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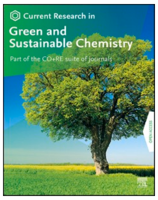

Tailoring zeolites for enhanced post-combustion CO_2 capture: A critical review

Ali H. Whaieb [a], Farah T. Jasim [a], Amer A. Abdulrahman [a], Idres M. Khuder [b], Saba A. Gheni [b,*], Islam Md Rizwanul Fattah [c], Nalan Turkoz Karakullukcu [d]

[a] *Department of Chemical Engineering, University of Technology- Iraq, 52 Alsinaa St., Baghdad PO Box 35010, Iraq*
[b] *Chemical Engineering Department, Tikrit University, Salahudin, 34001, Iraq*
[c] *Centre for Technology in Water and Wastewater (CTWW), School of Civil and Environmental Engineering, Faculty of Engineering and IT, University of Technology Sydney, 2007, Ultimo, NSW, Australia*
[d] *Karadeniz Advanced Technology Research and Application Center, Ondokuz Mayis University, Samsun, Turkey*

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ABSTRACT

Fossil combustion mainly contributes to global warming and increases atmospheric CO_2 levels, an essential greenhouse gas and environmental risk. The atmospheric CO_2 level increased, emphasizing the necessity to restrict the emission while maintaining it out of the carbon cycle. Various porous adsorbents were created as CO_2 capture sorbents, but they have been just moderately successful and require upgrading with more efficient porous adsorbents to address global climate issues caused by CO_2. Due to their tunable pore sizes, high chemical stability, superior adsorption selectivity, and large surface area, zeolite-based adsorbents are considered promising materials for CO_2 capture. Their framework structures allow for molecular sieving, ion exchange, and surface modifications, further enhancing their adsorption efficiency and regeneration capability.

1. Introduction

The increasing levels of atmospheric CO_2 due to fossil fuel combustion pose a critical environmental challenge. According to the IPCC estimation, greenhouse gas (GHG) emissions must peak by 2025 [1]. Consequently, a 43 % reduction in GHG emissions is projected by 2030. Fig. 1 provides a visual representation of the atmospheric composition of greenhouse gases. Conversely, a failure to implement substantial mitigation measures could lead to a substantial increase in global average temperature and atmospheric CO_2 levels, reaching 3.2 °C and 570 ppm, respectively, by the end of the 21st century [1,2].

Various CO_2 capture technologies have been explored, including solvent absorption, membrane separation, cryogenic processes, and solid sorbent adsorption. However, existing CCS technologies face several limitations that hinder their large-scale adoption. Carbon capture and storage (CCS) technologies encompass various approaches, including solvent absorption, membrane separation, cryogenic processes, and solid sorbent adsorption. While solvent-based technologies, such as amine scrubbing, remain widely used due to their high CO_2 capture efficiency, they suffer from drawbacks such as high energy consumption, solvent degradation, and corrosivity. Membrane-based and cryogenic separation methods, although promising, are often constrained by material selectivity, high operational costs, and the need for extreme conditions. Adsorption-based capture methods using solid sorbents have emerged as an energy-efficient alternative; however, conventional materials such as activated carbon and metal-organic frameworks (MOFs) often exhibit limited CO_2 selectivity, poor stability under humid conditions, or high regeneration energy demands.

Among adsorption-based technologies, zeolites have garnered significant attention due to their high thermal and chemical stability, tunable porosity, and superior adsorption properties. Unlike conventional adsorbents, zeolites offer a balance of high CO_2 affinity, recyclability, and selective separation, making them a promising candidate for scalable CO_2 capture. By modifying their pore structures and chemical composition, zeolites can be engineered to overcome the limitations of existing capture technologies. This study focuses on the advancements in zeolite modification techniques, including ion exchange, amine functionalization, and composite formation, to optimize their CO_2 capture performance for industrial applications.

Traditional solvent-based CO_2 capture methods, such as amine

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* Corresponding author.
E-mail address: ghenis@tu.edu.iq (S.A. Gheni).

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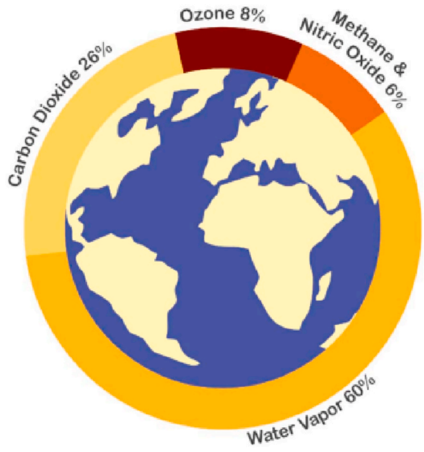


Fig. 1. Greenhouse gases percentage in the atmosphere.

scrubbing, suffer from high energy consumption, solvent degradation, and corrosion issues, making them costly and less sustainable. Membrane-based separation, while promising, is often limited by permeability-selectivity trade-offs, leading to reduced efficiency in real-world applications. Cryogenic separation requires extremely low temperatures, making it energy-intensive and economically challenging for widespread deployment. Furthermore, adsorption-based methods using conventional porous materials such as activated carbon, metal-organic frameworks (MOFs), and zeolites have demonstrated varying degrees of success, but most suffer from limitations in selectivity, adsorption capacity, and regeneration efficiency under industrial conditions.

The resulting climate crisis and environmental degradation necessitate the development of effective strategies to mitigate CO_2 emissions. Carbon capture and storage (CCS) emerges as a crucial technology aimed at reducing atmospheric CO2 concentrations. CCS involves capturing CO_2 from significant point sources, such as power plants and industrial facilities, followed by its transportation and secure storage in geological formations. Post-combustion CO_2 capture, a mature and widely applicable method, involves extracting CO_2 from flue gas post-combustion. This method is particularly advantageous as it can be retrofitted to existing power plants and industrial processes and other sources (shown in Fig. 2), making it a flexible and cost-effective option for reducing emissions.

The low concentration of CO_2 in flue gas, typically ranging from 10 % to 15 %, and the presence of other gases like nitrogen and oxygen present significant challenges in achieving efficient CO_2 separation. Post-combustion CO_2 capture remains a critical area of research due to its applicability in retrofitting existing industrial facilities. A recent review by Raganati and Ammendola [4] provides an extensive evaluation of current technologies, emphasizing the challenges of solvent-based and membrane-based methods. Our study builds upon this foundation by exploring recent advancements in zeolite modifications for improved CO_2 capture efficiency. CO_2 capture technologies are generally categorized into **pre-combustion, post-combustion, and oxy-fuel combustion** processes as shown in Fig. 3 [5], each with its own advantages and limitations. **Pre-combustion capture** involves the conversion of fossil fuels into syngas (a mixture of CO and H_2), followed by CO_2 separation before combustion. This method achieves high CO_2 removal efficiency but is limited by high capital costs, complex process requirements, and its applicability primarily to newly built facilities rather than existing power plants. **Oxy-fuel combustion**, on the other hand, burns fossil fuels in a high-purity oxygen environment instead of air, producing a flue gas composed mainly of CO_2 and water vapor. This simplifies CO_2 separation but requires significant energy input for oxygen production via air separation units (ASUs), making the process energy-intensive. Additionally, high flame temperatures in oxy-fuel combustion create operational challenges related to material degradation and process optimization. In contrast, **post-combustion CO_2 capture** is the most feasible option for existing industrial plants and power stations, as it does not require significant modifications to the combustion process. It involves capturing CO_2 from flue gases after combustion using solvent absorption, membrane separation, cryogenic processes, or solid sorbents such as zeolites. While post-combustion capture has historically been energy-intensive, recent advancements in materials, particularly modified zeolites, have significantly improved capture efficiency and regeneration performance, making it a more practical solution for near-term CO_2 mitigation efforts. Pre-combustion capture involves separating CO_2 after fuel reformation and produces syngas, a hydrogen and carbon monoxide mixture [6,7]. Oxy-fuel combustion technology includes burning fossil fuels in the presence of pure oxygen [7]. The post-combustion CO_2 capture approach involves capturing CO_2 from flue gas (end-of-pipe treatment approach). Given these considerations, post-combustion CO_2 capture remains a key research focus due to its **scalability, applicability to existing infrastructure, and ongoing advancements in adsorption-based technologies that enhance cost-effectiveness and efficiency.** The economic and environmental viability of CO_2 capture technologies is critical for their large-scale adoption. While post-combustion capture using **zeolite-based adsorbents** has demonstrated promising efficiency, its feasibility depends on factors such as **cost-effectiveness, energy consumption, scalability, and environmental sustainability.** This section provides a deeper analysis of these aspects, focusing on the cost-benefit trade-offs and environmental impacts associated with various CO_2 capture technologies. The **capital and operational costs** of CO_2 capture systems vary widely depending on the technology used. **Solvent-based CO_2 capture**, such as amine scrubbing, remains the most commercially developed method, but its high energy demand for solvent regeneration contributes to significant operational costs. Studies indicate that **amine-based systems cost \$40–80 per ton of CO_2 captured**, with additional expenses related to corrosion control and solvent degradation (IEA, 2023). In contrast, **solid sorbents such as zeolites offer lower regeneration costs**, with estimates ranging between **\$20–50 per ton of CO_2** due to

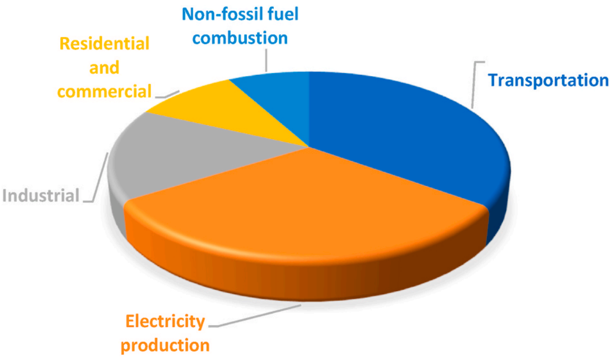


Fig. 2. Carbon dioxide emission from different sources [3].

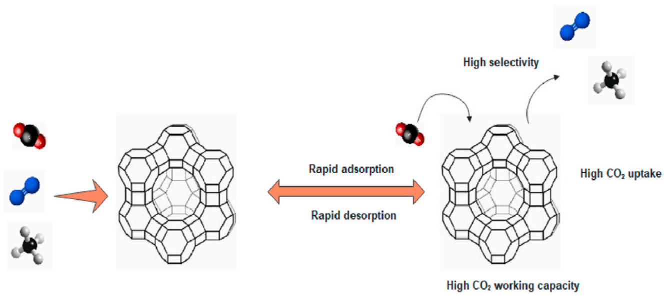


Fig. 3. Graphical describing of favorable properties of adsorbent for carbon dioxide capture [15].

their high stability and reduced thermal energy requirements [8]. Natural zeolites further reduce costs by eliminating the need for complex synthesis processes, making them an attractive option for large-scale deployment in cost-sensitive industries [9]. However, their **variable composition and lower adsorption selectivity** may require **pre-treatment and functionalization**, which could increase initial investment costs.

Post-combustion CO_2 capture, the simplest and foundational CCS technology, remains a crucial method for reducing emissions from large stationary sources like power plants and industrial facilities [11,12]. While pre-combustion and oxy-fuel capture offer advantages, they are unlikely to completely supplant post-combustion capture globally [11,13]. Post-combustion capture technology is considered an optimum capture route because there is no need to modify the existing emission technology without any major changes. Various separation techniques used for capturing CO_2 from flue gas streams are dependent upon the capture process principle, including solvent absorption, membrane technology, cryogenic methods, solid material adsorption, and the calcium looping cycle. Among these, adsorption offers several benefits, such as low energy consumption, economical regeneration, high loading capacity under ambient conditions, and a simple process that generates no liquid waste [14,15]. Further advantages include superior mechanical and chemical stability, high tolerance to flue gas pollutants, and easy maintenance. This suggests that this technology has a bright future in the capture and storage of CO_2. It is one of the mechanisms that has been studied the most and could eventually be applied as an emission-cleanup technology [16,17]. In addition, solid adsorbents with beneficial characteristics have been created; these include high adsorption capacity, insensitivity to moisture, variable properties, affordability, good CO_2 selectivity, ease of regeneration, and good reusability (Fig. 3).

Zeolites, a class of crystalline microporous aluminosilicates, have garnered significant attention as promising adsorbents for post-combustion CO_2 capture (see Table 1). Their unique structural characteristics, such as high surface area, tunable pore sizes, and chemical stability, make them ideal candidates for selectively adsorbing CO_2 over other gases. Additionally, the ability to tailor the properties of zeolites through chemical and structural modifications provides a pathway to enhance their CO_2 capture performance. Several recent review articles have explored various aspects of zeolite-based adsorbents and their applications in CO_2 capture. However, many of these reviews either focus on general adsorption materials, provide broad discussions without specific performance comparisons, or lack a comprehensive evaluation of emerging trends and future directions. To highlight the novelty of our review, Table 2 summarizes the scope, focus areas, and limitations of key review articles in the field:

The goal of the present review is to offer guidance for future endeavors in enhancing the performance of zeolite materials for post-combustion CO_2 capture in an effective and cost-efficient manner. Additionally, a comparison of zeolites with other CCS materials is presented to highlight their advantages and challenges. Understanding these modifications is crucial for optimizing zeolites as cost-effective and scalable adsorbents for CO_2 capture in industrial applications.

Table 2
Summary of recent review studies on zeolite-based adsorbents for CO_2 capture.

Reference	Year	Literature Reviewed Until	Key Focus Areas	Identified Gaps
[4,18]	2024	2023	Synthesis & Adsorption Mechanisms	Lacks performance-based comparisons & emerging trends
[19]	2022	2021	Zeolite Modifications	Limited industrial-scale feasibility analysis
[20]	2020	2019	Adsorption Kinetics & Capacity	Does not provide an economic or sustainability analysis
[21]	2023	2022	CO_2 Capture Performance	Focuses only on lab-scale studies
[22]	2022	2021	Zeolite Surface Functionalization	Minimal discussion on regeneration and durability
[23]	2024	2022	Hybrid Zeolite Composites	Lacks long-term stability assessments
[24]	2011	2010	Emerging CO_2 Adsorption Trends	Limited discussion on real-world applications
[25]	2024	2023	Zeolite-Based Industrial CO_2 Capture	Does not address economic feasibility

Table 1
Carbon dioxide capture approach and operating parameter [10].

Capture process	Method	Material used	Pressure (atm)	Temp. (°C)	CO_2 capture (vol%)	Removal of impurities
A. Post-combustion CO_2 capture						
Absorption	Chemical absorption	MEA, DEA, TEA	1	40–60	(3–25)	NO_X, SO_X, and PM
		Chilled ammonia				
Adsorption	Physical adsorption	Zeolite, carbonate sorbents, molecular sieve				
	Chemical looping	Activated carbon				
Membrane	Molten carbonate membrane	Ion transport membrane				
	Immobilized liquid membrane	Polymeric membrane				
Cryogenic	CO_2 liquefaction	Hybrid system (cryogenic + membrane)				
B. Pre-combustion CO_2 capture						
Absorption	Physical absorption	Selexol	(15–40)	200–450	(15–50)	NO_X, SO_X
	Chemical absorption	Fluor				
Adsorption		Zeolite				
		Carbonates				
		Activated carbon				
		Hydrotalcites, silicates				
Membrane		Metal membrane water gas shift reactor				
		Ion transport membrane				
Cryogenic	CO_2 liquefaction	Hybrid system (cryogenic + membrane)				
C. Oxy-fuel combustion						
Adsorption	Chemical looping	Zeolite	1	−55	(75–90)	NO_X, SO_X
	Physical adsorption	Activated carbon				
Membrane	Ion transport membrane	Polymeric membrane				
	Carbon molecular sieve					
Cryogenic	Distillation					

2. Fundamentals of zeolites

Ever since Cronstedt made the significant discovery in 1756, zeolites have garnered significant academic interest, leading to numerous practical applications in recent years [26]. Zeolites possess several advantages, including stability over repeated cycles, large surface area, and exceptionally rapid CO2 adsorption kinetics compared to other solid sorbents [27,28]. Additionally, zeolites exhibit strong adsorption sites and favorable mechanical properties, such as high abrasion resistance, density, and mechanical strength, enabling their formation into granules, spheres, and extrudate [29,30]. Furthermore, these CO_2 capture materials exhibit substantial adsorption capacity under moderate operating conditions (0–100 °C, 0.1–1 bar) [31], strongly influenced by temperature and positively correlated with pore size. However, CO_2 uptake by zeolites declines significantly as temperature approaches 100 °C. According to a recent review by Kumar et al. [32], the optimal temperature for CO_2 adsorption on zeolites is 70 °C, lower than typical flue gas temperatures (around 90 °C). Thus, either cooling flue gas or modifying adsorbents for high-temperature operation is necessary. However, cooling introduces additional energy consumption and cost to CO_2 capture technology. Therefore, it is essential to handle this component in the future adequately [27].

