of the MgO sample promoted with NaNO₃ at a concentration of 20 mol% before and after 10 cycles. The diffractograms are identical except that in the case of the sample after 10 cycles, the intensity of the signal for both MgO and NaNO₃ has increased.

9.4.2 Analysis of cyclic stability of MgO promoted by 30 mol % of LiNO₃

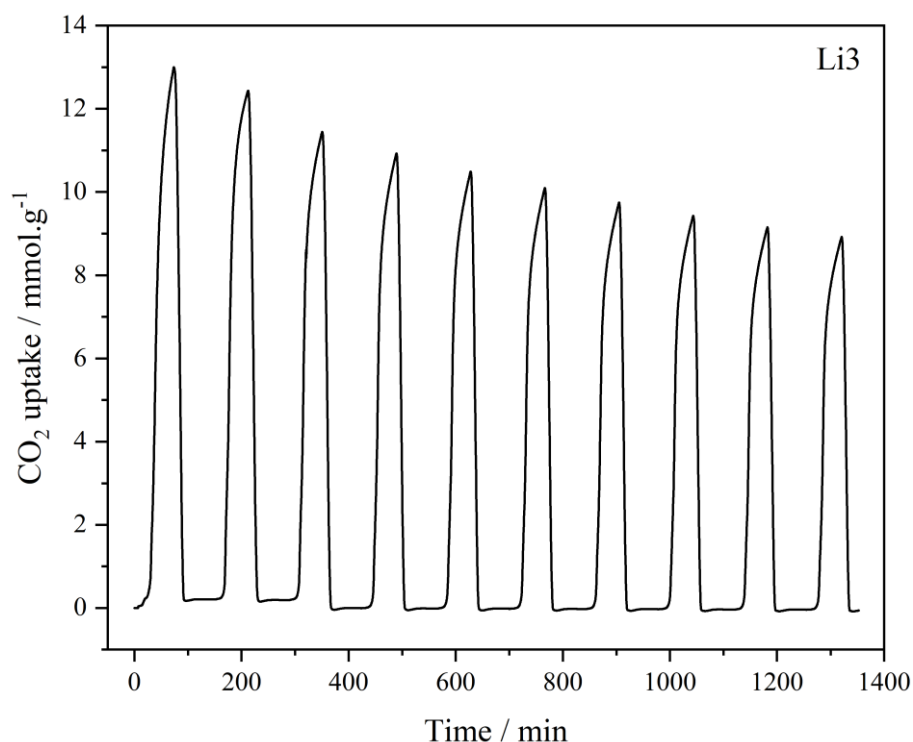


Figure 46. CO₂ uptake by MgO samples promoted by LiNO₃ at molar ratio 30 mol % (Li3) in the course of cyclic experiment.

Figure 46 illustrates the adsorption of CO₂ in individual cycles using MgO promoted with LiNO₃ at a concentration of 30 mol%. In the first cycle, 13 mmol.g⁻¹ of CO₂ was adsorbed, and this value gradually decreased with each cycle until it reached 8.92 mmol.g⁻¹ after the tenth cycle. The efficiency after 10 cycles of this sample is 69%.

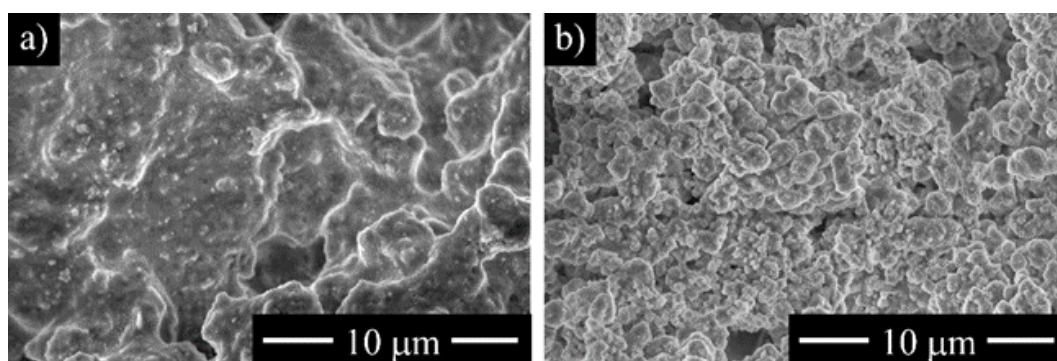


Figure 47. SEM images of MgO samples promoted by LiNO₃ at molar ratio 30 mol % (Li3) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 47 shows the morphology of the MgO sample promoted with LiNO₃ at a concentration of 30 mol% before and after the cyclic experiment. In the fresh sample, a melted structure can be observed, whereas in the sample after the cyclic experiment, the surface has become rougher.

