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Carbon Capture, Utilization and Storage

B. Ganesh Guptha[1]*, R . Sampath[2]*, A. Charan[3]*, G. Dileep [4]*

[1,2,3,4]Student, B-Tech III Year, Department of Chemical Engineering, GMR Institute of Technology, Rajam - 532127, India.
Email: 21341A0802@gmrit.edu.in[1], 21341A0822@gmrit.edu.in[2], 21341A0801@gmrit.edu.in[3], 22345A0805@gmrit.edu.in[4]

ABSTRACT:

The escalating levels of atmospheric CO2, emphasizing carbon capture and conversion techniques with a focus on metal-organic framework (MOF)-based materials. These materials, known for their unique structures and chemical stability, show promising potential for both CO2 capture and conversion. The review details advancements in synthesizing MOF-based materials and their application in reducing CO2 emissions. In addition to MOFs, the discussion touches on carbon capture, utilization, and storage (CCUS) as a sustainable technology. Chemical absorption technology is singled out for its commercial potential, summarizing the CO2 absorptive capacity of various solvents. The text also explores electrochemical conversion routes for turning CO2 into valuable chemicals, considering Faradaic conversion efficiencies. Graphitic carbon nitride (g-C3N4) is introduced as a two-dimensional material suitable for CO2 capture. To enhance its performance, the text describes the design of amine-functionalized g-C3N4 adsorbents, incorporating polyethylenimine (PEI) into the material's pores. This amine functionalization significantly improves CO2 capture, making PEI−g-C3N4 composites effective and recyclable for multiple cycles of adsorption and desorption. CO2, the primary greenhouse gas from human activities, mainly arises from fossil fuel combustion and industrial processes. Carbon Capture, Utilization, and Storage (CCUS) is a sustainable technology showing promise in reducing CO2 emissions linked to climate change. Chemical absorption technology, due to its commercial potential, is a key focus for carbon capture. Carbon utilization explores electrochemical conversion routes to turn CO2 into valuable chemicals. Successful carbon storage relies on a detailed understanding of fluid mechanics, geomechanics, and reactive transport.

INTRODUCTION

Carbon dioxide (CO2) stands as the prevalent greenhouse gas, and its buildup on Earth's surface has given rise to various issues. Notably, global warming and the elevation of sea levels are among the problems that could have detrimental effects on the planet's climate and environment.[1] Governments worldwide have entered agreements to rigorously regulate the rise in carbon dioxide (CO2) levels on Earth's surface. The initial measure involves the removal of CO2 from flue gas, a byproduct of fossil fuel combustion and a primary source of CO2 emissions.[2] The most widely used method for removing gas is absorption in liquids.[3] Due to its typical high temperature (e.g., 75−120 °C) and low CO2 content (e.g., 5−20 v/v %), the liquids employed to capture CO2 from flue gas need to display reversible chemical reactivity to CO2. [4] To gas is normally high in temperature (e.g., 75−120 °C), and low in CO2 content (e.g., 5−20 v/v %), the liquids used for capturing CO2 from flue gas should exhibit reversible chemical rectivity to CO2.meet this requirement, an amine scrubbing process was developed.[4] The global society's energy needs are predominantly fulfilled through the combustion of fossil fuels like coal, petroleum, and natural gas. This process generates a significant by- product: carbon dioxide (CO2), a major greenhouse gas (GHG). The substantial volume of CO2 emissions has given rise to critical environmental problems, including global warming, ocean acidification, and extreme weather events.

[5] Conducting Life Cycle Assessments (LCAs) is crucial to safeguard the integrity of CCUS projects and ensure the maintenance of essential balances. Additional obstacles to the widespread deployment of CCUS include the elevated costs linked to the capture process, challenges related to land area use, restricted geologic storage capacity, injection rate limitations, and infrastructure requirements.[6] Reducing the amount of CO2 in the air is crucial and needs urgent attention. Since we'll keep using fossil fuels for a while, a straightforward way to cut down on CO2 emissions is by taking out CO2 from places like power plants that burn fossil fuels. We can do this using technologies that capture and store carbon, but it comes with challenges like using a lot of energy for processes like separating and storing the captured carbon.[7,8] porous organic polymers,[9,10] and metal−organic frameworks,[11,12] various materials have been suggested for capturing CO2, but their use is restricted in real-life situations because they are either too expensive or not very stable.