2.1. *Zeolite adsorbent structure and types for CO_2 capture*

Zeolites are crystalline microporous aluminosilicates composed of corner-sharing TO_4 tetrahedra (see Fig. 4), where T can be silicon or aluminum. Aluminum atoms exhibit a strong affinity for the oxygen atoms in the structure, providing a favorable atmosphere for the transfer of cations [33,34].

Cations within zeolites play a crucial role in CO_2 capture by attracting CO_2 molecules to the zeolite structure [15]. These cations, which can be organic (e.g., alkylammonium) or inorganic (e.g., alkali, alkaline earth, and other metals), are incorporated into the zeolite framework during synthesis or post-synthesis treatments like calcination or ion exchange. This ion exchange property is a key characteristic of zeolites [35]. Cations enhance CO_2 adsorption by forming strong electrostatic interactions with negatively charged oxygen atoms. Moreover, they enhance the structural integrity of the zeolite lattice, assuring its endurance through the capture process. Zeolites promote ion exchange with CO_2, resulting in the creation of CO_2-cation complexes and enhanced adsorption capacity. The kind and concentration of cations markedly affect zeolite selectivity, augmenting their capacity to adsorb CO_2 from flue gas [36]. The structural and chemical properties of zeolites, particularly their Si/Al ratio and cationic composition, play a crucial role in their CO_2 adsorption performance. The Si/Al ratio determines the overall framework charge of the zeolite, influencing its hydrophilicity and affinity for polar molecules like CO_2. Zeolites with a low Si/Al ratio exhibit higher ion-exchange capacities and stronger electrostatic interactions with CO_2 due to the presence of more negatively charged aluminum sites. However, these low-silica zeolites tend to be more hydrophilic, which can reduce selectivity in humid environments. In contrast, high Si/Al ratio zeolites possess enhanced hydrophobicity, making them more resistant to moisture interference but potentially reducing CO_2 adsorption due to weaker electrostatic interactions. The presence and type of exchangeable cations also significantly impact zeolite adsorption behavior. Cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} interact with CO_2 molecules through electrostatic forces and polarization effects. Studies have shown that alkali metal cations (e.g., Na^+ and K^+) enhance CO_2 adsorption due to their moderate interaction strength, whereas alkaline earth cations (e.g., Ca^{2+} and Mg^{2+}) exhibit stronger binding with CO_2 but can lead to diffusion limitations in microporous structures. The selection of cation type and its distribution within the zeolite framework is critical in tuning adsorption selectivity, balancing CO_2 uptake, regeneration efficiency, and competitive adsorption with other gases such as N_2 and H_2O. By optimizing both the Si/Al ratio and cationic composition, zeolites can be engineered for higher CO_2 selectivity, improved adsorption capacity, and enhanced performance under real industrial conditions. In this study, we explore various modification techniques, including ion exchange and framework functionalization, to systematically improve the CO_2 capture efficiency of zeolites.

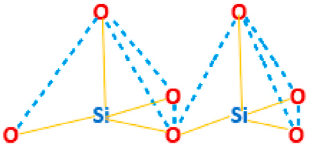


Fig. 4. Two corner-sharing SiO_4 tetrahedra [33].

Zeolites, classified as molecular sieves due to their microporous structure, can selectively adsorb gas molecules based on pore size. Thus, the zeolite can only adsorb gas molecules with a kinetic diameter smaller than its pore size. The topology and pore diameter of the crystal lattice are crucial factors in developing zeolite-based CO_2 capture materials. Introducing mesopores into microporous zeolites, achieved through synthesizing hierarchical porous materials, is one of the most promising approaches for creating novel structures with tailored chemical and textural attributes. Its flexible porous structure gets around molecule transport problems, leading to better CO_2 absorption and better mass transfer across the mesoporous channels [27,37,38].

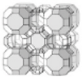
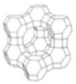
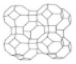
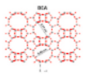
FAU-structured zeolites, including X and Y, have been thoroughly investigated owing to their stable crystalline morphologies and substantial pore volumes. X-type zeolites generally comprise 77–96 cations, whereas Y-type zeolites consist of 48–76 aluminium cations per site. The two zeolites exhibit analogous structures, with the principal distinction being the Si/Al ratio [39]. The electric field produced by cations affects their quantity within the zeolite. X-type zeolites typically possess a higher cation content than Y-type zeolites, mainly attributable to the presence of aluminium. FAU-structured zeolites, such as 13X and NaY, are extensively utilized for the adsorption and storage of CO_2 [34]. In 2009, Shao and colleagues demonstrated the effectiveness of NaY zeolite in capturing CO_2, attributing this capability to its substantial surface area of 732 m^2/g. The robust crystalline structure of NaY zeolite, along with its extensive three-dimensional pore network, further enhances its adaptability across diverse applications [40].

A well-established approach involves synthesizing 4A zeolites, which can then be transformed into 3A zeolites by substituting the sodium cation with a potassium cation, or into 5A zeolites by replacing the sodium ion with calcium or magnesium [41]. By adjusting the quantity of surfactants and alkanol groups, the surface areas of these zeolites can be modulated, allowing for optimized CO_2 adsorption at low pressures. Both 4A and 13X zeolites are effective in capturing CO_2, with zeolite 13X exhibiting a superior adsorption capacity. Table 3 presents examples of the aforementioned structures, and Fig. 5 illustrates the types of zeolites commonly used for CO_2 adsorption [27].

2.2. *CO_2 adsorption mechanisms in zeolites*

The process of CO_2 capture in zeolites encompasses both physical and chemical adsorption methods, as illustrated in Fig. 6. Weaker van der Waals interactions attract CO_2 molecules to the internal surface of the zeolite, resulting in physisorption. Here, dipole-dipole interactions and dispersion forces between the zeolite and CO_2 are the primary forces involved. The considerable quadrupole moment of CO_2 improves its capture by markedly interacting with the electric field gradient adjacent to the zeolite framework, so promoting the physical adsorption of CO_2 [45,46]. The quadrupole moment of CO_2 surpasses that of other gases, including carbon monoxide (CO), nitrogen (N_2), hydrogen (H_2), and methane (CH_4), in the following sequence. CO_2 surpasses CO, which exceeds N_2, followed by H_2, and finally CH_4 [47].

Table 3
Zeolite structures.

Zeolite structure	schematic	Example	Reference
KFI		ZK-5	[42]
FAU		Na-X,X,Y	[43]
LTA		3A,4A,5A	[32]
BEA		β	[44]

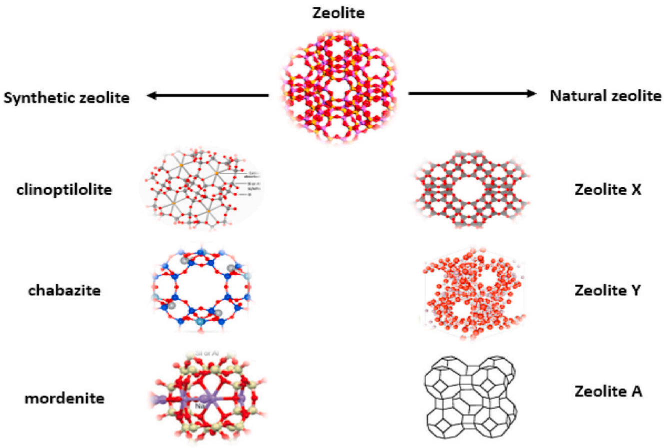


Fig. 5. Classification of zeolite for CO_2 capture application [27].

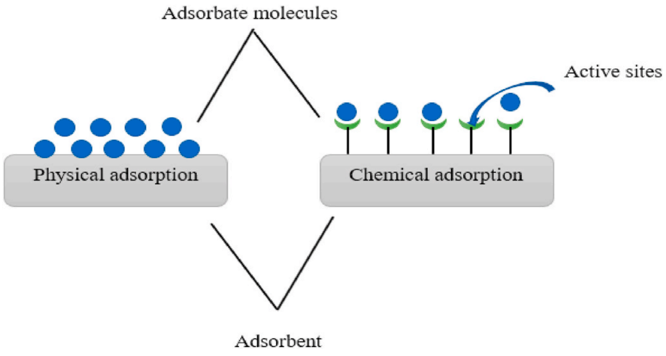


Fig. 6. Physical versus chemical adsorption [48].

In physical adsorption, CO_2 molecules are attracted to the zeolite surface through non-covalent interactions, leading to heat release and a reduction in enthalpy (ΔH). The entropy change (ΔS) is generally positive, signifying an increase in disorder as CO_2 molecules are adsorbed onto the zeolite surface. This process is reversible, allowing for the desorption of adsorbed CO_2 through either a decrease in pressure or an increase in temperature [36,49]. Chemisorption is defined as the formation of a direct chemical connection between an adsorbate and a surface, resulting in a significant change in the adsorbate's electronic structure. Bicarbonates and other related compounds chemically adsorb CO_2. Chemisorption is characterized by electron transfer or reconfiguration, resulting in a more dramatic change in enthalpy and heat release compared to physisorption [50]. Selective adsorption refers to the preferential adsorption of CO_2 over other gases present in the flue gas mixture. This selectivity is influenced by both the physical and chemical properties of the zeolite and is crucial for the effectiveness of CO_2 capture. Zeolites can be functionalized with amine groups or undergo ion exchange to incorporate specific cations. These modifications can increase the selectivity of CO_2 adsorption by enhancing the affinity of the zeolite for CO_2 molecules. In medium- and large-pore zeolites, two primary adsorption mechanisms frequently occur. The first mechanism involves the interaction between one oxygen atom of the CO_2 molecule and an extra-framework cation in the zeolite. The second, a bridging mechanism, occurs when both oxygen atoms of CO_2 interact with different extra-framework cations in the zeolite. A less commonly observed mechanism entails the formation of a carbonate or a carbonate precursor, in which one oxygen atom of CO_2 interacts with the cation site while the carbon of the CO_2 molecule bonds with an oxygen atom in the zeolite framework.

2.3. *Factors affecting adsorption rate on zeolites*

The CO_2 adsorption rate in zeolites is affected by pore size and surface area, where larger pores and increased surface areas enhance adsorption efficiency. The adsorption process is intricate and contingent upon several parameters, including temperature, pressure, and the chemical characteristics of the zeolite. Elevating the partial pressure of CO_2 enhances adsorption capacity by enhancing the availability of CO_2 molecules for adsorption [49]. Gardner et al. [51] observed that the adsorption capacity of H-ZSM-5 increases with increasing partial pressure. Conversely, higher temperatures weaken the interactions between CO_2 molecules and the zeolite, resulting in decreased adsorption capacity. Su et al. [52] found that the adsorption ability of unmodified Y-zeolite for CO_2 decreases as temperature rises. Chemical characteristics of the zeolite, such as cation density and the presence of active sites, also influence CO_2 adsorption at low pressures [53]. The basicity and electric field strength of the zeolite material are inversely related to its Si/Al ratio. Zeolite A, with a low Si/Al ratio and higher basicity, exhibits a higher capacity for CO_2 capture [54]. Table 4 summarizes the effects of various zeolite characteristics and operating conditions on the adsorption process.

Various zeolites exhibit different variations in their CO_2 adsorption characteristics, resulting in a variety of efficiencies when it comes to separating CO_2 from gas mixtures. The Zeolites are classified into two categories. One type is medium- and large-pore zeolites, which have pore diameters ranging from 0.45 to 0.60 nm and 0.60–0.80 nm, respectively. The second category consists of small-pore zeolites, which possess pores with dimensions ranging from 0.30 to 0.45 nm [15,56].

The reason for this distinction is that the molecules (CO_2, CH_4, and N_2) that zeolites are employed to separate have similar dimensions to the pore size of small-pore zeolites [15]. Electrostatic interactions primarily determine the adsorption behavior in medium- and large-pore

Table 4
Effect of zeolite characteristics and operation conditions on adsorption process [51,52,54,55].

Property	Impacts on the process	Reason
Higher CO_2 partial pressure	higher CO_2 adsorption capacity	More CO_2 molecules available for adsorption
Higher Temperature	Decreased CO_2 adsorption capacity	Weaker interactions between CO_2 molecules and the zeolite
The Si/Al ratio	Lower ratio results in higher CO_2 capacity	Basicity and electric field strength inversely proportional to Si/Al ratio
Pore diameter	Larger pore diameter negatively impacts capture	Multiple gases, including CO_2, can be adsorbed simultaneously

zeolites. In contrast, diffusion and size exclusion also contribute to the adsorption process in small-pore zeolites. Small-pore zeolites are composed of 8-membered rings (8 MRs), which are rings made up of 8 silicon or aluminum atoms or even smaller rings [15,56]. Fig. 7A [57] illustrates equilibrium separation, the process of separating CO_2 based on electrostatic interaction with the adsorbent (see Fig. 8).

The polarity and polarizability of gas molecules, coupled with the electrical field gradient of the zeolite surface, influence their electrostatic interactions. As the aluminum content in the zeolite increases, so does the electrical field gradient [15,42]. Despite its nonpolar nature, CO_2 is preferentially adsorbed by zeolites due to its larger quadrupole moment and polarizability compared to other gases like N_2 and CH_4 (Table 5). This enhanced affinity for the zeolite surface enables superior CO_2 adsorption and subsequent separation from N_2 or CH_4.

Medium- and large-pore zeolites generally separate CO_2 based on equilibrium adsorption. In contrast, in small-pore zeolites, the diffusion rate of adsorbates into the pores often determines the selectivity of the separation process. According to Table 5, CO_2 has a smaller kinetic diameter than N_2 and CH_4, which can significantly influence diffusion through narrow pores, particularly in zeolites with low aluminum content. For example, CO_2 diffuses more rapidly than CH_4 in certain small-pore zeolites, such as all-silica LTA and CHA [58]. Kinetic separation, which exploits differences in molecular diffusivity through micropores, can achieve selectivity as illustrated in Fig. 7B [57].

The ideal scenario for kinetic separation is molecular sieving, where the zeolite's pore size is large enough to allow CO_2 entry but restricts N_2 and/or CH_4 (Fig. 7C) [59]. Although this appears optimal, it is achievable only in zeolites with pore sizes smaller than 3.6 Å, the kinetic diameter of N_2. In such constrained spaces, CO_2 exhibits low diffusivity (known as configurational diffusion), which slows its uptake. This limitation can also reduce working capacity, as CO_2 may become trapped within the pores [60].

3. Tailoring zeolites for CO_2 capture

The effectiveness of zeolites in CO_2 capture can be significantly enhanced through various tailoring strategies. These modifications focus on improving the interaction between CO_2 molecules and the zeolite material, optimizing the physical and chemical properties of the zeolite to achieve higher adsorption capacity, selectivity, and efficiency. The key strategies include chemical modification, pore size and structure optimization, surface functionalization, and the development of hybrid zeolites. Tailoring techniques have a lot of advantages and disadvantages, which are listed in Table 6.

3.1. *Chemical modification*

Chemical modification of zeolites enhances their affinity for CO_2 through alterations to their chemical composition, commonly via methods such as ion exchange and metal oxide impregnation (see Table 7). A prevalent technique for chemical modification is ion exchange, where native cations within the zeolite framework (e.g., Na^+, K^+, Ca^{2+}) are substituted with cations that exhibit a higher affinity for CO_2. For example, replacing native cations with Li^+, Mg^{2+}, or Zn^{2+} enhances CO_2 adsorption due to stronger electrostatic interactions between CO_2 molecules and the new cations, thereby improving CO_2 selectivity over other gases such as N_2.

The choice of cation influences the electric field within the pores and available pore volume, providing an effective method to tune the adsorptive properties of the porous material. Cations serve as preferential adsorption sites, especially for polar or easily polarizable molecules. However, the type of cation can also impact the adsorption of nonpolar molecules through induced electrostatic interactions with the ionic surface [75]. The extent of adsorption in zeolitic pores is largely driven by interactions between the adsorbate and the cation-induced electric field, although the acid-base properties of the zeolite framework can also significantly impact adsorption under specific pressure conditions. The exchangeable cation functions as an acid site, while the nearby framework oxygen acts as a basic site, with basicity increasing as framework aluminum content rises and cation electronegativity decreases [76]. The acid-base strength of these zeolite sites can be readily adjusted by cation exchange or changes in aluminum content within the framework [77].