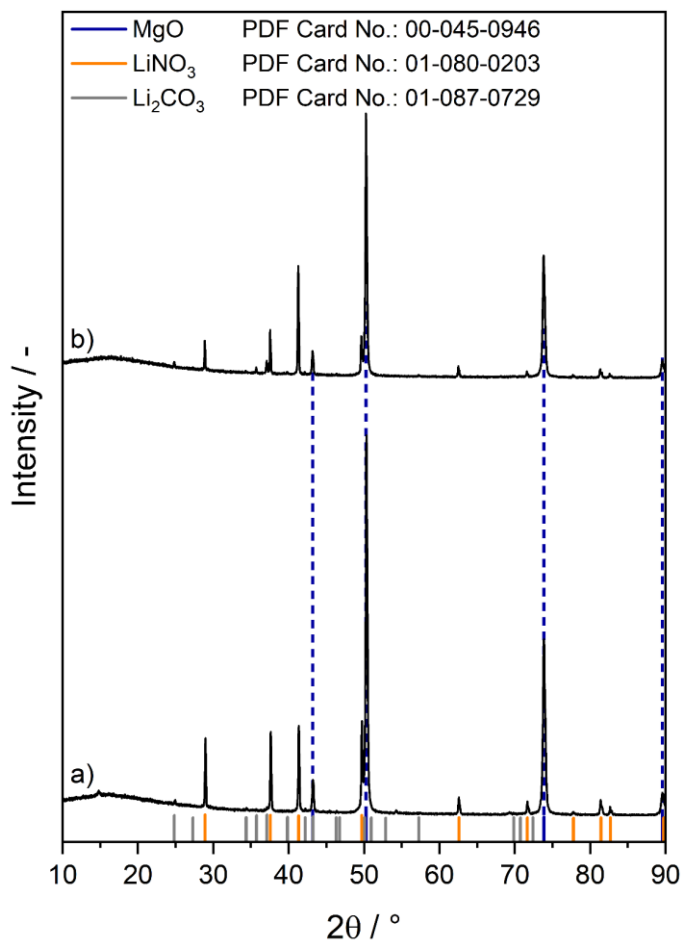


Figure 48. Diffractograms recorded for MgO samples promoted by LiNO_3 at molar ratio 30 mol % (Li3) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 48 illustrates the diffractograms of the MgO sample promoted with LiNO_3 at a concentration of 30 mol% before and after the cyclic experiment. In the case before the cyclic experiment, the presence of MgO and LiNO_3 can be observed. In the sample after the cyclic experiment, a slight peak for Li_2CO_3 appears, which is formed from the transformation of the nitrate.

9.4.3 Analysis of cyclic stability of MgO promoted by 20 mol % of $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$

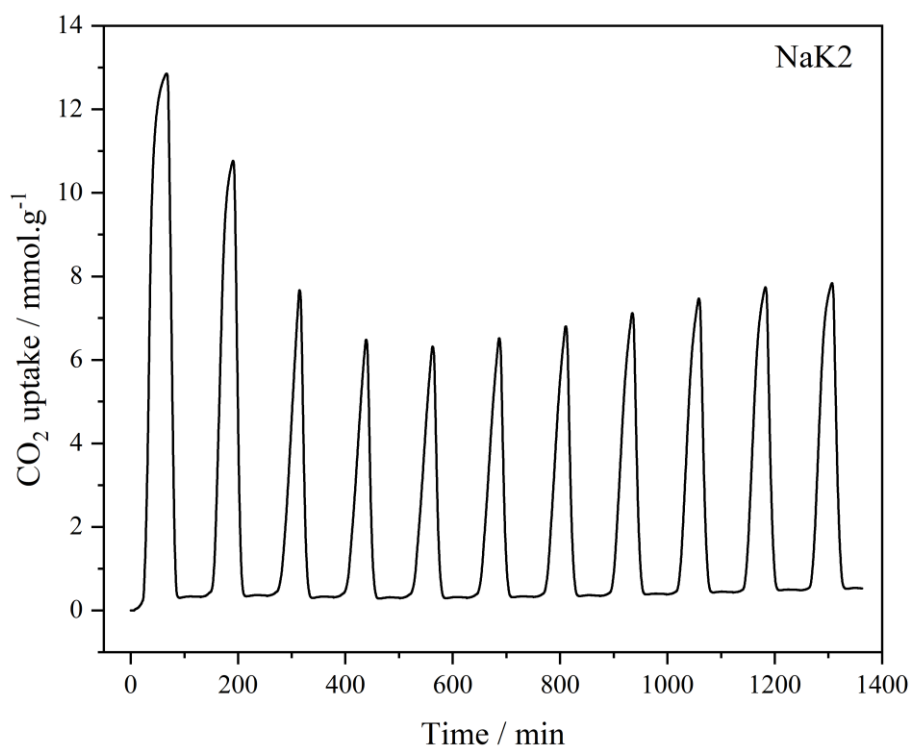


Figure 49. CO₂ uptake by MgO samples promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at molar ratio 20 mol % (NaK2) in the course of cyclic experiment.