In the last ten years, there has been significant interest in graphitic carbon nitride (g-C3N4) within both academic and industrial circles. [13,14] g-C3N4 is a type of two-dimensional (2D) material with a structure similar to graphene, and it has garnered attention for its unique properties such as high stability and hardness. These characteristics make it promising for various applications, including photocatalysis, [15−19] electrocatalysis, [15−19] electronic devices, [23] energy storage, [15] and gas adsorption. [24−30] Importantly, g-C3N4 can be easily synthesized through the direct pyrolysis of nitrogen-rich precursors (like urea, dicyandiamide, and melamine) via polycondensation reaction, making it appealing for industrial use. In terms of CO2 capture, there have been pioneering efforts using g- C3N4.

MATERIALS FOR CARBON CAPTURE

MOF COMPOSITES:

[31]MOF composites refer to hybrid materials that combine metal-organic frameworks (MOFs) with other substances, resulting in enhanced or unique properties. These composites leverage the strengths of both MOFs and the incorporated materials, offering a versatile platform for various applications. Here are key aspects and applications of MOF composites: (i). Enhanced Functionality: Synergistic Effects: Combining MOFs with other materials can create synergistic effects, enhancing the overall performance of the composite material. [32] Tailored Properties: The properties of MOF composites can be tailored by selecting suitable secondary components, allowing for customization based on specific application requirements. [33] (ii). Diverse Combinations: Inorganic Materials: MOFs can be combined with various inorganic materials such as metals,metal oxides, or nanoparticles to impart specific functionalities or improve structural stability. Organic Polymers: Integration with organic polymers can enhance flexibility, mechanical strength, or introduce additional functionalities to the MOF composite. 34 (iii). Fabrication Techniques: □ In Situ Synthesis: Some MOF composites are synthesized by incorporating additional materials during the MOF formation process. □ Post-Synthetic Modification: MOFs can be modified after synthesis by introducing secondary components, allowing for precise control over the composite's composition and properties. MOF composites offer a versatile and tunable platform, combining the unique properties of MOFs with other materials for a wide range of applications, from gas storage to catalysis and sensing. Their design and fabrication require careful consideration to optimize performance for specific uses.

Carbon materials derived from MOFs for electrocatalytic CO2 reduction:

[35] Carbon materials derived from metal-organic frameworks (MOFs) have garnered attention for electrocatalytic carbon dioxide (CO2) reduction due to their unique properties. Here's a brief overview:

i. (i). Synthesis Approach: Carbon materials are often derived by pyrolyzing MOFs, subjecting them to high temperatures in an inert atmosphere. This process leads to the removal of organic ligands, leaving behind a carbon framework. [36]

ii. Graphitic Nature: The resulting carbon materials typically exhibit a graphitic structure, providing excellent electrical conductivity, which is crucial for efficient electron transfer during electro catalysis.

iii. Active Sites and Metal Incorporation: The metal nodes present in the original MOF can be retained in the carbonized structure, acting as active sites for electro catalytic reactions. Common metals include Fe, Co, Ni, and Cu.

iv. [37] High Surface Area: The porous nature of MOFs is often preserved in the derived carbon materials, resulting in a high surface area. This enhances the exposure of active sites and facilitates the diffusion of CO2 to the catalytic centers.

v. Tunable Functionality: The carbonization process allows for the introduction of heteroatoms (e.g., N, S) into the carbon matrix, providing additional catalytic sites and improving the material's overall electro catalytic performance.

vi. Stability and Durability: Carbon materials derived from MOFs tend to exhibit good stability and durability during electro catalysis, contributing to their suitability for long-term CO2 reduction applications.

vii. Enhanced Selectivity: The structural features and composition of these carbon materials can be tailored to enhance selectivity toward specific CO2 reduction products, such as carbon monoxide (CO) or formate.

viii. Integration into Devices: carbon materials can be easily integrated into various electrochemical devices, such as electrodes, for use in CO2 reduction cells. Carbon materials derived from MOFs provide a versatile platform for designing efficient and selective electro catalysts for CO2 reduction, contributing to the development of sustainable technologies for carbon capture and utilization.

Conductive Graphitic Carbon Nitride as an Ideal Material for Electrocatalytically Switchable CO2 Capture:

Carbon Capture and Storage (CCS): This involves capturing CO2 emissions from industrial sources such as power plants, cement factories, and other heavy industries. The captured CO2 is then transported to a suitable storage site, such as underground geological formations, where it is stored permanently to prevent it from entering the atmosphere.