Sun et al. [78] demonstrated the potential of transition metal cation-exchanged SSZ-13 zeolites for post-combustion CO_2 capture, exhibiting higher CO_2/N_2 selectivity (over 40) than alkali metal ion-exchanged zeolites (23–36). Zhao et al. [79] utilized Li^+-exchanged ZSM-25 zeolites (LZZs) to enhance CO_2 adsorption kinetics without reducing selectivity. Their results, obtained through single (isotherm) and binary (breakthrough) gas tests, showed that LZZ has a CO_2 adsorption rate 9.84 times that of Na-ZSM-25, with a CO_2 adsorption capacity increase of 6.1 % at 303 K and 9.5 bar. Additionally, LZZ inherited Na-ZSM-25's high CO_2/CH_4 selectivity in both single and binary-gas adsorption. Tao et al. [80] investigated the adsorption behavior of CO_2, N_2, and CH_4 on metal cation-exchanged LTA zeolites (Si/Al = 3 and 6) with various cations (Na+, Ca2+, Mn2+, and Ce^{3+}). Mortazavi et al. [81] explored enhancing the CO_2 adsorption capacity of clinoptilolite (Si/Al ratio 3.5–4) through cation exchange with Li^+, Mg^{2+}, and Ca^{2+}, finding that clinoptilolite exchanged with Li $^+$ exhibited the highest CO_2 adsorption capacity. This enhancement was attributed to Li $^+$ ions' small atomic radius and high basicity, which increase the CO_2 capture capacity and selectivity.

The efficiency of ion exchange is contingent upon variables like cation concentration and type, reaction time, and temperature. Smaller cations with greater CO_2 affinity, such as Li^+, demonstrate enhanced CO_2 capture capacity and selectivity owing to their reduced atomic

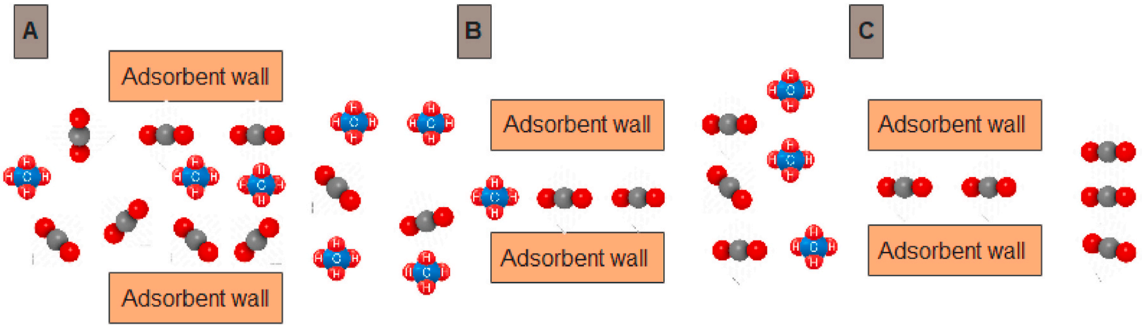


Fig. 7. Types of CO_2 Separation Mechanisms for CO_2/CH_4 Mixtures ((A) *Equilibrium Separation*: In this mechanism, CO_2 preferentially adsorbs onto the surface of the adsorbent, while CH_4 continues to diffuse through.(B) *Kinetic Separation*: Here, CO_2, with a smaller kinetic diameter than CH_4, diffuses more rapidly through the pores. (C) *Molecular Sieving Separation*: In this mechanism, only CO_2 molecules can enter the pores due to their smaller size, whereas CH_4 molecules are too large to access the pores effectively [15].

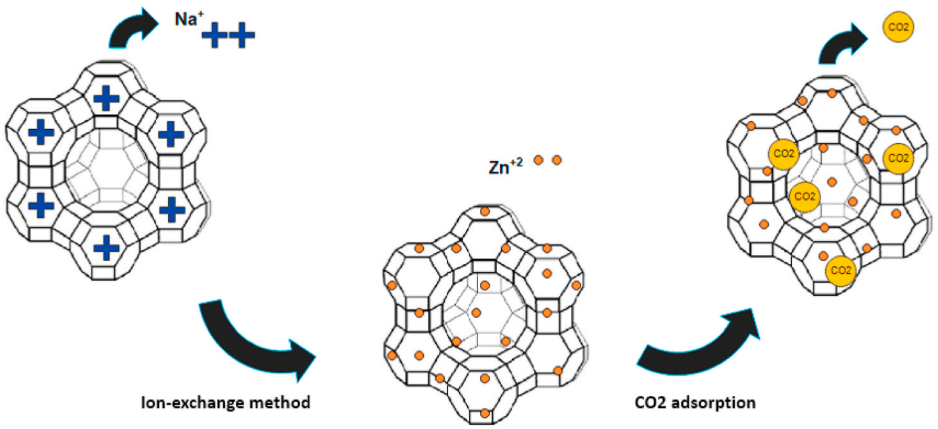


Fig. 8. Schematic representation of zeolite modifications by ion exchange for carbon dioxide capture [82].

Table 5
Properties of gases relevant to CO_2 separation from flue gas or biogas [15].

Gases	Kinetic diameter (Å)	Quadrupole (cm^{-2})	Polarizability (cm^3)
CO_2	3.30	$13.4*10^{-40}$	$2.65*10^{-24}$
N_2	3.64	$4.6*10^{-40}$	$1.76*10^{-24}$
CH_4	3.80	0	$2.60*10^{-24}$

radius and increased basicity, facilitating a tighter interaction with the zeolite framework and a stronger affinity for CO_2.

Another approach is the impregnation of zeolites with metal oxides such as MgO, CaO, or ZnO. These metal oxides can introduce the base strength of zeolites by the creation of new basic sites on the zeolite surface, which enhances the chemisorption of CO_2. Bordawekar [92] and Davis [93] have observed that the addition of cesium oxide to NaX zeolites leads to an increase in both the basicity and adsorption efficacy. The investigations conducted by Kovacheva et al. [94] on the NaX sample impregnated with MgO demonstrated that the inclusion of this oxide contributed to an improvement in the basicity of the NaX structure. A frequent observation is that the basic sites of metal oxides exhibit a higher degree of basicity compared to those of ion-exchanged zeolites [49]. Mesoporous MgO is theoretically advantageous for carbon dioxide adsorption due to its superior thermal stability and regeneration characteristics compared to NaX zeolite [95]. The mesoporous MgO material achieves a high adsorption capacity of 8 wt% at low temperatures and ambient pressure [96].

3.2. *Hybrid zeolites*

Hybrid zeolites are composite materials that combine the properties of zeolites with other materials, such as polymers, carbons, silica, chitosan, and metal-organic frameworks (MOFs) [97–102]. The development of hybrid zeolites aims to synergistically enhance the CO_2 capture performance beyond what is achievable with zeolites alone, particularly in terms of selectivity, improved mechanical strength and higher thermal stability under varying operating conditions. Besides that, they can offer increased resistance to fouling, making them more suitable for industrial applications in post-combustion CO_2 capture. Table 8 summarizes the CO_2 adsorption efficiency of zeolite-composites

Table 7
Adsorption capacity of different types of zeolites modified with ion-exchange method.

Zeolite	Ion exchange	P (bar)	T (°C)	CO_2 uptake (mmol/g)	Ref.
RHO	Cu (3.5,2.3 %)	1	25	3.2, 2.3	[84]
SSZ-13	(Co^{+2})	1	0	4.49	[78]
SSZ-13	(Ni^{+2})	1	0	4.47	[78]
13X	(Li^{+})	1	25	1.1	[85]
13X	(K^{+})	1	25	1.2	[85]
13X	(Ca^{+2})	1	25	1.7	[85]
13X	(Li^{+})	1	25	6.98	[86]
13X	(Na^{+})	1	25	6.28	[86]
Natural zeolite (NZ)	(Cu^{+2})	1	20	7.6	[83]
Natural zeolite (NZ)	(Fe^{+3})	1	20	6.23	[83]
Zeolite A	Ca^{+}	0.15	40	3.72	[87]
Na-X	Li^{+}	1	25	5.57	[88]
NaX	La^{+3}	1	0	4.36	[89]
NaX	Ce^{+3}	1	0	3.85	[89]
Mordenite	Fe^{+}	1	25	2.07	[90]
NaX	Ca^{+}	0.95	25	5.48	[91]
NaY	K^{+}	0.95	25	5.9	[91]

Table 6
Advantages and disadvantages of different zeolite modification [55].

Route	Advantages	Disadvantages	References
Carbon modification	Improved adsorbent stability, enhanced resistance to moisture and temperature, tunable surface properties	Limited scalability, lower CO_2 adsorption capacity	[61]
Ion exchange	Simple and cost-effective modification method, widely applicable to various zeolite types	Limited control over the ion exchange process	[62]
Amine functionalization	Enhanced CO_2 adsorption capacity, regenerable and reusable adsorbents, selective CO_2 capture	Potential structural changes, decreased thermal stability	[53] [63] [64–69]
MOF modification	Enhanced stability under high temperature, increased adsorption capacity and selectivity	Challenging synthesis and MOF-zeolite integration	[70,71]
Chitosan modification	Non-toxic and cheap, excellent morphological stability, better adsorption capacity	Potential structural changes, decreased thermal stability	[72,73]
Silica modification	Increased hydrophobicity	Altered zeolite structure and properties	[43]
Acid Treatment	Enhanced surface acidity, improved selectivity	Potential changes in zeolite structure, limited control	[74]

in the literature.

3.2.1. *Zeolite-geopolymer based composite*

Geopolymers can be characterized as amorphous zeolites that have not undergone the process of crystallization [114] (see Fig. 9). As depicted in Fig. 10, the geopolymer structure comprises an amorphous arrangement of SiO_4 and AlO_4 tetrahedral units interconnected by oxygen atoms. Hydrated alkali cations stabilize this structure by neutralizing the system's charges [113,115]. Geopolymers inherently possess porosity comparable to zeolites. Specifically, geopolymers are mesoporous materials, whereas zeolites are microporous. However, unlike zeolites, geopolymers exhibit favorable mechanical properties and are easily shapeable [116]. These attributes render geopolymers highly suitable for structural applications, thermal and acoustic insulation, or catalyst support [117,118]. Furthermore, geopolymers demonstrate excellent mechanical strength and can be easily shaped and reproduced, even on a large scale.

Adsorption is invariably associated with substantial thermal effects, which stem from the exothermic characteristics of the process. These thermal effects can significantly influence the kinetics and efficacy of sorption [120]. The adsorption of CO_2 on zeolites exhibits isosteric heat ranging from 33 to 41 kJ/mol [121]. Composite materials incorporating zeolites can mitigate the released heat. Studies have demonstrated that geopolymers exhibit notable selectivity for CO_2 over N_2 in gas adsorption [122,123]. A geopolymer-zeolite 13X composite has been investigated for CO_2 capture using techniques such as thermogravimetric analysis, pressure decay tests [113], and differential adsorption tests in CO2/N2 gas mixture flow [124], demonstrating promising capacity and selectivity. Khalid et al. [98] and Wang et al. [125] utilized geopolymer-zeolite composites as adsorbents, exhibiting comparable properties to pure zeolites but with higher BET surface areas and metal cation-exchange capacities.

Typically, zeolites are synthesized via hydrothermal techniques that activate silica (SiO2) and alumina (Al_2O_3) sources in an alkaline medium. Following synthesis, zeolites must be shaped into larger forms through processes such as pressing, sintering, spray coating, or utilizing porous supports to produce spherical granules or coarse powders suitable for industrial applications. This shaping process significantly increases fabrication complexity and cost. The CO_2 capacity and selectivity of three various granular and monolithic shapes of geopolymers synthesized from potassium silicate (K1–SiO_4) and metakaolin were claimed to be in the range between 0.27 and 0.3 mmol/g with CO_2 selectivity of around 100 % for CO_2-methane or CO_2 nitrogen mixtures. It is anticipated that the incorporation of zeolite into the geopolymer matrix may enhance adsorption performance due to the geopolymer's high selectivity for CO_2 [122]. The sodium form of zeolite 13X is recognized as a standard material for carbon dioxide capture applications owing to its relatively high CO_2 uptake, which is significantly greater than that of geopolymers while maintaining acceptable selectivity. The integration of the regular, ordered microporous phase of Na13X zeolite with the mesoporous and macroporous phases of the geopolymer structure presents an opportunity to optimize the properties of this zeolite-geopolymer composite for effective carbon dioxide capture. Typically, a monolith is fabricated by blending the conventional sodium form of zeolite 13X (20–40 wt%) with a metakaolin-based geopolymer matrix, which features a microstructure with nanoparticles exhibiting both microporosity and mesoporosity [126].

Table 8
The CO_2 adsorption efficiency of zeolite composites.

Zeolite	Pressure (atm)	Temperature (°C)	CO_2 uptake **(mmol/g)**	References
Zeolite X/AC	1	0	2.5	[103]
Na-X/AC	1	25	1.81	[104]
Zeolite 13X/AC	1	10	6	[105]
Zeolite 13X/AC	2.2	10	6.3	[106]
MCM-41/13X	1	25	1.2	[107]
P-ZSM/MCM-41	1	25	1.51	[108]
5A/MCM-41	1	25	4.08	[101]
Zeolite/MIL-100 (Fe)	2	25	7.01	[109]
Zeolite 5A/MOF-74	20	25	13.8	[110]
Zeolite/Fe-MOF	1	27	8.4	[111]
Zeolite Y/Carbon	1	30	2.39	[61]
FAU(X)/Chitosan	–	−20	0.71	[99]
ZSM-5/MCM-48 P60 (PEI)	1	25	3.28	[112]
ZSM-5/MCM-48 T60 (TEPA)	1	25	4.97	[112]
13X−geopolymer composite	0.2	35	1.5	[113]

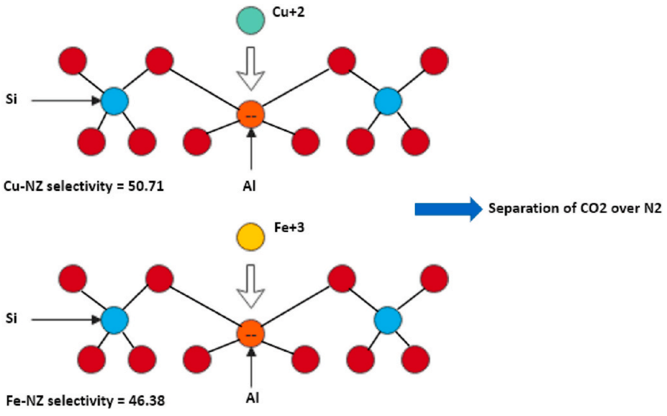


Fig. 9. Schematic of transition metal–exchanged [83].

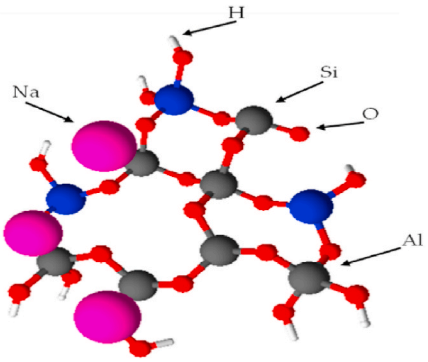


Fig. 10. The scheme of the geopolymer framework [119].

3.2.2. *Zeolite-carbon based composite*

Carbon sources can effectively improve zeolite's mechanical properties and durability and enhance its chemical migration and ion exchange ability. Porous carbon typically has micropores that are significantly larger, often exceeding 1 nm. This property is advantageous for CO_2 adsorption and storage [127]. Nevertheless, ultra-micropores (with a size smaller than 1 nm) exhibit superior CO_2 uptake and selectivity compared to larger pores (with a size greater than 1 nm) [128, 129]. Zeolites' microporous structure, adjustable acidity, abundance, and excellent thermal stability have led to their widespread use as silicon-based CO_2 adsorbents [130].