Figure 49 shows the progression of the cyclic experiment for the MgO sample promoted with $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ at a concentration of 20 mol%. In the first cycle, 12.85 mmol/g of CO₂ was adsorbed. In the following cycles, the adsorbed amount gradually decreased until the fifth cycle, where 6.32 mmol/g was adsorbed, which is 49% of the first cycle. After that, the adsorbed amount of CO₂ gradually increased to 7.84 mmol/g. Thus, the adsorption decreased by 51% after the fifth cycle and then increased by 10% until the end of the experiment. Therefore, the efficiency of cycling for this sample is 61%.

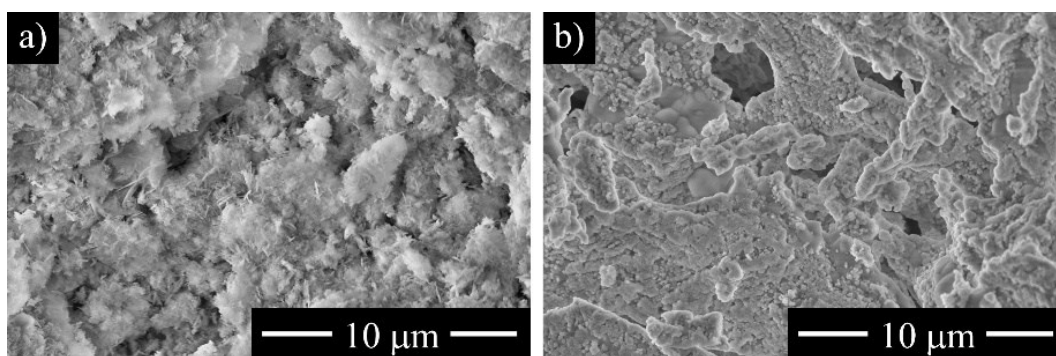


Figure 50. SEM images of MgO samples promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at molar ratio 20 mol % (NaK2) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 50 shows the change in surface morphology of the MgO sample promoted with NaK at a concentration of 20 mol% before and after the cyclic experiment. In the sample before the cyclic experiment, MgO nanowires can be observed, whereas in the sample after the cyclic experiment, these nanowires are absent, and the surface has segregated.

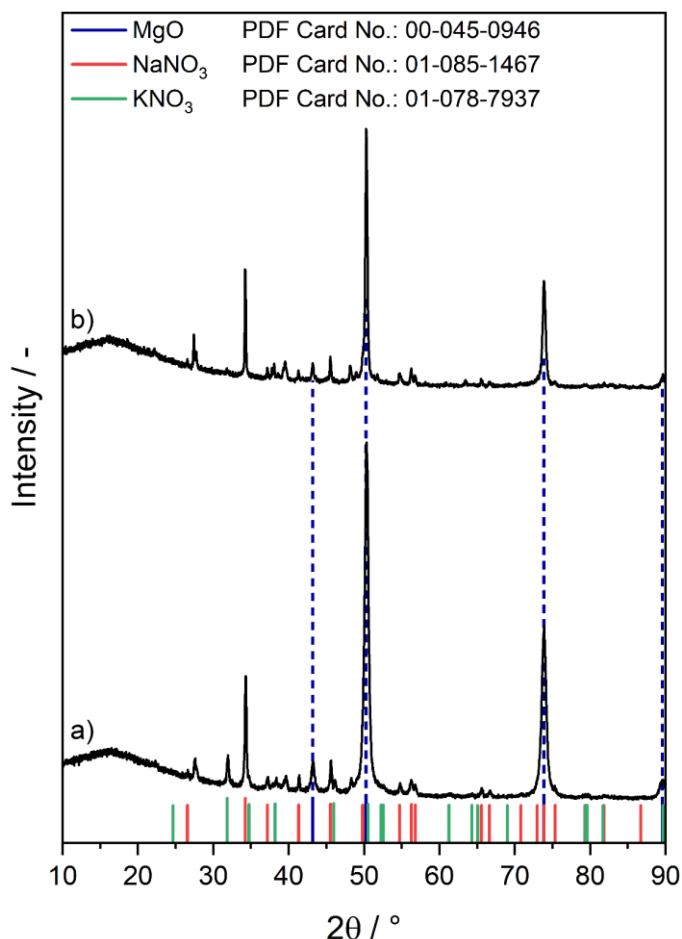


Figure 51. Diffractograms recorded for MgO samples promoted by $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ alkali metal salt mixture at molar ratio 20 mol % (NaK2) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 51 shows the diffractograms of the MgO sample promoted with $(\text{Na}_{0.54}\text{K}_{0.46})\text{NO}_3$ at a concentration of 20 mol% before and after the cyclic experiment. The diffractograms before and after the experiment are very similar, except that the intensity of the peaks after the experiment is not as high compared to the sample before the experiment. Peaks from MgO, KNO_3 , and NaNO_3 are present.