[38]A novel electrocatalytically switchable scheme for capturing carbon dioxide (CO2) has recently been proposed as an effective and reversible strategy for bare hexagonal boron nitride (h-BN) nanomaterials. In this approach, CO2 molecules initially weakly adhere (physisorption) to neutral h-BN. Through the injection of additional electrons into the h-BN adsorbent, density functional theory (DFT) calculations demonstrate a substantial enhancement in CO2 adsorption through a charge-induced chemisorption interaction. The chemically adsorbed CO2 can theoretically be released by removing the extra electrons. Unlike previous methods, the capture and release of CO2 happen spontaneously upon introducing or removing extra electrons. Notably, this electrocatalytic process can be conveniently controlled and reversed by toggling the charges carried by h-BN, presenting a promising solution for managing CO2 capture with high selectivity and reversibility.

However, the electrocatalytic scheme faces a hurdle with h-BN being a wide-gap semiconductor featuring a band gap of approximately 5.8 eV[39,40]. The insulating nature of h-BN raises uncertainties regarding the process of charging it up, as conventional semiconductor charging methods may not be as straightforward or effective in this particular context.

To overcome the above disadvantage, Jiao et all have investigated carbon nanotubes with pyridinic- nitrogen as an alternative absorbent to electrocatalytically switchable CO2 capture because of their good electron conductivity. On the other hand, we have proposed layered h-BN and graphene (hybrid BN/G) nanosheets, consisting of a single or double-layer h-BN and a substrate graphene layer, as an experimentally feasible approach to induce the requisite charge on h-BN for electrocatalytically switchable CO2 capture.

Utilization: The utilization of captured carbon, often referred to as carbon capture utilization and storage (CCUS), involves the capture of carbon dioxide (CO2) emissions from industrial processes or directly from the atmosphere and its utilization in various applications rather than releasing it into the atmosphere. This approach aims to mitigate climate change by reducing the amount of CO2 that contributes to the greenhouse effect.

There are several ways carbon capture can be utilized:

Carbon Utilization: Instead of storing the captured CO2, it can be utilized in various ways:

a. Carbon Utilization in Products: CO2 can be converted into valuable products such as chemicals, fuels, building materials, plastics, and other materials through chemical processes. For instance, CO2 can be used in the production of methanol, which is a versatile chemical feedstock.

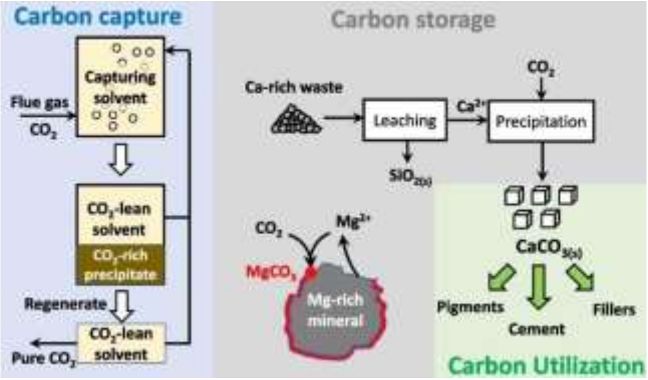
b. Carbon Utilization in Agriculture: CO2 can be used in agriculture for enhanced plant growth through carbon dioxide fertilization. This involves directing captured CO2 to greenhouses or specific agricultural settings to improve crop yields.

c. Mineralization: CO2 can be mineralized by reacting it with certain minerals to form stable carbonates. This process can be used to create construction materials like cement or to permanently store CO2 in a solid form.

d. Bioenergy with Carbon Capture and Storage (BECCS): This technique involves capturing CO2 emitted during the combustion of biomass for energy production and storing it using CCS technology.

The utilization of captured carbon has the potential to not only reduce greenhouse gas emissions but also create new economic opportunities by turning CO2 into valuable products or enhancing existing industrial processes. However, challenges such as cost-effectiveness, technological advancements, infrastructure development, and policy frameworks need to be addressed to scale up these utilization methods effectively.

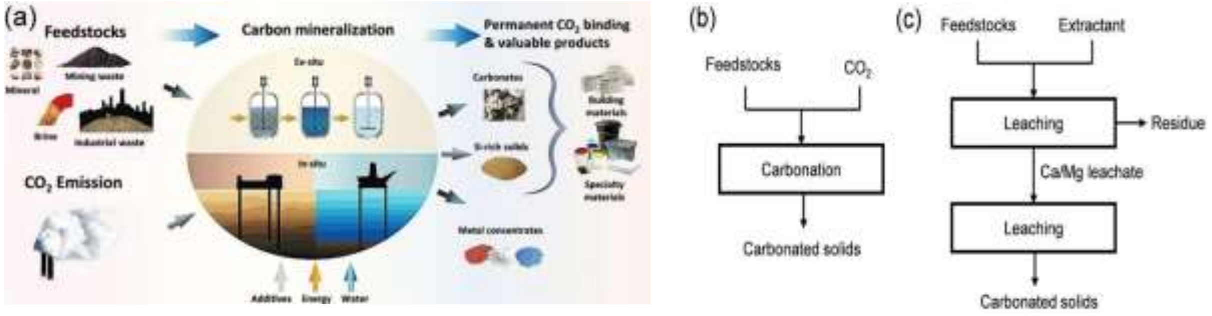
Several industries, research institutions, and governments are investing in research and development to explore and implement various techniques for the utilization of captured carbon, aiming to make these methods more feasible, economically viable, and widespread in the fight against climate change.