Zeolite was easily poisoned with carbon dioxide in the presence of moisture, while the porosities of zeolite are higher than those of carbon material [131]. Gunawan et al. [36] utilized a carbon source to induce adjustments in zeolite Y's structure to enhance its capacity for carbon dioxide capture. The procedure has two stages. Initially, the synthesis of zeolite; then, the extraction of its template with a saturation method, as illustrated in Fig. 11.

Rebeiro et al. [100] employed a composite consisting of an activated carbon (AC) monolith and zeolite 13X for CO_2 capture from flue gas within an electric swing adsorption (ESA) process. The CO_2 adsorption capacity of the resulting composite exhibited a threefold increase compared to the single AC monolith when the zeolite mass ratio reached 18 %. Regufe et al. [132] developed novel hybrid materials, shaped via extrusion and suitable for ESA-based CO_2 capture. Their findings indicated that pellets composed of 50 % AC and 50 % 13X demonstrated favorable CO_2 adsorption capacity and intermediate performance during the electrification step, making them the most viable candidates for ESA applications. While pellets comprising 30 % AC and 70 % 13X exhibited high CO_2 adsorption capacity and CO_2/N_2 selectivity, they failed to heat adequately via the Joule effect within the experimental voltage and current range, rendering them unsuitable for ESA under those conditions. Gan et al. [104] synthesized a porous carbon-zeolite composite utilizing silicon-rich biomass. The composite demonstrated superior CO_2 adsorption and separation performance compared to pure porous biochar. This enhancement is attributed to the synergistic combination of the excellent properties of porous carbon and Na-X zeolite. Porous biochar, characterized by both micropores and mesopores, provides a robust foundation for CO_2 adsorption. The study highlighted the crucial role of ultra-micropores in the range of 0.7–0.9 nm, particularly due to their dynamic diameter of 0.33 nm, in CO_2 adsorption. Larger micropores ($>$1 nm) exhibited a less significant impact [133,134]. Khoramzadeh et al. [106] observed substantial improvements in adsorption capacity and rate upon the addition of approximately 5 wt% carbon black (CB) to zeolite 13X. Moreover, the composite exhibited higher adsorption heat and CO_2/N_2 selectivity compared to pure 13X.

3.2.3. Zeolite-silica based composite

Mesoporous silica, characterized by thin-walled pores and amorphous apertures, is prone to collapse under elevated temperatures or moisture conditions [45,135]. To address the limitations associated with zeolite microporous materials and mesoporous molecular sieves, research has increasingly focused on developing a novel composite that features a uniform and tunable mesoporous and microporous structure [136,137]. Zhou et al. [101] demonstrated that incorporating metal ions into micro/mesoporous 5A-MCM-41 composites can result in very effective adsorbents for CO_2 adsorption and separation. At 100 kPa and 298 K, the 5A-MCM-41 composites have an impressive CO_2 adsorption capacity of up to 4.08 mmol/g. The combination of zeolite 5A with MCM-41 results in a material that has greater size and more abundant pores, which improves its ability to adsorb CO_2. The better performance is because mesoporous silica channels form inside the zeolite structure. These channels make it easier for CO_2 to get into the material's active sites.

Santos et al. [138] created micro-mesoporous composite materials (ZSM-12/MCM-41) using the hydrothermal technique. The composite materials consist of a silica/alumina matrix that contains the ZSM-12 zeolite, either on the surface or within the pores. The composite material showed a greater capacity for adsorbing CO_2 compared to MCM-41 mesoporous materials. The higher degree of crystallinity of the zeolitic phase within its structure explains this. These findings confirm the material's potential applicability in the field of CO_2 capture. Finally, they suggest that the specific interaction between the micro- and mesoporous structures influences the process of CO_2 adsorption onto the composite materials. Ma et al. [108] demonstrated that the CO_2 adsorption capacities of micro/mesoporous composites were significantly enhanced compared to those of pure microporous or mesoporous materials. Among the composites studied, P-ZSM-MCM-41 exhibited the highest CO_2 adsorption capacity, measuring 1.51 mmol g^{-1}, which is approximately twice the capacity of the original ZSM-5. These materials leverage the high adsorption capacity and thermal stability of microporous materials, along with the rapid diffusion and mass transfer properties of mesoporous materials, resulting in improved CO_2 adsorption capacities relative to pure microporous or mesoporous counterparts. Ji et al. [107] developed micro-mesoporous MCM-41/13X composites using both two-step and one-step crystallization processes. The results revealed that MCM-41/13X-2 composites exhibited the highest CO_2 adsorption capacity of 1.2 mmol/g. This enhanced performance is attributed to their well-organized mesoporous structure and large specific surface area, nearly double that of the MCM-41 sample. Furthermore, these materials benefit from the significant adsorption capacity and thermal stability of the microporous component, coupled with the rapid diffusion and mass transfer capabilities of the mesoporous phase. This synergistic combination leads to superior CO_2 adsorption compared to the use of either microporous or mesoporous materials alone.

3.2.4. Zeolite-chitosan based composite

Various researchers are studying the amine functionalization of porous materials like zeolite for increased CO2 adsorption [55,139]. Chitosan consists of a glucosidic residue with one amino and two hydroxyl groups. The adsorbent molecule absorbs acidic CO_2 because of the chitosan structure's numerous amine groups (Fig. 12).

Amine functional groups on zeolite may increase its surface area and carbon dioxide selectivity. The acid-base interaction between carbon dioxide molecules, the acid gas, and amine, the basic centre, controls carbon dioxide adsorption on zeolite/chitosan. Zeolites and chitosan are affordable, non-toxic, recyclable solid catalysts. Kumar et al. [130] found that zeolite and chitosan composite material absorbed CO_2 better than either alone. Due to their high surface area and pore volume, chitosan-based zeolite bio-composites absorbed CO_2 and H_2 better than CS or standard zeolites. Chitosan-based zeolite bio-composites can store CO_2 and H_2 in numerous sectors, according to the findings. Kumar et al. [141] thoroughly investigated the synthesis and physicochemical characteristics of chitosan-based zeolite-Y and ZSM-5 porous bio-composites. The process involved solvent exchange and subsequent calcination, as depicted in Fig. 13. The chitosan-based zeolite bio-composites exhibit improved gas storage capabilities for tiny molecules

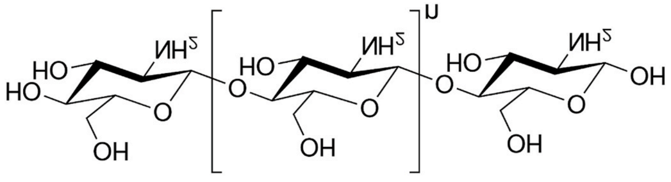


Fig. 12. Structures of chitosan [140].

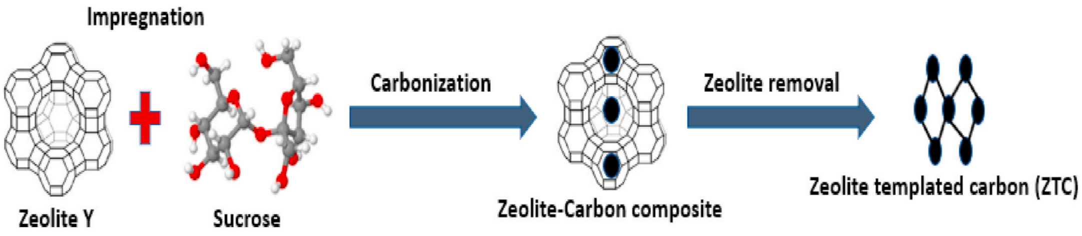


Fig. 11. Zeolite modification with carbon source [45].

such as CO_2 and hydrogen. Hence, chitosan-based zeolite bio-composites are well-suited for energy storage and CCS applications.

Phase inversion and freeze-drying were used to embed Zeolite 13X powder in chitosan to make composite aerogel beads [142]. The beads' CO_2 adsorption was remarkable due to the well-dispersed zeolite powder, which maintained its specific surface area at high loadings (561 m^2 g^{-1} at 90 wt %). In addition to mechanical coherence, chitosan may have actively captured CO_2 at low quantities. When the polymer is tightly confined in zeolite microparticles, amino groups become more accessible. The optimized microstructure of the beads and the additives worked synergistically to trap CO_2. The sample containing 90 % zeolite has a CO_2 capture capability of 4.23 mmol/g.

Phuoc et al. [99] synthesized zeolite X-chitosan composite utilizing phase inversion, solvent exchange, and air drying. This straightforward approach prepares the zeolite-chitosan composite without complicated, time-consuming, or energy-intensive steps. Results showed that beads with zeolite X or Cu^{+2}-exchanged zeolite X can capture significant CO_2. Despite multiple adsorption and desorption cycles, the composite remains reusable. The zeolite-chitosan composite is ideal for sustainable carbon capture due to its unique properties. Regenerating the chitosan-zeolite bead at 98 % was also considered. SEM examination showed zeolite X crystals with particle sizes of 1–3 μm (Fig. 14). The ZX-CS composite pictures (Fig. 14 a, b, c, d) show that the zeolite X crystals have developed intricate interactions with the chitosan framework. The Fourier transform infrared (FTIR) study of Zeolite X-chitosan before and after CO2 adsorption (Fig. 15) shows significant peak pattern changes, indicating that adsorption affects molecular structure.

3.2.5. *Zeolite-metal organic framework based composite*

Porous materials like zeolites and metal-organic frameworks (MOFs) have garnered significant attention from researchers due to their exceptional properties, including large surface area, tunable pore size, and diverse functional group [143]. Within the MOF structure, metal centers, which may consist of metal ions or clusters, coordinate with organic components through covalent bonds [144]. Additionally, numerous intermolecular interactions—such as hydrogen bonds, van der Waals forces, chelation, dipole-dipole interactions, and π-π interactions—are critical in facilitating the formation of MOF frameworks [145–147]. Although the specific covalent bonds present in this framework demonstrate thermodynamic stability, they lack kinetic stability [147,148]. As a result, incoming ligands can readily displace the organic linkers, significantly enhancing structural connectivity, flexibility, and the variety of MOF types [148]. Zeolites have coordinated unsaturated aluminum metal sites, which give them strong Lewis-acid and Brønsted sites [149,150]. Zeolite and MOF share similar characteristics, including high surface areas and uniformly distributed open pores [143,151]. However, they vary in terms of their thermal stability, mechanical stability, and structural flexibility [152]. Researchers have explored the combination of zeolites and MOFs to overcome these limitations and harness the synergistic benefits of both materials. Coating zeolites with MOF layers makes enhancing surface area possible and generate more adsorption sites for CO_2. This hybrid approach leads to materials with enhanced adsorption capacity, selectivity, and stability, as illustrated in Fig. 16.

Al-Naddaf et al. [154] synthesized a composite material (Zeo-A@-MOF-74-1) by integrating zeolite-5A with MOF-74. This composite material exhibits a high capacity for capturing CO_2. It is clear that Zeo-A@MOF-74-1 exhibits more adsorption than MOF-74 when subjected to low-pressure conditions (below 2 bar). With increasing pressure, the Zeo-A@MOF-74-1 uptakes reached 13.8 mmol/g at 20 bar, exhibiting a 30 % improvement compared to MOF-74. The observed results can be attributed to the recently developed mesopores that exist at the interface between MOF-74 and zeolite 5A [155].

Lestari et al. [102] found that incorporating 20 % by weight of natural zeolite into the metal-organic framework (MOF) MIL-100(Fe) significantly enhanced its CO_2 adsorption capacity by 300 %. This resulted in a maximum capacity of 7.01 mmol/g. The authors attribute this improvement to the increased number of pores and the presence of hydroxyl (OH) and ammonium (NH_4^+) groups in the activated zeolite. These functional groups interact with the unsaturated iron metal sites within MIL-100(Fe), creating additional CO_2 binding sites. Zeolite modifications, such as ion exchange and surface functionalization, significantly enhance CO_2 adsorption performance by improving selectivity, stability, and regeneration efficiency. The ion exchange process alters the electrostatic potential of the zeolite framework by replacing native cations with alternative metal ions, influencing CO_2 adsorption through polarization effects. Studies have shown that Li^+-exchanged zeolites (Li-X) exhibit up to 6.2 mmol/g CO_2 uptake at 1 bar, compared to 4.5–5.5 mmol/g for unmodified NaX zeolites [8]. This improvement is attributed to the stronger binding affinity of Li^+ ions for CO_2 molecules, enhancing physisorption without significantly increasing regeneration energy requirements. Similarly, Ca^{2+}-exchanged zeolites (Ca-X) demonstrate higher CO_2/N_2 selectivity ratios (35–45) compared to Na-X (20–30), making them more effective for flue gas applications where nitrogen competition is a concern [156]. The presence of divalent cations improves electrostatic interactions with CO_2, thereby increasing adsorption efficiency while maintaining rapid desorption kinetics. Amino-functionalization is another effective strategy for increasing CO_2 adsorption capacity, particularly in humid environments. By grafting primary or secondary amine groups onto the zeolite surface, CO_2 uptake can be enhanced through chemisorption interactions. Functionalized ZSM-5 zeolites with amine groups have demonstrated a 50–70 % increase in CO_2 adsorption capacity under wet conditions, overcoming the common limitation of zeolites in humid flue gas applications [157]. Moreover, amine-modified zeolites exhibit stable performance over multiple adsorption-desorption cycles, with >95 % retention of initial

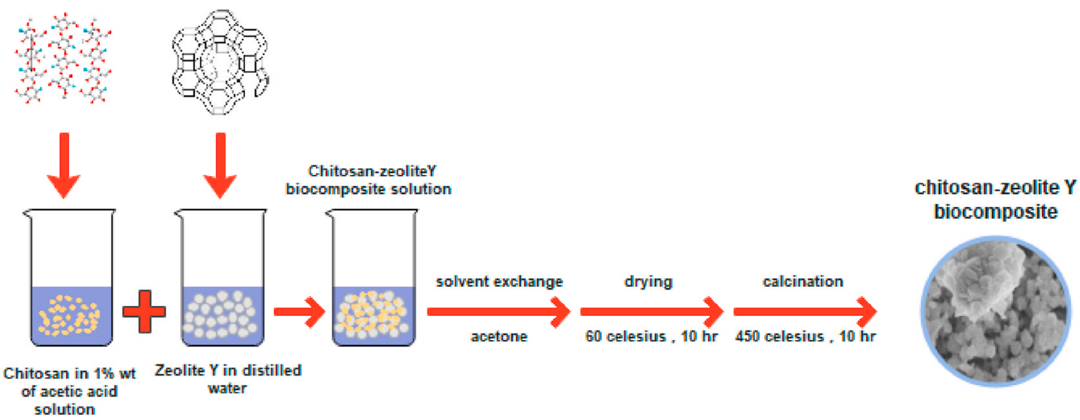


Fig. 13. Experimental step for the preparation of chitosan-zeolite Y bio-composite [141].

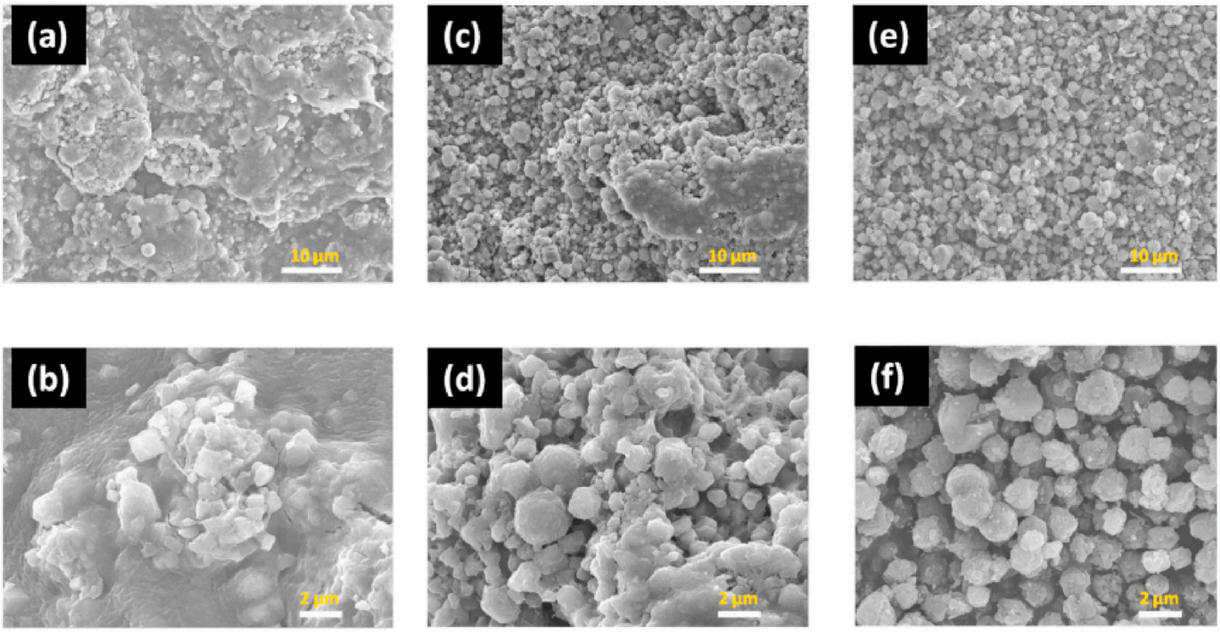


Fig. 14. SEM micrographs of (a, b) Z2C1, (c,d) Z9C1 and (e, f) ZX sample [99].