9.4.4 Analysis of CO₂ uptake of MgO samples promoted by 30 mol. % of (Li_{0.38} Na_{0.18}K_{0.44})NO₃

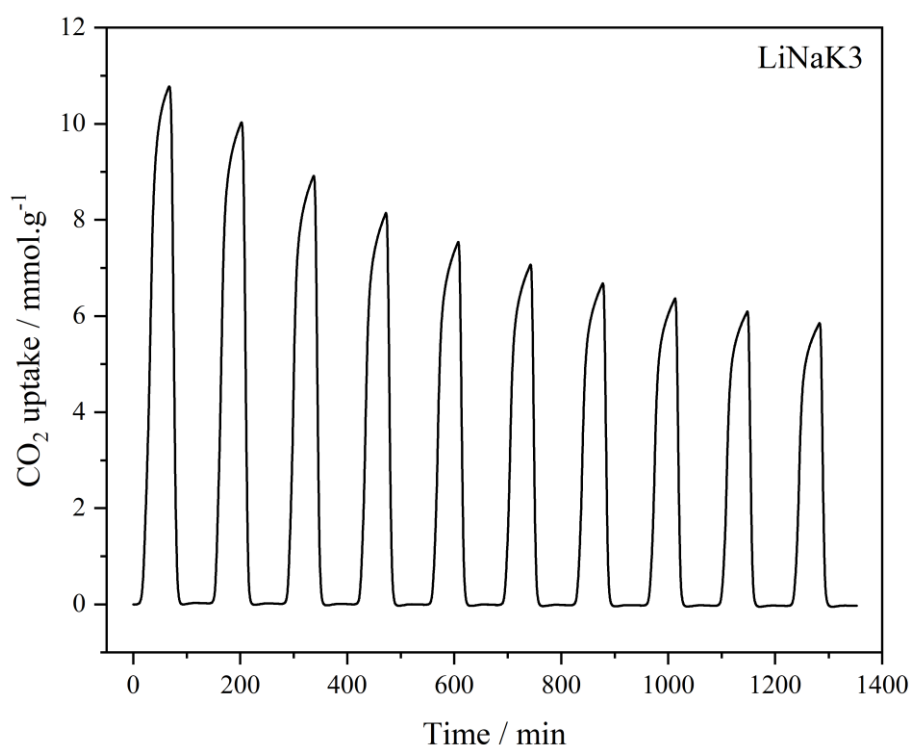


Figure 52. CO₂ uptake of MgO sample promoted by (Li_{0.38} Na_{0.18}K_{0.44})NO₃ alkali metal salt mixture at 30 mol % (LiNaK3) in the course of cyclic experiment.

Figure 52 shows the progression of the cyclic experiment for the MgO sample promoted with (Li_{0.38} Na_{0.18}K_{0.44})NO₃ at a concentration of 30 mol%. After the first cycle, 10.78 mmol.g⁻¹ of CO₂ was adsorbed. With each cycle, the adsorption decreased until the tenth cycle, where the adsorbed amount of CO₂ was 5.86 mmol.g⁻¹. The efficiency after ten cycles for this sample is 54%.

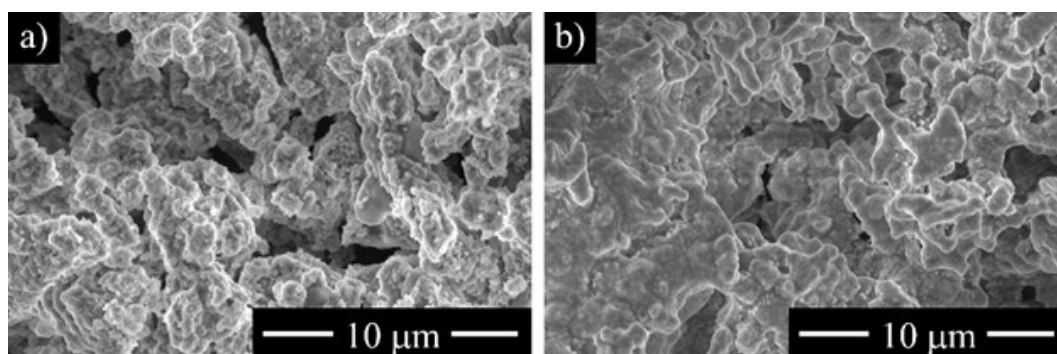


Figure 53. SEM images of MgO samples promoted by (Li_{0.38} Na_{0.18}K_{0.44})NO₃ alkali metal salt mixture at 30 mol % (LiNaK3) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 53 shows the morphology of the MgO sample promoted with (Li_{0.38} Na_{0.18}K_{0.44})NO₃ at a concentration of 30 mol% before and after the cyclic experiment. In the case of the fresh

sample, sharp large crystals with very little segregation can be observed. In contrast, the sample after 10 cyclic experiments is much more segregated, and the shape of the crystals is not as sharp.