Storage: Mineral carbonation is a geological process that stabilizes CO2 by creating carbonate minerals through reactions with metal cations like Ca2+, Mg2+, or Fe2+

The materials used for this process vary from naturally occurring minerals and mining residues to industrial by-products. As the end products of carbonation are thermodynamically stable, they can be reused or stored above ground without continuous supervision . Mineral carbonation can be either in-situ or ex-situ , as depicted in Figure 6a. In in-situ mineral carbonation, CO2 captured from post-combustion streams in off-site facilities, compressed, and injected into a geologic reservoir reacts with host rocks to form carbonates. Thus, studies often focus on the direct geochemical reactions between pressurized CO2 and minerals to simulate in-situ mineral carbonation. Conversely, ex-situ carbonation occurs in a reactor using captured CO2 or flue gas, where solid feedstocks undergo carbonization through direct or indirect processes . Direct carbonation involves a single-step reaction where the feedstocks directly react with CO2, as depicted in Figure 6b. However, as this method enables both metal dissolution and carbonate precipitation simultaneously, the reaction rate is typically compromised

. In contrast, indirect carbonation divides the process into multiple stages to expedite and optimize carbonation. These stages include extracting metal from feedstocks, converting the metal into metal hydroxides, and using metal hydroxides to precipitate CO2 into carbonates . This section focuses on the precipitation of carbonate minerals based on various feedstocks, including natural minerals, mining wastes, and industrial by-products.



Mineral carbonation and industrial uses

This section deals with two rather different options for CO2 storage. The first is mineral carbonation, which involves converting CO2 to solid inorganic carbonates using chemical reactions. The second option is the industrial use of CO2, either directly or as feedstock for production of various carbon-containing chemicals.

Mineral carbonation: technology, impacts and costs Mineral carbonation refers to the fixation of CO2 using alkaline and alkaline-earth oxides, such as magnesium oxide (MgO) and calcium oxide (CaO), which are present in naturally occurring silicate rocks such as serpentine and olivine. Chemical reactions between these materials and CO2 produces compounds such as magnesium carbonate (MgCO3) and calcium carbonate (CaCO3, commonly known as limestone). The quantity of metal oxides in the silicate rocks that can be found in the earth's crust exceeds the amounts needed to fix all the CO2 that would be produced by the combustion of all available fossil fuel reserves. These oxides are also present in small quantities in some industrial wastes, such as stainless steel slags and ashes. Mineral carbonation produces silica and carbonates that are stable over long time scales and can therefore be disposed of in areas such as silicate mines, or re-used for construction purposes, although such re-use is likely to be small relative to the amounts produced. After carbonation, CO2 would not be released to the atmosphere. As a consequence, there would be little need to monitor the disposal sites and the associated risks would be very low. The storage potential is difficult to estimate at this early phase of development. It would be limited by the fraction of silicate reserves that can be technically exploited, by environmental issues such as the volume of product disposal, and by legal and societal constraints at the storage location.

RESULTS AND DISCUSSIONS

The relationship between the CO2 capture capacity of MOF-based materials and their catalytic performance for CO2 conversion is an intricate interplay influenced by various factors. Here are some key aspects of this relationship:

(i). Pore Structure and Surface Area: The CO2 capture capacity of MOFs is often associated with their high surface area and well-defined pore structures. However, for catalytic performance, the accessibility of catalytic sites within the MOF structure becomes crucial. A balance must be struck to ensure that the high surface area translates into effective catalytic activity.

(ii). Metal Centers and Active Sites: The metal nodes in MOFs that contribute to CO2 capture (e.g., through coordination) can also serve as active sites for catalysis. The nature of these metal centers and their coordination environments plays a significant role in both CO2 capture and conversion reactions.

(iii). Adsorption and Desorption Dynamics: The kinetics of CO2 adsorption and desorption in MOFs are critical for capture/release efficiency. In the context of catalysis, the ability of the MOF to dynamically interact with CO2 during the conversion process is essential for sustained catalytic activity.