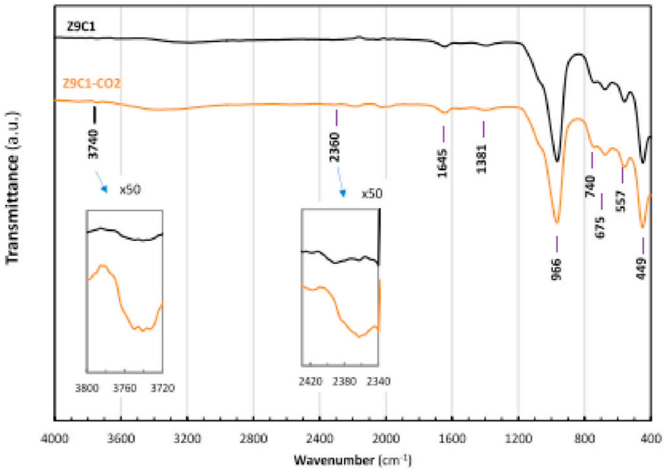


Fig. 15. Comparison of FTIR of the Zeolite X-chitosan (Z9C1) before and after CO_2 adsorption [99].

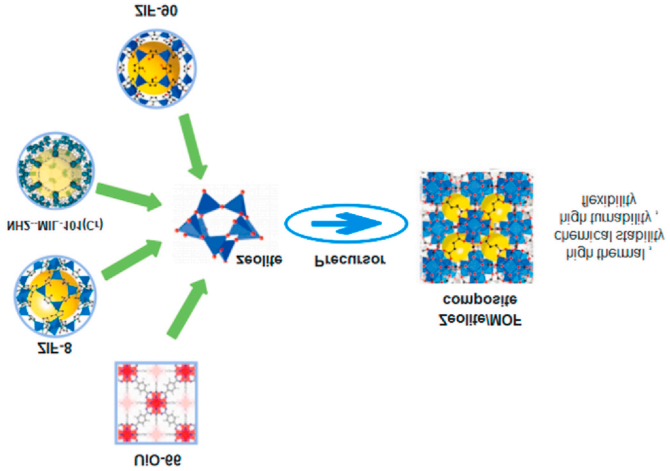


Fig. 16. Zeolite/MOF composite [153].

CO_2 uptake after 50 cycles, highlighting their durability for industrial applications [158]. Table 9 summarizes the improvements in CO_2 adsorption capacity and selectivity for various modified zeolites, reinforcing the advantages of ion exchange and functionalization strategies.

These findings highlight that modifications such as ion exchange and amine functionalization can significantly improve CO_2 uptake, selectivity, and long-term stability, making them viable solutions for enhancing zeolite-based CCS technologies.

3.3. Pore size and structure optimization

The size of the pores in zeolites determines the accessibility of CO_2 molecules to the internal surface area. By carefully controlling the synthesis conditions or through post-synthesis modifications, it is possible to create zeolites with pore sizes that are ideally suited for CO_2 capture. For example, smaller pores may enhance the interaction with CO_2 molecules through confinement effects, while larger pores might be more suitable for capturing larger volumes of CO_2. The crystalline framework structure of zeolites can also be tailored to optimize CO_2 adsorption. Zeolites with high framework density and specific topologies, such as CHA (chabazite), MFI (ZSM-5), and LTA (Linde Type A), are known for their high CO_2 capture capacities. Modifying the framework structure can enhance the diffusion of CO_2 molecules within the zeolite, reducing mass transfer limitations and improving overall adsorption efficiency.

Amari et al. [159,160] and Lenarda et al. [159,160] explored how acid treatment modifies surface properties by generating new active sites on zeolite surfaces. Natural zeolites, including clinoptilolite, chabazite, and mordenite, exhibit increased CO_2 adsorption capacity following acid treatment, which introduces more acid sites on their surfaces. In CO_2 adsorption processes, pore volume plays a more critical role than surface area. Consequently, the application of acid modification methodologies to zeolites, resulting in increased pore volume, leads to a corresponding enhancement in CO_2 adsorption potential.

The effectiveness of CO_2 capture is influenced by different factors, such as the concentration and type of acid employed, reaction time, and temperature. Generally, longer reaction times and higher acid concentrations yield more acid sites and greater CO_2 adsorption capacity. However, excessive acid treatment can damage the zeolite structure,

Table 9
Effect of different modification methods on zeolite performance for CO_2 adsorption.

Modification Type	Zeolite Type	CO_2 Adsorption Capacity (mmol/g)	CO_2/N_2 Selectivity	Regeneration Efficiency (%)	Stability (Cycles Retaining >90 % Capacity)	Reference
None (Baseline)	NaX	4.5–5.5	20–30	85–90	25–30	Li et al. [1]
Ion Exchange (Li^+)	Li-X	5.8–6.2	40–50	90–95	40–50	Wang et al. [2]
Ion Exchange (Ca^{2+})	Ca-X	5.2–5.9	35–45	88–93	35–45	Zhang et al., [3]
Amine Functionalization	ZSM-5	3.5–4.8 (dry), 5.5–6.2 (wet)	25–40	95+	50+	Chen et al. [4]
Composite Formation	ZSM-5/AC	4.9–5.7	30–42	92–96	45–50	Kumar et al. [5]

diminishing its CO_2 capture performance [45]. Bhavani et al. [74] demonstrated that the synthetic sodium form of zeolite-MFI, with varying Si/Al ratios (5, 30, 100, 200), modified with HCl, enhances porosity and CO_2 adsorption capacities. This HCl modification exhibited promising adsorption activity without compromising crystal structure. All modified zeolite-MFI samples were characterized using X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) methods to assess crystallinity, pore volume, and BET surface area in relation to the physical sorption of CO_2. Following HCl treatment, zeolite pore volume and BET surface area improved significantly, with adsorption capacity influenced by interactions with the electric field. The modified ZSM zeolite demonstrated the highest adsorption capacity (4.49 mmol/g) at 279 K and 0.8 bar with a Si/Al ratio of 5. However, as the Si/Al ratio increased to 200, a decrease in adsorption capacities to 2.86 mmol/g and 1.96 mmol/g was observed, confirming that gradual dealumination reduces the electrostatic field within the zeolite voids [161].

Kongnoo et al. [162] studied the CO2 adsorption capacity of zeolite 13X prepared from fly ash, both in its original and acid-treated form (Fig. 17). Acid treatment led to increased CO_2 adsorption by enhancing the porosity and creating additional mesopores. Gentle acid treatment with H_3PO_4 was found to be more effective in improving the microporous structure without compromising crystallinity, compared to strong acids like HCl and HNO_3 (see Fig. 18).

Ertan et al. [163] modified natural and synthetic zeolites with acid and observed that acid treatment significantly enhanced CO_2 adsorption while having a relatively minor impact on N_2 adsorption. Table 10 summarizes the CO_2 adsorption performance of acid-treated zeolites reported in the literature.

3.4. Surface functionalization

Surface functionalization involves incorporating functional groups onto the zeolite surface to enhance its interactions with CO_2 molecules, effectively boosting CO_2 adsorption capacity, particularly under low-pressure conditions. Among the various approaches, introducing amine groups on the zeolite surface is one of the most effective methods for achieving this functionalization. The modification of zeolites with amines has garnered significant scientific interest, establishing them as promising candidates for CO_2 adsorption at low pressures due to the synergistic interactions between amine-CO_2 and CO_2-metal sites on the zeolites. The incorporation of amine groups can lead to several beneficial effects, including activation of aluminum sites, increased surface area, reduced pore size, enhanced porosity volume, and improved stability and regeneration properties [36]. Moreover, the strong affinity of amines for CO_2 allows for chemical binding through carbamate formation, further boosting adsorption capacity, especially in low-CO_2 concentration environments.

The proposed reaction mechanism for amine-modified adsorbents includes the formation of covalent bonds between acidic CO_2 molecules and active surface sites, producing carbamate species. This reaction can be represented by the following equations [36,49,167]:

$$CO_2 + 2\ RNH_2 \Longleftrightarrow RNH_3 + RNHCOO^- \quad (1)$$

$$RNHCOO^- + H_2O \Longleftrightarrow RNH_3 + HCO_3 \quad (2)$$

Primary, secondary, and tertiary amines can all be used, with the choice depending on the desired adsorption properties. In addition to amines, other functional groups, such as hydroxyl, thiol, or carboxyl groups can be grafted onto the zeolite surface. These groups can provide additional sites for CO_2 interaction, enhancing the overall adsorption capacity. The choice of functional group depends on the specific requirements of the CO_2 capture process, such as the operating temperature and pressure. Amine-modified adsorbents are classified into three main types: amine-impregnated, amine-grafted, and a combined approach incorporating both grafting and impregnation techniques [167,168]. In the amine grafting method, amino silane reacts with the surface hydroxyl groups of zeolites through a base-catalyzed condensation reaction, forming stable Si–O–Si bonds, which covalently attach

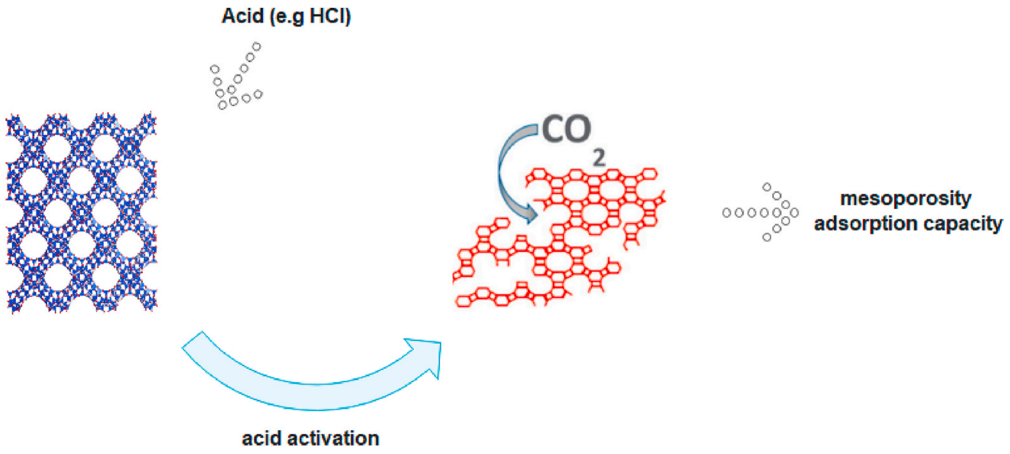


Fig. 17. Schematic of surface modification of zeolite Using acid [162].

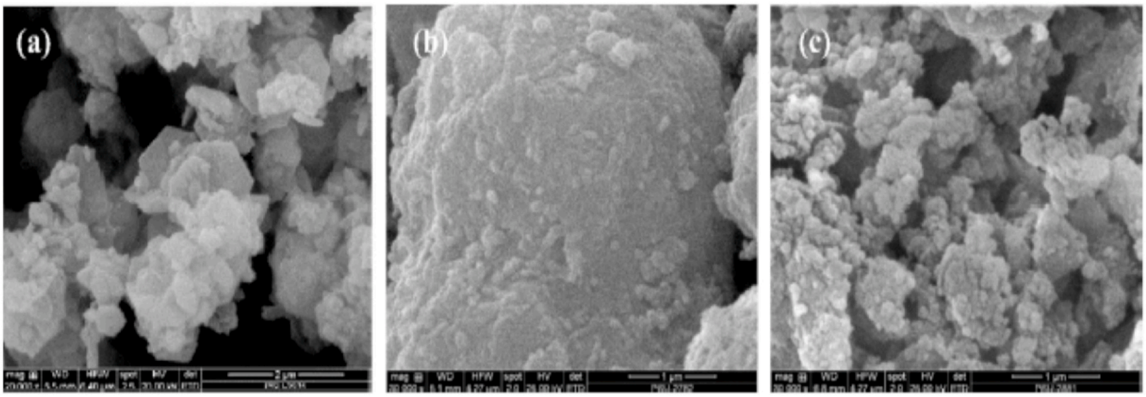


Fig. 18. (a) SEM micrographs zeolite 13X and (b) acid-activated POMFA-zeolite 13X at 6 M HCl for 4 h [164].

Table 10
Performance of acid-modified zeolite for CO_2 adsorption.

Zeolite/Acid	Press. (atm)	Temp. (°C)	CO_2 uptake (mmol/g)	References
Zeolite 13X/HCl	4	32	6.42	[162]
Natural Montmorillonite/HCl	5	0	1.53	[165]
Clinoptilolite/HCl	4	25	32.56	[166]
Na-ZSM-5/HCl	0.8	6	4.49	[74]

the amine to the porous solid support. In contrast, the amine impregnation technique relies on the diffusion of amine molecules into the porous cavities of a solid matrix due to chemical affinity and concentration gradients; no chemical bonding occurs between the amine groups and the zeolite support in this process. Table 11 presents a comparative overview of different functionalization approaches, while Fig. 19 illustrates a flow diagram of the amine modification process.

Banaei et al. [175] modified a novel type of synthesized zeolite, NaY, using an impregnation method to examine how surface modifications affect CO_2 adsorption. This was achieved by employing TEPA, DEA, and 2-MAE amines. The CO_2 adsorption capacity was evaluated using the volumetric method at 25 °C and 75 °C, with results showing increased adsorption capacity at the higher temperature. Prior to modification, the CO_2 adsorption capacity of NaY zeolite was 82.8 mg/g and 73.51 mg/g at 25 °C and 75 °C, respectively. After modification, CO_2 adsorption capacities for TEPA-NaY, DEA-NaY, and 2-MAE-NaY adsorbents were recorded as 60.63, 65.21, and 72.93 mg/g at 25 °C, and 92.9, 78, and 85.42 mg/g at 75 °C, respectively. These findings demonstrate that the surface characteristics of NaY zeolite are altered by amine modification, suggesting that amine-modified NaY has substantial potential for CO_2 adsorption at elevated temperatures. Panda et al. [176] explored the effect of various aliphatic amines on the CO_2 adsorption capacity of binder-containing zeolite 4A. The introduction of amine groups into the zeolite pores led to increased CO_2 uptake, attributed to enhanced interactions between the amine functional groups and CO_2 molecules. The adsorption capacity was found to be influenced by factors such as the amine's chain length, branching, and electronic properties. Cheng et al. [177] investigated the effects of different amines—monoethanolamine (MEA), triethanolamine (TEA), diethanolamine (DEA), and aminoethylethanolamine (AEEA)—on CO_2 adsorption capacity in zeolite H-ZSM-5. As illustrated in Fig. 20, MEA and AEEA exhibited the highest CO_2 adsorption efficiencies, attributed to their larger surface areas and pore volumes. AEEA-modified H-ZSM-5 demonstrated the highest adsorption capacity, reaching 4.44 mmol/g at 321 K under a pressure of 1 atm. The desorption process required minimal activation energy due to the presence of free H^+ ions in H-ZSM-5. Additionally, regeneration cycle tests showed that carbamate nitrogen atoms bond with aluminum (Al) atoms, enhancing stability and making CO_2 capture cost-effective. The CO_2 adsorption by the AEEA adsorbent was determined to be exothermic, with an enthalpy change (ΔH) of −41.68 kJ/mol, indicating a process involving both chemical and physical adsorption. Generally, physical adsorption presents ΔH values below 20 kJ/mol, while chemical adsorption typically has ΔH values in the range of 80–200 kJ/mol. Fashi et al. [167] modified zeolite 13X using piperazine. Their findings, illustrated in Fig. 21, show that increasing piperazine concentration

Table 11
Comparison of different functionalization techniques for zeolite [55,170–174].