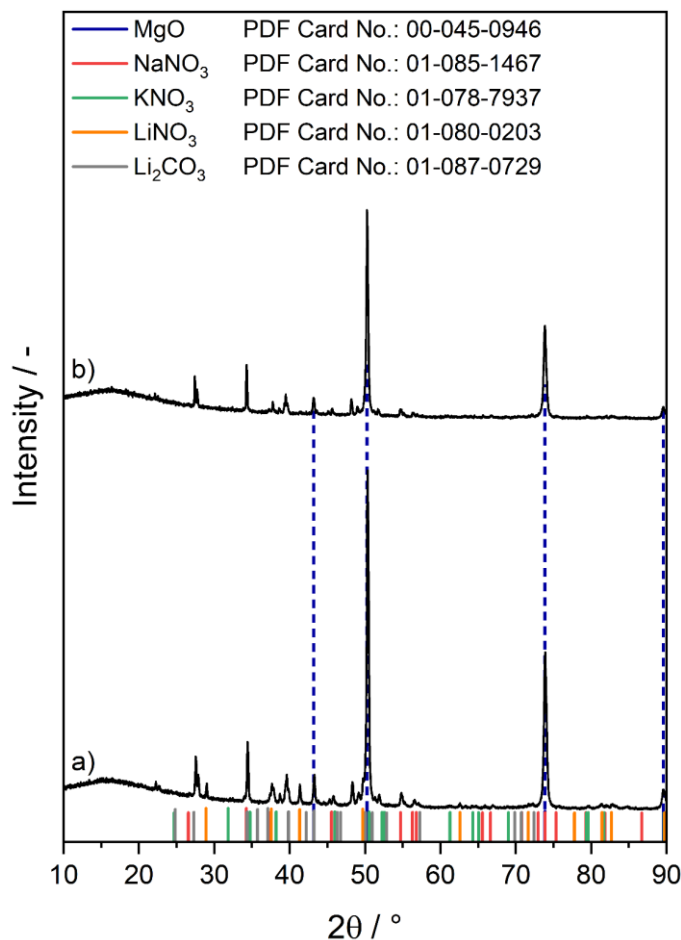


Figure 54. Diffractograms recorded for MgO samples promoted by $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ alkali metal salt mixture at molar ratio 30 mol % (LiNaK3) for a) *fresh* and b) sample collected after completed cyclic experiment.

Figure 54 shows the diffractograms of the MgO sample promoted with $(\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44})\text{NO}_3$ at a concentration of 30 mol% before and after the cyclic experiment. The diffractograms before and after the experiment are very similar, except that the intensity of the peaks after the experiment is not as high compared to the sample before the experiment. Peaks from MgO, KNO₃, NaNO₃, LiNO₃, and Li₂CO₃ are present.

Table 9. Summary of maximum CO₂ uptake and textural characteristics for MgO samples promoted by NaNO₃ at molar ratio 20 mol% (Na2), (Na_{0.54}K_{0.46})NO₃ alkali metal salt mixture at molar ratio 20 mol% (NaK2), LiNO₃ at molar ratio 30 mol% (Li3) and (Li_{0.38}Na_{0.18}K_{0.44})NO₃ alkali metal salt mixture at molar ratio 30 mol % (LiNaK3). Textural properties were evaluated for both *fresh* samples and samples collected *after* 10 cycles TG experiment.

Sample	CO ₂ uptake (mmol. g _{sorbent} ⁻¹)	*BET (m ² . g ⁻¹)		**V _T (cm ³ . g ⁻¹) ***d _p (nm)		****Dc (nm)*	
		fresh	After 10 cycles	fresh	After 10 cycles	fresh	After 10 cycles
Na2	11,8	16,67	6,49	0,183/43,93	0,037/23,0	19,5±4,5	38,7±14,7
Li3	10,4	7,27	3,33	0,046/39,96	0,014/17,2	62,9±8,9	196,0±127,5
NaK2	9,8	24,57	3,11	0,292/47,60	0,017/22,4	20,5±7,9	48,0±5,5
LiNaK3	11,1	2,42	1,48	0,025/41,21	0,006/16,4	50,2±15,0	60,9±23,3