(iv). Stability under Reaction Conditions: Catalytic conversion of CO2 often involves harsh reaction conditions. The stability of MOFs under these conditions is crucial for maintaining their structural integrity and, consequently, their catalytic performance. Instability could lead to a decrease in both CO2 capture and conversion efficiency over time.

(v). Functionalization and Tunability: MOFs can be functionalized to introduce specific groups or modify the metal centers, influencing both CO2 capture and catalytic activity. Tuning the MOF structure to optimize both capture and conversion functionalities is a challenging but promising approach.

(vi). Electrical Conductivity: While CO2 capture typically involves adsorption phenomena, catalytic conversion requires electron transfer processes. The electrical conductivity of MOFs, or their derived carbon materials, becomes crucial for efficient charge transfer during catalysis.

(vii). Synergy with Other Materials: Integrating MOFs with other materials, such as conductive polymers or nanoparticles, can create hybrid systems with synergistic effects. This integration may enhance both CO2 capture and conversion capabilities, leading to improved overall performance.

(viii). Selectivity in Catalysis: The design of MOFs can be tailored to influence the selectivity of CO2 conversion products. For instance, controlling the coordination environment of metal centers may favor specific reaction pathways. Understanding and optimizing the intricate balance between CO2 capture and catalytic conversion in MOF-based materials is a current focus of research in the field of sustainable energy and environmental applications. The challenge lies in designing multifunctional materials that excel in both aspects for integrated carbon capture and utilization processes.

In summary, we have shown that modification of the charge state of conductive g-C4N3 nanosheets provides an experimentally feasible approach for electrocatalytically switchable CO2 capture. Compared with other CO2 capture approaches, the process of CO2 capture/release occurs spontaneously without any energy barriers once extra electrons are introduced or removed, and these processes can be simply controlled and reversed by switching on/off the charging voltage. In addition, these negatively charged g-C4N3 nanosheets are highly selective for separating CO2 from mixtures with CH4, H2 and/or N2. Good electrical conductivity and high electron mobility of the sorbent materials are prerequisite for electrocatalytically switchable CO2 capture. The aim of the present paper is to explore conductive and easily synthetic sorbent material as an experimentally feasible adsorbent for electrocatalytically switchable CO2 capture. These predictions may prove to be instrumental in searching for a new class of high-capacity CO2 capture materials with ideal thermodynamics and reversibility, and we hope that this work will stimulate further theoretical and experimental research in this direction.

CONCLUSIONS

The development of MOF-based materials has ushered in promising advancements in CO2 capture and conversion. The success of MOFs as CO2 adsorbents relies on their tunable chemical properties, facilitating improved interactions with CO2 and other substrates. Key interactions include those with open metal sites, Lewis basic sites, polar functional groups, and micropores, leading to impressive adsorption capacities and selective capture. Post-synthetic strategies, such as modification and composite construction, address challenges in introducing functional groups. The catalytic efficiency of MOF-based materials is attributed to their high surface areas, porous structures, and synergistic effects from multiple functionalities. The high CO2 capture capacities of MOFs are crucial for their efficacy as catalysts, influencing local CO2 concentrations at active sites and enhancing catalytic performance, even in mixed gas environments. While significant progress has been made, challenges remain, including addressing harsh reaction conditions, reducing the reliance on co-catalysts, improving mass transfer limitations, and ensuring longterm stability. Collaboration across disciplines is essential for advancing understanding and practical applications in CO2 conversion. MOF-based materials hold great promise for the future of CO2 capture and conversion systems, with ongoing research expected to drive further advancements. In a summary, interstitially phosphorus-doped g-C3N4 nanotubes have been successfully synthesized with one- step thermal reaction between sodium hypophosphite monohydrate and melamine. The phosphorus doping leads to the formation of nanotubes instead of micro-sheets, increases the surface area, and creates more amino groups on the surface with lower zeta potential for better CO2 adsorption due to the possible acid-base interaction. The optical absorption is enhanced due to the shift of the electronic band structure. The more disorders are created due to less polymerization in the graphitic framework and less ternary nitrogen in triazine rings. Photogenerated charge carriers (electrons & holes) are better separated and migrated to the photoreactions for CO2 and water reductions with much higher activities. Thus, phosphorus doping leads to many modifications on g-C3N4, ranging from morphology change, to better optical absorption and charge separation, enlarged surface area and adsorption capability, in realizing higher activities in both photocatalytic reductions of CO2 to CO and CH4, and H2O producing H2.

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