Comparison	Grafting	Impregnation	Double functionalization	Polymerization
Description	Covalently attaching functional groups to the zeolite's surface.	Dissolving the zeolite in a functional agent-containing solution, then calcining or drying it.	Combining two different agents or functionalization strategies.	Using a polymer that interacts with CO_2 to coat the zeolite surface.
Advantages	- Stability: Produces robust chemical connections that result in stable functionalized surfaces. -Specificity: Provides exact control over the kinds and numbers of functional groups. -Regeneration: Functionalized zeolites frequently show excellent regeneration abilities.	-Simplicity: Reasonably easy to use and economical. -Versatility: Able to use a wide range of functional agents. -Scalability: More easily extended for industrial use.	-Enhanced Performance: CO_2 capture efficiency can be increased through synergistic effects. -Tailored attributes: Enables surface features to be altered to specifically target certain capture processes.	-High Capacity: Polymers have a high CO_2 uptake capacity and high surface area. -Versatility: Different polymers can be engineered to have particular capture properties. -Reusability: Polymers are frequently regenerable using easy procedures.
Challenges	-Complexity: Usually requires a number of steps in the synthesis process. -Cost: This process can be costly because pure reagents and regulated conditions are required.	-Leaching: Over time, functional agents can spread out and become less effective. -Uniformity: It can be challenging to distribute functional agents uniformly.	-Complexity: Synthesis and optimization procedures are more intricate. -Cost and Time: Because there are numerous processes involved in the preparation process, there are higher expenses and longer preparation times.	-Durability: Under harsh conditions or over time, polymers can degrade. Compatibility: It can be difficult to ensure that the polymer and the zeolite are compatible.

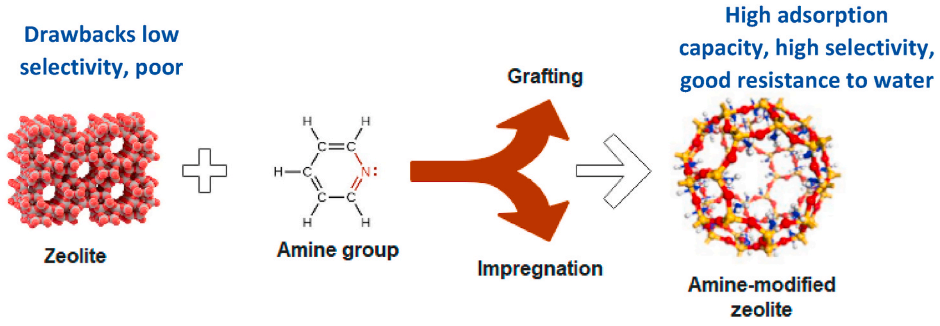


Fig. 19. Amine functionalization of zeolite [169].

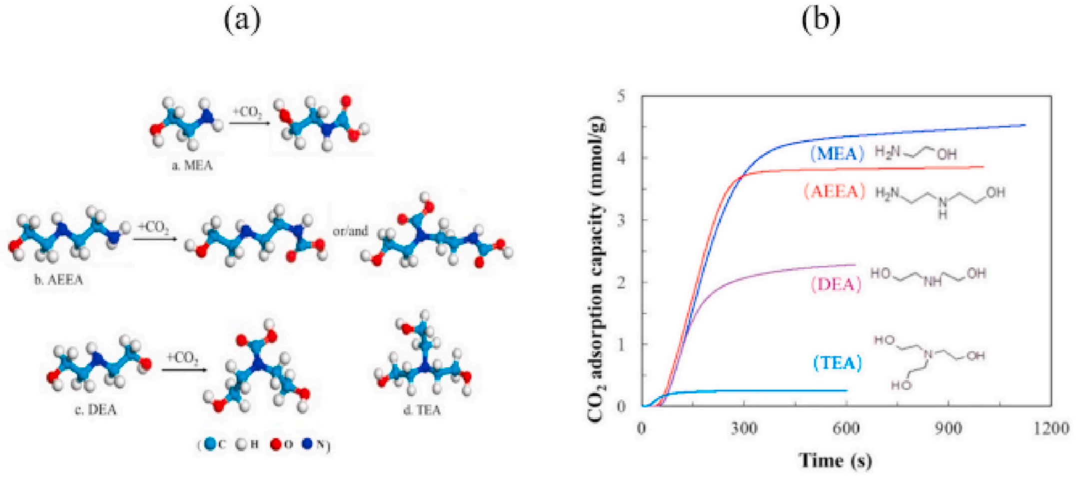


Fig. 20. **(a)** Structures of various amines and their respective reactivity with CO_2, **(b)** CO_2 adsorption capabilities of the distinct amine-based HZSM5-25-2 [177].

significantly enhanced CO_2 adsorption capacity without altering the morphology of the zeolite.

Heshmatollah et al. [178] reported the chemical modification of NaY zeolite through the grafting of amine groups, including monoethanolamine (MEA), tetraethylenepentamine (TEPA), and morpholine (MOR) (Fig. 22). This modification resulted in a significant enhancement of the CO_2 adsorption capacity. Notably, NaY-TEPA exhibited the highest adsorption capacity of 4.756 mmol/g at 70 °C and 5 bar. CO_2-temperature programmed desorption (TPD) analysis of NaY and amine-modified NaY zeolites indicated that the primary adsorption mechanism involves the interaction of CO_2 with amine groups on the zeolite surface at ambient pressure and 323 K.

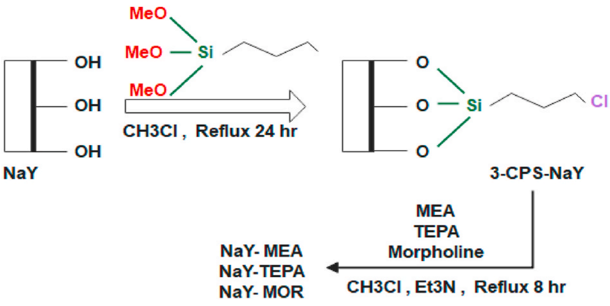


Fig. 22. Preparation of modified NaY zeolite [178].

However, excessive acid treatment could compromise the structural integrity of the zeolite, reducing its CO_2 adsorption capacity. Although composites exhibit rapid CO_2 adsorption rates, they are relatively expensive due to complex manufacturing processes and the high cost of surfactants. Table 12 provides a summary of CO_2 adsorption performance for amine-modified zeolites as reported in the literature.

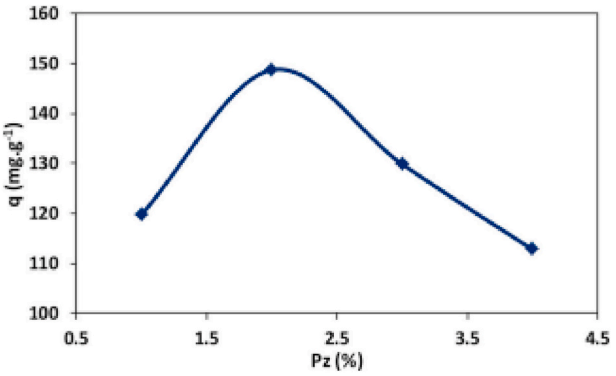


Fig. 21. Effects of Pz concentration on equilibrium CO_2 adsorption capacity at temperature of 25 °C, pressure of 5 bar, adsorbent amount of 1 g, particle size of 200 mm [167].

4. Performance metrics for CO_2 capture

The effectiveness of zeolites in CO_2 capture is evaluated based on several key performance metrics. These metrics include adsorption capacity, selectivity, regeneration and stability, and energy efficiency. Understanding and optimizing these factors is essential for developing zeolites that can meet the demands of large-scale post-combustion CO_2 capture.

Table 12
Adsorption capacity of different amine-modified zeolite.

Zeolite	Amine type	P (bar)	T (°C)	CO_2 uptake (mmol/g)	Ref.
LTA	APTMS	1	60	2.3	[69]
NaY	TEPA	1	75	2.11	[175]
13X	Piperazine	5	25	4.54	[167]
Zeolite Y	TEPA	1	30	2.6	[179]
Beta-25	APTES	1	35	4.7	[180]
Beta-25	TEPA	1	35	2.56	[180]
HZSM-5	MEA	1	20	4.27	[177]
HZSM-5	AEEA	1	48	4.44	[177]
β- zeolite	TEPA	1	30	2.9	[65]
Zeolite 4A	IBA	1	25	2.56	[181]
13X	PEI	1	75	1.2	[182]
Hollow zeolite (HZ)	MEA (3 wt %)	1	30	0.295	[183]
Natural zeolite (NZ)	Allylamine	1	25	0.32	[184]
NaY	PEI (15 wt %)	1	25	0.045	[185]
Zeolite Y	MEOH	1	30	2.26	[186]
Zeolite Y	DEOH	1	30	1.84	[186]
Zeolite Y	TEOH	1	30	1.62	[186]
Clinoptilolite	TEA	5	25	5	[81]
Zeolite 4A	DEA	5	25	9.4	[55]
Zeolite 13X	MEA	0.15	30	1	[187]
Zeolite Y60	TEPA	0.15	60	4.27	[52]

4.1. *Adsorption capacity*

Adsorption capacity is a fundamental metric that measures the amount of CO_2 a zeolite can adsorb per unit mass or volume under specific conditions. The adsorption capacity is influenced by the zeolite's surface area, pore volume, chemical composition, and the presence of active sites. Tailored zeolites often show enhanced CO_2 adsorption capacities compared to their unmodified counterparts. For example, zeolites modified through ion exchange or impregnation with metal oxides tend to exhibit higher capacities due to increased interaction sites for CO_2 molecules [188]. Zeolites such as Li-exchanged LTA or CaO-impregnated ZSM-5 have significantly improved CO_2 adsorption, particularly at high pressures and low temperatures. Moreover, hierarchical zeolites with a combination of micro- and mesopores can enhance mass transfer and provide additional adsorption sites, further increasing the overall capacity.

4.2. *Selectivity*

Selectivity is a critical performance metric that measures the ability of a zeolite to preferentially adsorb CO_2 over other gases, particularly N_2, the major component of flue gas. High CO_2/N_2 selectivity is essential for efficient post-combustion CO_2 capture. Tailored zeolites can achieve high CO_2/N_2 selectivity through several strategies, such as ion exchange and surface functionalization. For instance, zeolites modified with cations like Li^+ or Mg^{2+} show improved selectivity due to stronger electrostatic interactions with CO_2 compared to N_2. Additionally, surface functionalization with amine groups significantly enhances CO_2 selectivity by forming stable carbamate complexes that are not formed with N_2. Zeolites with pore sizes that exclude larger N_2 molecules while allowing CO_2 to enter can achieve high selectivity. Moreover, the introduction of polar functional groups that interact specifically with the quadrupole moment of CO_2 further enhances selectivity. Zeolites X and Y display the highest adsorption capacities among zeolites (Table 13). Zeolite X [FAU] is a highly regarded zeolite for its ability to adsorb CO_2. It is commonly used as a benchmark when comparing other adsorbents, such as carbons or MOFs, as well as other zeolites.

Zeolites are widely studied for post-combustion CO_2 capture due to their high adsorption capacity, selectivity, and thermal stability. The CO_2 adsorption capacity of zeolites varies significantly depending on the Si/Al ratio, cation type, and pore structure. Low-silica zeolites, such as NaX (Si/Al = 1.0–1.5), typically exhibit CO_2 adsorption capacities in the range of 4.5–5.5 mmol/g at 1 bar and 25 °C, while high-silica zeolites such as ZSM-5 (Si/Al > 10) show lower uptake (~2.0–3.5 mmol/g) but improved resistance to humidity. Cation-exchanged zeolites further enhance adsorption efficiency. Studies have reported that Li^+ and Ca^{2+}-exchanged zeolites achieve up to 25–30 % higher CO_2 uptake than their Na^+ counterparts due to increased electrostatic interactions between CO_2 molecules and framework cations. In particular, Li-X zeolites exhibit adsorption capacities exceeding 5.8 mmol/g at 1 bar, making them competitive with amine-based adsorbents. Apart from adsorption capacity, selectivity is a crucial performance metric in real flue gas applications. The CO_2/N_2 selectivity of zeolites is often used to determine their efficiency in separating CO_2 from power plant emissions. Conventional NaX zeolites exhibit selectivity ratios of 20–30, while optimized ion-exchanged zeolites (e.g., Li-X, Mg-X) can achieve selectivity values exceeding 40–50, significantly outperforming many commercial solid sorbents. The working capacity (i.e., the amount of CO_2 captured and released per cycle) is another important metric, with modified zeolites demonstrating superior regeneration efficiency over multiple adsorption/desorption cycles. Table 14 presents a summary of adsorption capacities and selectivity ratios for various zeolite structures,

Table 14
Comparative CO_2 adsorption performance of various zeolites structures

Zeolite Type	Si/Al Ratio	Cation	CO_2 Adsorption Capacity (mmol/g)	CO_2/N_2 Selectivity
NaX	1.0–1.5	Na^+	4.5–5.5	20–30
Li-X	1.0–1.5	Li^+	5.8–6.2	40–50
Ca-X	1.0–1.5	Ca^{2+}	5.2–5.9	35–45
ZSM-5	10–100	H^+	2.0–3.5	15–25

Table 13
Silica/Alumina ratio, adsorption capacity and pure CO_2 selectivity for different Types of zeolites at 1 bar and 25 °C.

Zeolite type	Si/Al	nCO_2 (mmol g^{-1})	nN_2 (mmol g^{-1})	nCH_4 (mmol g^{-1})	Pure selectivity CO_2/N_2	Pure selectivity CO_2/CH_4	Ref.
Na-CHA-4	4	4.7	0.7	1.3	7	4	[189]
Na-CHA-25	2.5	3.6	0.8	0.3	5	12	[189]
Na-X	1	6.3		0.8		8	[86]
Li-X	1	7		0.5		13	[86]
Ca-X	≤ 1.5	5.2	0.3		17		[87]
Cu-SSZ-13	6	3.8	0.3	13			[190]
Na–Y	2.2	4.7					[191]
Na-RHO	3.9	4.9		0.1		49	[192]
K-RHO	3.9	4.5		0.1		45	[192]
Cs-RHO	3.9	1.2		0.1		17	[192]
Na-FER (20 °C)	8.7	2.8					[193]
Na-FER (60 °C)	8.7	2.1					[193]
SAPO-56 (20 °C)	0.3	3.9		0.7		6	[194]
Zeolite T	4 or 5	3.1	0.2	0.5	16	6.2	[195]

highlighting their comparative performance with other CCS materials. A comprehensive **Life Cycle Analysis (LCA)** of CO_2 capture technologies highlights the trade-offs between energy consumption and emissions reduction. **Membrane-based and cryogenic CO_2 capture methods** require **higher energy inputs** (~2–3 GJ per ton of CO_2 captured), whereas **zeolite-based adsorption systems operate at 1.0–1.5 GJ per ton**, making them one of the most energy-efficient solid sorbent-based methods [196]. Moreover, **vacuum-temperature swing adsorption (VTSA)** has further improved the energy efficiency of zeolite-based systems, achieving up to **30 % lower energy consumption** compared to conventional thermal swing adsorption (Kumar et al., [197]). For CO_2 capture technologies to reach large-scale deployment, further improvements in **cost-efficiency, energy consumption, and policy incentives** are required. Governments and industry stakeholders are investing in **carbon pricing mechanisms, tax credits, and subsidies** to incentivize CO_2 capture adoption. The integration of **zeolite-based capture technologies with renewable energy sources** (e.g., solar-assisted regeneration systems) could further **reduce the carbon intensity of the process** and make these technologies more economically attractive in the future.

X- and Y-type zeolites, renowned for their extensive pore volumes and robust crystal structures, have found significant commercial applications. While sharing a comparable cage structure, X-type zeolites exhibit a higher aluminum content and, consequently, a greater number of cations than Y-type zeolites. These cations, acting as acid sites, and the neighboring framework oxygen atoms, functioning as basic sites, contribute to the zeolites' acid-base properties. The elevated aluminum content within the framework is primarily responsible for this enhanced basicity [76,198]. Modifying the aluminum content in the framework or replacing the cations makes it possible to adjust the strength of these zeolite acid-base pairs [77,198].