*Specific surface area estimated based upon Brunauer-Emmet-Teller analysis

**total pore volume

***mean pore diameter

****average crystalline domain size estimated by Halder-Wagner method

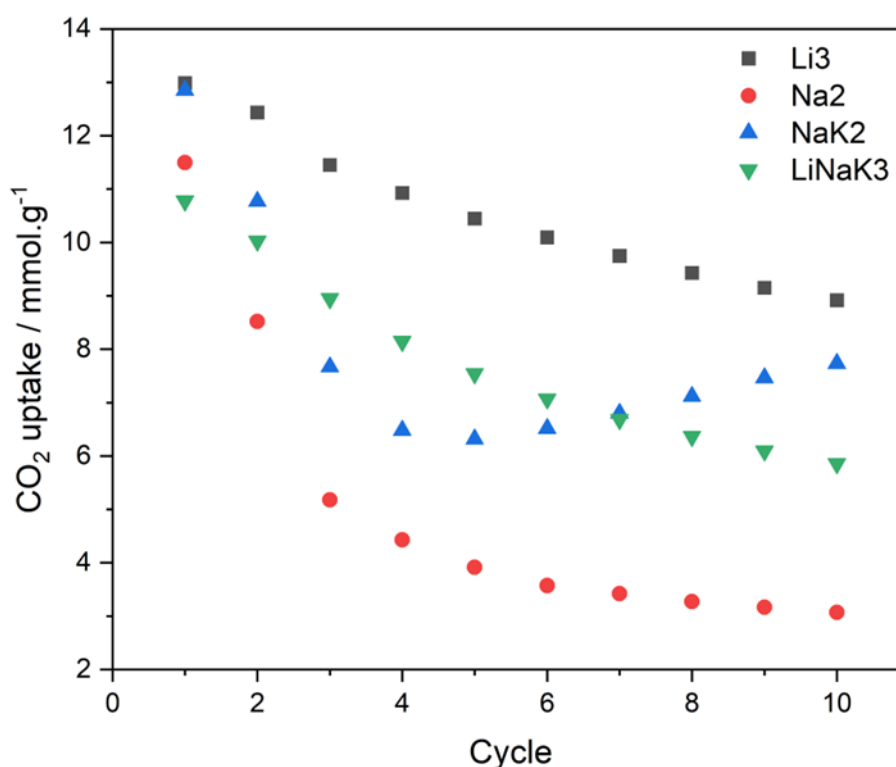


Figure 55. Comparison of CO₂ uptake of MgO samples promoted by NaNO₃ at molar ratio 20 mol% (Na2), (Na_{0.54}K_{0.46})NO₃ alkali metal salt mixture at molar ratio 20 mol% (NaK2), LiNO₃ at molar ratio 30 mol% (Li3) and (Li_{0.38}Na_{0.18}K_{0.44})NO₃ alkali metal salt mixture at molar ratio 30 mol % (LiNaK3) across individual cycles

Figure 55 provides an overview and comparison of the individual samples across the adsorption cycles. It can be observed that the sample Li3 exhibits the smallest decline in CO₂ adsorption capacity, whereas Na2 shows the most significant decrease. Interestingly, the NaK2 sample initially shows a decrease in adsorption, which then slightly increases after the fifth cycle

CONCLUSION

MgO is considered a suitable candidate for solid-state CO₂ capture owing to its desirable properties such as relative adsorption capacity, abundance, low cost, operating temperature, and toxicity, in comparison to other metal oxides. However, the current adsorption capacity for pristine MgO is still significantly lower for practical applications. Therefore, MgO is typically modified with additional components to increase surface area, porosity, stability, and regeneration to enhance CO₂ adsorption capacity. MgO modification with metal salts have recently emerged as a viable strategy to further optimize the MgO adsorption capacity. In this study, we synthesized morphology optimized MgO via thermal decomposition and utilized the obtained MgO rods to investigate its CO₂ adsorption capacity by promoting it with three metal salt nitrates with varied molar ratios, i.e., Li, Na, and K and their derivatives. The results revealed that out of 12 different metal-salt promoted MgO samples, MgO-NaNO₃ > MgO(Li_{0.38}Na_{0.18} K_{0.44})NO₃ > MgO-LiNO₃ > MgO-(Na_{0.54}K_{0.46})NO₃ yielded highest CO₂ adsorption capacity. Specifically, CO₂ adsorption capacities of 11.8, 11.1, 10.4, and 9.8 mmol.g⁻¹ were obtained, respectively, which were significantly higher in comparison to pristine MgO. Similarly, BET results of the samples indicated that metal promotion endowed enhanced structural properties in comparison to the pristine MgO sample, resulting in favorable adsorption of the optimized samples. Moreover, the high performing samples have significant effect on the operating temperature regime of the modified samples in which MgO-NaNO₃ exhibited highest CO₂ adsorption at 300°C while the lowest was recorded for MgO(Li_{0.38}Na_{0.18} K_{0.44})NO₃ at 125°C. This study provides useful insights by which the adsorption capacity of CO₂ using MgO as an adsorbent can be significantly improved by modifying MgO with metal salts and their derivatives for mitigation of excess environmental CO₂.