Despite their exceptional adsorption capacities, X and Y zeolites are ill-suited for efficient CO_2 separation from N_2 or CH_4 due to their large pore size. This limitation results in lower selectivity compared to small-pore zeolites, such as zeolite A, merlinoite, and chabazite, which exhibit superior CO_2 selectivity over N_2 or CH_4. Zeolite A, a widely recognized small-pore zeolite, is commonly employed for CO_2 adsorption. Ion exchange can be utilized to adjust the pore size of Zeolite NaA, which is approximately 4 Å, rendering it highly desirable. A fully potassium-exchanged Zeolite A possesses a pore size of around 3 Å, insufficient for CO_2 adsorption [198,199]. However, partial ion exchange, replacing sodium ions with potassium ions, allows for pore size adjustment that enables CO_2 entry while restricting larger molecules like methane and nitrogen due to kinetic limitations. This strategy has led to significant enhancements in the pure selectivity for CO_2 over N_2 and CH_4, while maintaining a relatively high CO_2 adsorption capacity [194,198,199].

In contrast, RHO-type zeolites, with their unique 3D structures comprising cages and small pore openings, are particularly promising for CO_2 capture. Confalonieri et al. have demonstrated that CO_2 uptake is strongly correlated with the sodium content in nanosized RHO crystals. Adsorption tests have shown that 1 bar CO_2 is sufficient to saturate RHO samples, and no further increase in pressure up to 5 bar is observed at room temperature [194,198,200].

While Zeolite RHO (with a pore size of 3.6 Å) does not exhibit the highest adsorption capacity or selectivity, K-RHO offers a slightly lower adsorption capacity and selectivity compared to Na-RHO. However, its adsorption isotherm shows a less rapid increase at low CO_2 pressure, resulting in an improved working capacity in the low-pressure domain (0–1 bar) [192]. In comparison, Cs-RHO showed substantially lower adsorption capacity at low pressure (up to 1 bar), but while Na-RHO and K-RHO reached adsorption plateaus around 1−2 bar, Cs-RHO reached its plateau around 6 bar, showing potential for pressure swing adsorption (PSA) due to its high working capacity (approximately 3 mmol/g between 1 and 6 bar) [192].

ZSM-5, renowned for its exceptional chemical and thermal stability, high surface area, and frequent application in gas separation and catalysis [201–203], utilizes extra-framework cations to neutralize the negative charge within the silica-alumina framework. These cations also influence the electrostatic field, internal pore structure, and crystallinity of the zeolite [78,204,205]. Moreover, such cations can enhance the application performance and significantly impact the physicochemical properties, though the effects of various extra-framework cations on CO_2 adsorption performance remain underexplored [206]. Additionally, dehumidification remains a major concern in CO_2 adsorption and separation processes due to its high energy demands. However, low-silica zeolites are critical in this context as their CO_2 adsorption capability decreases substantially when exposed to water vapor [32].

A core-shell zeolite, comprising a hydrophilic ZSM-5 core and a hydrophobic silicalite-1 shell, was employed for the adsorptive separation of CO_2 in humid environments [207]. This hybrid material exhibited remarkable water resistance and sustained CO_2 adsorption capacity without requiring additional heat treatment for regeneration. In contrast, the original ZSM-5 material experienced a significant decline in CO_2 adsorption capacity in the presence of water vapor. ZSM-5, characterized by a moderate pore size and a dense microporous structure, facilitates efficient CO_2 physisorption through van der Waals forces or hydrogen bonding. The CO_2 uptake of ZSM-5 was measured at 25 °C and 1 bar CO_2 partial pressure, yielding a value of 1.35 mmol g-1. Upon increasing the CO_2 partial pressure to 10 bar, the adsorption capacity exceeded 2.34 mmol/g [208]. Masala et al. [209] synthesized a ZSM-5-800 adsorbent by subjecting ZSM-5 to a temperature of 800 °C. They found that this adsorbent had a CO_2 adsorption capacity of 2.2 mol kg^{-1} at a temperature of 25 °C and a pressure of 1.1 bar. Kalantarifard [210] successfully produced ZSM-5 with significant surface structures and large pores. They subsequently improved its properties by modifying it with ED, resulting in a remarkable CO_2 adsorption capacity of 6.13 mmol/g. The man-made zeolite had a maximum amine adsorption capacity of 450 mg g^{-1}. This is because it has large internal channels and pores that are spread out evenly. To facilitate the efficient reuse of the adsorbents, they employed microwave radiation to eliminate the adsorbed carbon dioxide. The samples containing 70 and 50 wt percent (wt%) of ED achieved a desorption efficiency of 100 % after undergoing microwave irradiation for 9 and 13 min, respectively. However, the sample with 10 % ED had a maximum desorption efficiency of 60 %. Liu et al. [211] made a ZSM-5 (MFI-type) material that is very porous by using organosilanes to stop growth. At a temperature of 273 K and under atmospheric pressure, the CO_2 capture capacity of HP-ZSM-5 was 2.6 mmol/g, significantly higher than that of ZSM-5.

4.3. Regeneration and stability

Regeneration efficiency and long-term stability are crucial metrics for assessing the practicality of using zeolites in cyclic CO_2 capture processes. The ability of a zeolite to maintain its adsorption capacity over multiple cycles without significant degradation is essential for sustainable operation. Tailored zeolites should exhibit high regeneration efficiency, meaning that the adsorbed CO_2 can be easily desorbed with minimal energy input, allowing the zeolite to be reused in subsequent cycles. Zeolites that rely primarily on physisorption for CO_2 capture generally have better regeneration properties, as the weak van der Waals forces can be overcome by mild heating or pressure reduction. The stability of zeolites under cyclic adsorption and desorption conditions is critical for their long-term use. Tailored zeolites should resist structural degradation, loss of active sites, or fouling over multiple cycles. Zeolites impregnated with metal oxides or those functionalized with organic groups must be designed to withstand thermal cycling and exposure to moisture, which can otherwise lead to performance deterioration.

One of the primary challenges in adsorption technology lies in ranking the performance of various adsorbents, as isotherm-based selectivity and working capacity often fall short in providing satisfactory metrics [212]. Adsorbent screening processes utilize simplified cycles, allowing for rapid pre-selection of suitable adsorbents for specific tasks, with solutions achievable within seconds to minutes [213–215]. Furthermore, efficient engineering approaches are essential for developing practical and cost-effective adsorption technologies. Optimizing both adsorbent performance and process design is critical for the successful commercial deployment of adsorption technologies [216]. Most adsorbents exhibit a strong preference for CO_2 over other key components like N_2 and O_2, owing to CO_2's high quadrupole moment and polarizability. As a result, adsorbents typically adsorb and regenerate CO2 as the primary component. The low concentration of CO_2 in various applications, such as confined spaces (0.7 %) [217], ambient air (0.04 %), and flue gas from natural gas-fired (3–5 %) and coal-fired (10–15 %) power plants, makes CO_2-selective adsorbents particularly attractive.

CO_2 capture through adsorption is typically classified into temperature swing adsorption (TSA) and pressure swing adsorption (PSA), depending on the primary regeneration mechanism, which involves either increasing the temperature or reducing the pressure [218]. Other factors essential to consider include heat and mass transfer, pressure drop, and energy consumption. At present, there is no straightforward method for designing regeneration cycles in adsorption processes [213].

The sorbent can be regenerated by adjusting either temperature or pressure, referred to as temperature swing adsorption (TSA) or pressure/vacuum swing adsorption (PSA/VSA), respectively. It is also possible to integrate both processes by varying temperature and pressure, leading to a hybrid regeneration mode (VTSA/PTSA). Table 15 outlines the advantages and disadvantages of the various swing adsorption methods.

4.3.1. *Temperature swing adsorption (TSA)*

In the TSA process, CO_2 adsorption occurs at relatively low temperatures (around 50–60 °C) to efficiently capture CO_2 [13]. Conversely, sorbent regeneration and subsequent CO_2 desorption are achieved by heating the system to approximately 150–200 °C [13]. One potential approach involves using steam as the purging gas, as it can be easily separated from the captured CO_2. However, utilizing steam also presents challenges, which constitute the primary disadvantage of TSA with direct heating [220]. Although condensation effectively separates water, an additional system for water removal is necessary before compressing CO_2 for transit and storage. Furthermore, it is crucial that the sorbent exhibits a high tolerance to water, considering both its reactivity and mechanical properties [221]. Many CO_2 sorbents, particularly physisorbents, experience a significant reduction in CO_2 adsorption capacity in the presence of water, necessitating an additional drying process [221]. Moreover, even sorbents that are highly reactive with water but do not experience a decrease in CO_2 adsorption capacity may suffer from mechanical degradation [222]. These additional operations increase process complexity, energy consumption, and overall cost. Alternatively, CO_2 can be used as a hot purging gas, eliminating the need for additional units associated with steam usage [222]. Nonetheless, it is essential to recognize that using CO_2 as a purging gas will diminish the driving force for desorption. Provided the sorbent can withstand the requisite temperatures, employing a higher regeneration temperature will escalate overall thermal energy consumption [222]. In this context, Ntiamoah et al. [222] demonstrated a TSA process using NaUSY zeolite as the sorbent, where recovered CO_2 was heated to 250 °C and used as a purging gas. This process achieved a CO_2 purity exceeding 91 %, a recovery rate of 83.6 %, and a thermal energy consumption of 4.5 MJ kg^{-1} of CO_2. With respect to the alternative approach of modifying the heating method, one potential solution involves using a heat exchanger within the reactor to indirectly heat the sorbent (indirect heating) [223]. This method does not require purging gas, thus eliminating dilution and the need for additional operational units. Thermal expansion can desorb CO_2 with 100 % purity, requiring minimal energy for evacuation [224]. This heating mode has been proposed for fixed-bed reactors due to its simplicity and the capability to recover CO_2 with very high purity, resulting from the absence of purging gas. Clausse et al. [225] proposed an indirect temperature swing adsorption (TSA) method, incorporating an internal heat exchanger and utilizing 13X and 5A adsorbents. This approach achieved a CO_2 purity exceeding 95 %, a recovery rate of 81 %, and a specific energy consumption of 3.23 GJ per ton of CO_2.

Table 15

Different swing adsorption methods, operation, advantages, and disadvantages [219].

Adsorption process	Operation	Advantage	Disadvantage
Pressure Swing Adsorption (PSA)	Decrease the pressure in an adsorbent bed	Simple system with high stability	Requires pressurization before adsorption; high energy consumption for air intake; incomplete regeneration
Temperature Swing Adsorption (TSA)	Increase temperature and maintain constant pressure in an adsorbent bed	High adsorption efficiency with thorough regeneration	High thermal inertia; lengthy regeneration time; potential dilution of gas purity by hot gas medium; significant energy consumption
Electric Swing Adsorption (ESA)	Apply the heating effect (Joule effect) to an adsorbent bed	High energy efficiency; rapid heating rate	The process is still immature
Vacuum Swing Adsorption (VSA)	Reduce pressure below atmospheric levels in an adsorbent bed	Ideal for low-pressure, large-scale applications	High energy consumption for capture

4.3.2. *Electric swing adsorption (ESA)*

Electric swing adsorption (ESA) presents a potential alternative to traditional thermal swing adsorption (TSA). The European Space Agency (ESA) has pioneered the use of electric current to regenerate sorbent materials through the Joule effect [226,227]. Compared to conventional TSA, ESA offers the advantages of a higher heat transfer rate and faster desorption kinetics [226,227]. However, the regeneration process in ESA is subject to stringent constraints. The sorbent material must possess electrical conductivity and exhibit high CO_2 adsorption capacity and selectivity. Given their high electrical conductivity, activated carbons (ACs) are considered the most suitable candidates for ESA [226,227]. In addition to the limitations associated with sorbent selection, another significant drawback of ESA is its exceptionally high electrical energy consumption. Indeed, the cost of electrical energy is considerably greater than that of low-grade heat, which is typically utilized for sorbent regeneration in TSA, and often includes waste heat [226,227]. Within this context, Grande et al. [228] investigated the application of ESA for capturing CO_2 from flue gases with a CO_2 concentration of 3.5 %, typical of natural gas power plants. Using an adsorption temperature of 293 K and a desorption temperature of 423 K, they achieved a CO_2 purity of 16 % and a recovery rate of 89 %. More recently, Zhao et al. [227] explored an ESA method for a feed stream containing 15 % CO_2 balanced with N_2. Employing a carbon monolith as a sorbent, they observed that increasing the electric current and electrification duration significantly improved CO_2 purity and reduced energy consumption. Under optimal conditions, they attained a CO_2 purity of 52 % and a recovery rate of 76 % with an energy consumption of 5.64 MJ kg^{-1} of CO_2. It is crucial to note that the theoretical energy cost for separating a component (CO_2) from a mixture can be assessed by analyzing the energy balance of a closed adiabatic system [229]. The required energy for separation increases as the initial concentration of the component decreases.

4.3.3. *Pressure swing adsorption (PSA) and vacuum swing adsorption (VSA)*

Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA) are techniques that utilize pressure variations to regenerate sorbent materials. PSA captures CO_2 at high pressure, releases it (desorbs) the captured CO_2, regenerates the sorbent, and reduces the pressure to ambient levels [230]. While widely used in industry, PSA has limitations for post-combustion capture due to the low CO_2 concentration in flue gas (typically less than 20 % by volume).

To address these challenges, VSA has been proposed as a viable alternative. VSA operates by adsorbing CO_2 at atmospheric pressure, while CO_2 desorption and sorbent regeneration occur under vacuum conditions [231]. However, basic VSA systems often suffer from low CO_2 purity or low CO_2 recovery [220]. This limitation is primarily attributed to the low CO_2 partial pressure in the feed, which complicates the achievement of both high CO_2 purity and high recovery rates in a straightforward one-stage configuration that meets CCS specifications [232]. Consequently, for VSA to be effectively applied in post-combustion capture, it necessitates a minimum of two stages to capture CO_2 with a purity exceeding 90 % while maintaining a relatively high recovery rate. Moreover, vacuum-temperature swing adsorption (VTSA) is an advanced CO_2 capture method that integrates both vacuum and thermal regeneration processes to optimize energy efficiency. Unlike conventional pressure swing adsorption (PSA) or temperature swing adsorption (TSA), which rely solely on either pressure reduction or heat input, VTSA combines these strategies to achieve lower energy consumption and improved desorption kinetics. This dual-mode regeneration approach enhances CO_2 recovery while minimizing thermal degradation of adsorbents. VTSA is particularly advantageous in CO_2 capture applications where reducing energy intensity is a priority. Studies have shown that VTSA processes can achieve up to 30–40 % lower energy consumption compared to TSA alone, as the vacuum stage reduces the desorption temperature required for complete CO_2 release [233]. The integration of vacuum conditions also enhances desorption rates, enabling faster regeneration cycles and increasing overall process throughput. Additionally, VTSA helps prevent thermal deactivation of amine-functionalized zeolites, which are susceptible to degradation under high-temperature regeneration conditions. Zeolites, particularly low-Si/Al ratio zeolites (e.g., NaX, Li-X, and Ca-X), have demonstrated high CO_2 adsorption capacity under post-combustion conditions, making them ideal candidates for VTSA applications. Research indicates that Li-X zeolites subjected to VTSA exhibit CO_2 working capacities of 6.0–6.5 mmol/g, compared to 5.2–5.8 mmol/g under TSA alone (Chen et al., 2020). The combination of vacuum and temperature cycling also improves regeneration efficiency, exceeding 95 % CO_2 recovery over multiple adsorption-desorption cycles. While VTSA offers notable energy savings, industrial-scale implementation requires further optimization of adsorbent durability, cycle timing, and vacuum system integration. Recent advancements in hybrid zeolite-activated carbon composites have shown promise in enhancing VTSA efficiency by reducing heat loss during desorption [234]. Future studies should focus on refining adsorbent formulations to further reduce energy costs, improve selectivity, and extend adsorbent lifespan under VTSA conditions.

An alternative method that has been shown to enhance the efficiency of both PSA and VSA is the implementation of a two-stage vacuum pressure swing adsorption (VPSA) process [235]. Typically, the first stage achieves a CO_2 recovery rate of approximately 95 %, with CO_2 purity levels ranging from 40 % to 60 %. The second stage is then employed to elevate the CO_2 purity to 95 % [230]. Wang et al. [236] developed a framework to model a two-stage VPSA process for capturing CO_2 from flue gas containing 16.5 % CO_2, utilizing 13X-APG and activated carbon (AC) as sorbents in the first and second stages, respectively. This approach resulted in an energy consumption of 2.44 MJ kg^{-1} of CO_2, yielding a CO_2 purity of 95.6 % and a CO_2 recovery of 90.2 %. Nikolaidis et al. [237] examined a two-stage VPSA system, employing zeolite 13X in the first stage and Mg-MOF-74 in the second stage. Their system achieved a CO_2 purity of 97.57 % and a CO_2 recovery rate of 90.16 %, requiring a total energy input of 0.7 MJ kg−1 of CO_2.