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LIST OF ABBREVIATIONS

GHG	Greenhouse gas
GWP	Global Warming Potential
CAP	Climate Action Plan
IPPC	Intergovernmental Panel on Climate Change
UNEP	United Nations Environment Program
WMO	World Meteorological Organization
UN SDGs	United Nations Sustainable Development Goals
UNFCCC	United Nations Framework Convention on Climate Change
CCUS	Carbon Capture, Utilization and Storage
IEA	International Energy Agency
MEA	Monoethanolamine
IGCC	Integrated gasification combined cycle
syngas	Synthetic gas
MOFs	Metal-Organic frameworks
CO ₂ -EOR	CO ₂ -enhanced oil recovery
BE	Binding energy
ORNL	Oak Ridge National Laboratory
AEC	Atomic Energy Commission
LMFBR	Liquid Metal Fast Breeding Reactor
MSRE	Molten-Salt Reactor Experiment
CSP	Concentrated solar power
SEM	Scanning electron microscope
XRD	X-ray diffractometer
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda

TG	Thermogravimetry
AMS	Alkali metal salt
TGA	Thermogravimetry analysis
V_r	Total pore volume
d_p	Mean pore volume
Dc	Average crystalline domain size

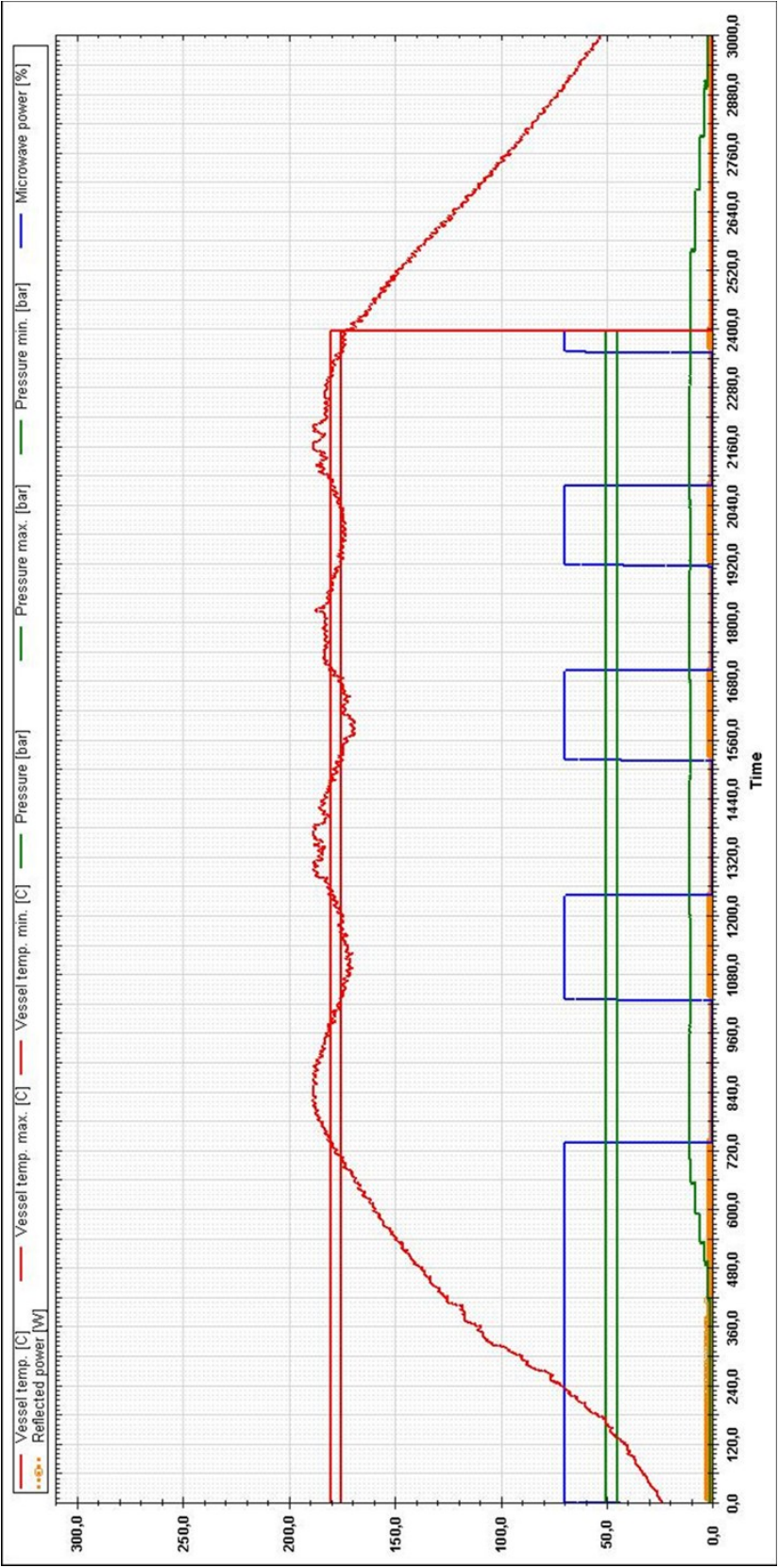
APPENDICES

Appendix P I: Microwave synthesis

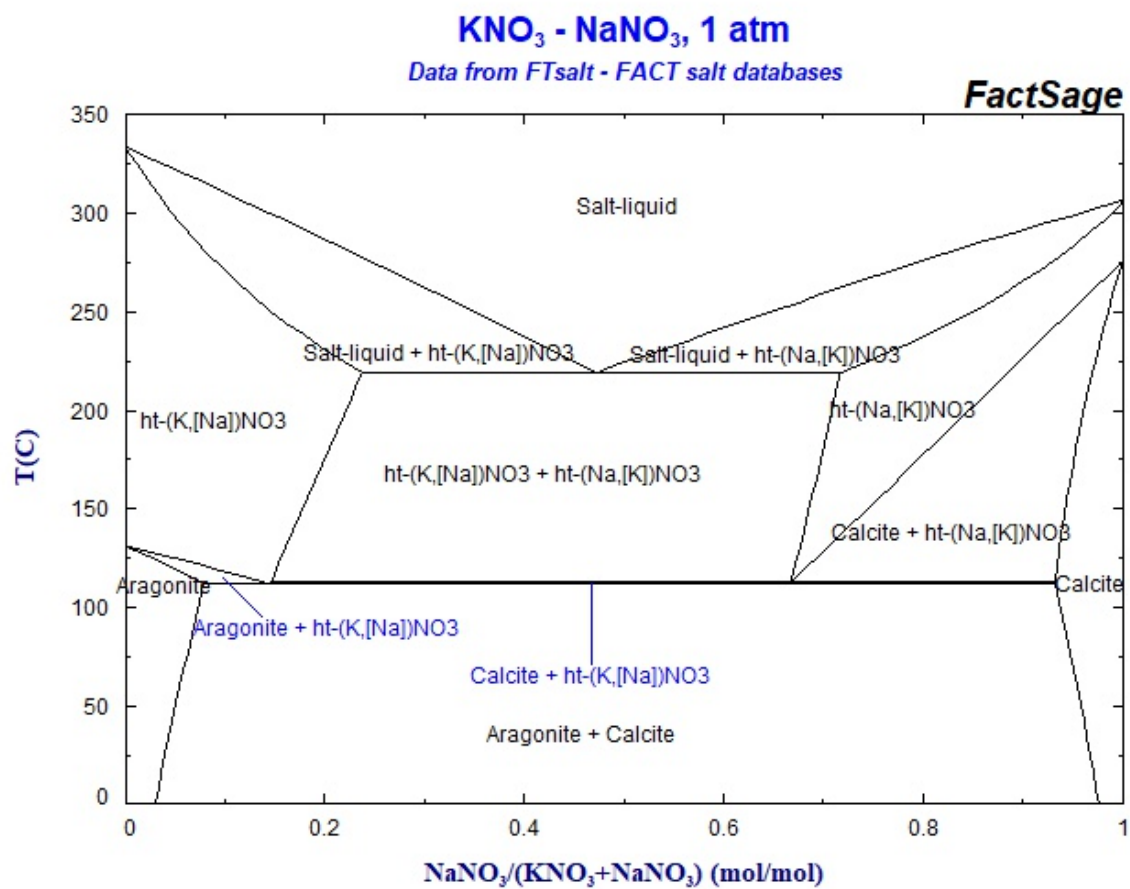
Appendix P II: eutectic mixture ($\text{Na}_{0.54}\text{K}_{0.46}\text{NO}_3$)

Appendix P III: Eutectic mixture ($\text{Li}_{0.38}\text{Na}_{0.18}\text{K}_{0.44}\text{NO}_3$)

APPENDIX P I: MICROWAVE SYNTHESIS



APPENDIX P II: EUTECTIC MIXTURE ($\text{Na}_{0.54}\text{K}_{0.46}\text{NO}_3$)



APPENDIX P II: EUTECTIC MIXTURE (Li_{0.38}Na_{0.18}K_{0.44})NO₃ [33]