A standard Pressure/Vacuum Swing Adsorption (P/VSA) cycle involves high-pressure adsorption and low-pressure desorption stages. Additionally, P/VSA energy consumption is often underestimated, as high-grade energy (electricity) is required for pressure variation, necessitating thermal energy conversion for fair comparison with amine processes [238].

4.3.4. Hybrid regeneration strategies

Hybrid regeneration strategies have emerged as a promising approach to address the limitations of pressure- or temperature-based regeneration modes. Hybrid Vacuum Temperature Swing Adsorption (VTSA) offers a solution that combines the benefits of VSA and TSA. This hybrid approach mitigates the need for extremely high desorption temperatures in TSA and the difficulties associated with achieving deep vacuums in large-scale VSA systems, leading to reduced energy consumption and capture costs as well as high CO_2 recovery rates [220, 239]. Consequently, VTSA facilitates the recovery of the used sorbent under less severe operating conditions compared to both VSA and TSA [239]. In this context, Jiang et al. [230] demonstrated a VTSA process using zeolite 13X, achieving a CO_2 purity of 97.27 %, a recovery of 97.66 %, and an energy consumption of 3.22 MJ kg^{-1} CO_2. Webley et al. [240] proposed a nontraditional hybrid microwave-assisted VTSA method that employs 13X zeolite. They found that brief exposure to microwave radiation significantly enhanced the rates of CO_2 and water release at the studied vacuum levels, indicating that the use of microwaves could potentially reduce overall energy costs.

Another type of hybrid cycle, known as pressure temperature swing adsorption (PTSA), has the potential to address these challenges by leveraging the combined effects of temperature and pressure. Large-scale CO_2 capture facilities may find PTSA more user-friendly due to its milder regeneration conditions. Specifically, PTSA necessitates lower regeneration temperatures compared to TSA and higher desorption pressures than PSA [232]. A fundamental PTSA process encompasses sequential steps of adsorption, heating, depressurization or evacuation, cooling, and/or pressurization [241]. More intricate cycles, such as a seven-step cycle, have also been reported, which include adsorption, pressure equalization, depressurization, vacuum heating, vacuum cooling, pressure equalization, and pressurization [242]. To prevent a decline in capacity resulting from heat released during the adsorption process, it is essential to supply cooling water to regulate the temperature of the column. Tsutsumi et al. [243] demonstrated a 40 % reduction in energy penalty through energy recovery techniques like expanders and chemical heat transformers. Fig. 23 provides a simplified schematic of an adsorptive cycle.

4.4. Energy efficiency

Energy efficiency is a key consideration in the overall evaluation of CO_2 capture technologies. It encompasses the energy required for both

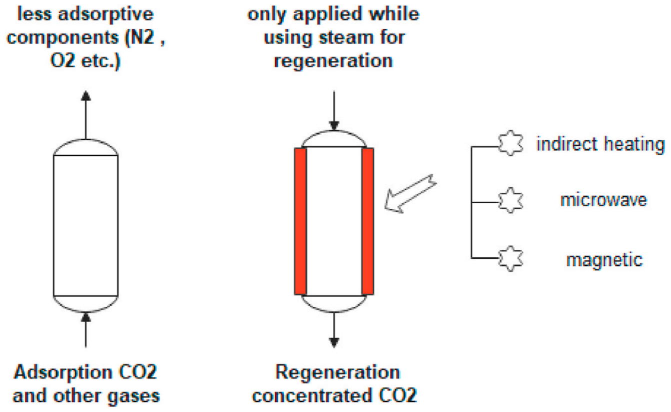


Fig. 23. A simplified schematic adsorptive cycle.

the adsorption and regeneration phases and is directly influenced by the tailoring strategies employed in zeolite development.

The energy efficiency of CO_2 capture using zeolites is partly determined by the heat of adsorption. Tailored zeolites with strong chemisorptive interactions may require more energy to adsorb CO_2, but they also benefit from higher selectivity and capacity. However, the balance between adsorption capacity and the associated energy cost must be carefully managed to ensure overall process efficiency.

The energy required to regenerate zeolite is a critical component of overall energy efficiency. Zeolites that rely on physisorption typically require lower desorption energy, making them more energy-efficient for cyclic processes. Tailoring strategies that enhance CO_2 capture without significantly increasing desorption energy are essential for optimizing the energy efficiency of the process. Optimizing the balance between **adsorption capacity and regeneration energy** is critical in the design of tailored zeolites for CO_2 capture. While high adsorption capacity is desirable for maximizing CO_2 uptake, excessive binding strength can lead to increased regeneration energy, reducing process efficiency. Therefore, the ideal zeolite should exhibit strong CO_2 affinity while ensuring low-energy desorption to enable cost-effective cyclic operation. Zeolites with **low Si/Al ratios** (e.g., NaX, Li-X) tend to have **higher CO_2 adsorption capacities** due to their strong electrostatic interactions with CO_2 molecules. For instance, **Li-X zeolites can achieve CO_2 uptakes of 5.8–6.2 mmol/g at 1 bar** but require moderate desorption temperatures (120–150 °C) [244]. Conversely, high-Si/Al zeolites, such as **ZSM-5 and siliceous faujasites**, exhibit lower adsorption capacity (∼2.0–3.5 mmol/g) but benefit from **reduced regeneration energy demands**, making them more suitable for vacuum-swing or hybrid regeneration processes [245]. Ion-exchanged zeolites offer a **tunable balance** between capacity and regeneration. Studies have shown that **Ca^{2+}-exchanged zeolites achieve a CO_2 working capacity of 5.2–5.9 mmol/g** while maintaining desorption temperatures below 140 °C, reducing the energy input required for regeneration [246]. Similarly, **amine-functionalized ZSM-5 demonstrates improved CO_2 capture in humid environments**, with a **50 % lower energy penalty compared to unmodified ZSM-5** due to weaker CO_2 binding interactions [247]. For large-scale CO_2 capture applications, **hybrid regeneration techniques** such as vacuum-temperature swing adsorption (VTSA) help mitigate the trade-off between adsorption and desorption efficiency. Recent advancements in **zeolite-carbon composite adsorbents** have demonstrated **up to 25 % lower regeneration energy** while maintaining high working capacities, making them a promising alternative to conventional amine scrubbing (Kumar et al., 2023). Further research into hierarchical pore structures and framework doping strategies could enhance zeolite selectivity while minimizing energy costs in cyclic CO_2 capture operations.

5. Comparative analysis of zeolites with other adsorbents

Carbon-based materials have been extensively utilized as effective agents for capturing CO_2 due to their inexpensive nature, stable physiochemical properties, affordability, low susceptibility to moisture, high thermal stability, and the ability to adjust their porosity [15,27,32,198,248]. However, these materials weakly absorb CO_2 in the 50–120 °C temperature range, leading to low operational selectivity and relatively high-temperature sensitivity. Compared to zeolites or metal-organic frameworks (MOFs), which will be discussed later, carbon materials are less polar and exhibit a lower affinity for CO_2 adsorption. This common limitation can be mitigated by introducing heteroatoms (typically nitrogen, and occasionally other elements) into the carbon frameworks or by employing surface functional groups [249,250]. Additionally, CO_2, being acidic, tends to be adsorbed onto basic groups, such as nitrogen species. The incorporation of nitrogen atoms into activated carbons, particularly on the surface, provides a more stable alternative to utilizing oxygenated functional groups such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O) groups.

Ordered mesoporous silica materials possess unique characteristics that make them highly promising as CO_2 adsorbents. These attributes include a high pore volume, elevated surface area, excellent thermal properties, adjustable pore sizes, and mechanical stability. Various types of these materials, such as SBA-16 (Santa Barbara Amorphous) and SBA-15, as well as MCM-41 and MCM-48, have been utilized, each exhibiting different pore geometries (cubic and hexagonal) and morphologies (rods, spheres, and surfactant-templated mesoporous silica) [198,251,252]. However, their limited CO_2 adsorption capacity at ambient pressure hinders practical applications. A significant challenge associated with the use of porous and mesoporous silica adsorbents is the degradation of their structure in the presence of steam, which can lead to the release of attached or incorporated amines. This degradation not only diminishes their CO_2 adsorption capacity but also contributes to corrosion issues [252]. MOFs have garnered considerable interest due to their remarkable properties, including tunable pore structures, high surface areas, and favorable pore surface characteristics. These properties can be easily modified by altering the constituent clusters or organic ligands, positioning MOFs as promising candidates for CO_2 capture applications [17].

In terms of active surface area per unit weight, MOFs typically range from 1500 to 6000 $m^2\ g^{-1}$, while activated carbons and zeolites fall within 400–2000 $m^2\ g^{-1}$ and up to 1500 $m^2\ g^{-1}$, respectively [198,253].

A previous researches focused on the integration of MOFs with various solid adsorbents, including activated carbon, graphene, graphene oxide (GO), and carbon nanotubes (CNTs). This technique provides the benefits of enhanced surface area and readily adjustable places for altering the characteristics of the composite material [254]. Most of the previously reported solids have a significant capacity for adsorption processes. However, synthesis on a large scale would significantly increase the cost of CCS, making it impractical. To reduce costs, researchers have developed low-cost adsorbents that are readily available and use less energy for regeneration in order to capture CO_2 [17]. Researchers have identified natural zeolites as alternative adsorbents for gas purification and separation [33,255]. Clay minerals, which are plentiful on the Earth's surface, have a diverse variety of uses in the fields of adsorption and catalysis [256,257]. Several authors have investigated clay minerals as CO_2 adsorbents by using, for example, kaolinite [258,259], montmorillonite [260,261] or sepiolite [262,263], bentonite [260,264], and attapulgite [265,266] as starting materials. Typically, the structure consists of layers formed by arranging tetrahedra and octahedra sheets [267,268], as shown in Fig. 24.

The optimization of these features can be achieved by introducing organic, inorganic, or organometallic species between the adjacent sheets [256,270], by functionalization [266], or by acid treatment [165,271]. Clay minerals are resistant to chemical changes, although

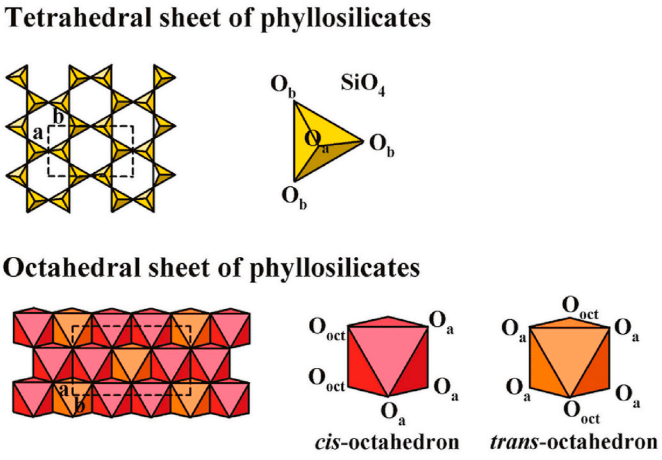


Fig. 24. Tetrahedral and Octahedral sheet of phyllosilicates [269].

enhancing their textural qualities and improving their microporosity is possible. Furthermore, certain circumstances can enhance the adsorption capability of CO_2.

The POPs are constructed by the cross-linking of lighter elements (C, H, B, O, N, S, P, etc.) through covalent bonds [272]. The main feature of POPs is their ability to undergo reversible adsorption of CO_2 gas under specific environmental conditions. So far, researchers have investigated different types of POPs for the purpose of capturing CO_2. Polymers with covalent aromatic frameworks (CTF), porous melamine-formaldehyde (MF), covalent organic polymers (COP), polymers with intrinsic microporosity (PIMs), conjugated microporous polymers (CMPs), and polymers with intrinsic microporosity (PIMs) are some of these [198,272], as displayed in Fig. 25.

TThe microporous structure of polymers is a crucial factor in CO_2 capture. Ultra-micropores ($d < 1.0$ nm) can significantly enhance adsorption capacity and selectivity due to size-selective effects [24]. Therefore, the design of POPs for CO_2 capture should prioritize high surface area (SBET), heteroatom content, and micropore content [272].

The choice of metal oxides influences their CO_2 adsorption capacity, kinetics, regeneration heat requirements, availability, thermal stability, and structural and textural characteristics. When CO_2 molecules react with certain porous metal oxides, such as MgO and CaO, they form thermodynamically stable carbonates. Recent research has also focused on silicates, zirconates, and perovskites based on lithium, sodium, and potassium due to their demonstrated enhanced CO2 trapping capabilities [27,273].

Among most of these materials, Li_2O, MgO, and CaO have exhibited superior performance; however, due to their reactivity and kinetic factors, Li_2O and MgO are not considered potential candidates for CO_2 capture [17]. In contrast, CaO is viewed as a promising alkaline earth metal oxide with viable commercial applications. Additionally, lithium and sodium phase ceramics have shown higher thermal stabilities and volume changes compared to CaO. In the cases of Li_4SiO_4 and Li_8SiO_6, the highest adsorption was attributed to the moles of CO_2 captured in each phase. Furthermore, sodium phase ceramics demonstrate CO_2 adsorption capabilities in the presence of steam, producing $NaHCO_3$ as the carbonated phase, which exhibits a twofold capacity compared to Na_2CO_3 under dry conditions [17,27,198]. Table 16 provides a comprehensive overview of various adsorbents used in carbon dioxide capture.

In summary, the selection of an optimal sorbent material hinges on a complex interplay of factors, including adsorption capacity, selectivity, adsorption/desorption rates, temperature requirements, thermal and mechanical stability, cycling stability, tolerance to moisture and other impurities in the flue gas, and production cost (Table 17). Among all the adsorbents reviewed, zeolites and MOFs exhibit the greatest level of industrial maturity.

Table 16
Previous work of carbon dioxide adsorption using different adsorbent material.

Adsorbents	Temperature (°C)	Pressure (bar)	CO_2 uptake (mmol g^{-1})	Ref.
Silica-based materials				
SiO2-NS (PEI)	75	1	4.01	[274]
SBA-15 (PEI)	25	1	0.83	[275]
KIL-2 (TEPI)	25	1	3.37	[276]
Carbon based materials				
Walnut shell (Biochar)	25	1	1.86	[277]
Soybean straw (Biochar)	30	1	1.80	[278]
NH_3-AC (black locust)	25	1	5.05	[279]
AC/CuO	30	1	6.78	[280]
TEPA-CNT	60	–	5	[281]
TEPA-graphite oxide	25	30	2.08	[282]
PEI-graphene oxide	75	1	2.91	[283]
Metal organic frameworks				
Dehydrated-MIL-53 (Cr)	30.85	20	8.5	[284]
hydrated-MIL-53 (Cr)	30.85	20	7.7	[284]
MIL-53(Al)	30.85	30	10.53	[285]
MIL-53(Cr)	30.85	25	10.04	[285]
Li-HKUST-1	25	18	7.89	[286]
Na-HKUST-1	25	18	8.11	[286]
K-HKUST-1	25	18	8.64	[286]
MOF-177	25	50	35.23	[287]
MOF-210	25	80	65.23	[287]
Porous organic polymers				
CMP@2	0	1	2.28	[288]
ZnP–50 %F-CMPs	25	1	2.05	[289]
SIOC–COF-5	0	1	4.5	[290]
TPE–COF–II	0	1	5.27	[291]
HCPs-5 %	0	1	2.25	[292]
HC-Pcz-8	25	1	3.5	[293]
Zeolite materials				
Zeolite 4A	25	20.7	4.8	[294]
Zeolite 13X	25	20.7	5.2	[294]
Zeolite Y	25	1	4.5	[191]
PDY-3	25	1	5.1	[191]
PDY-6	25	1	5.2	[191]
PDY-7	0	1	5.9	[191]
Metal oxides				
Alumina-aerogel/K_2CO_3	56.1	–	7.20	[295]
Rod-like MgO	25	1	1.56	[296]
Mesoporous MgO	350	10	6.25	[297]
CaO-based pellets	650	1	11.4	[298]

Both natural and synthetic zeolites can be employed for post-combustion CO_2 capture. Their CO_2 adsorption mechanism is influenced by factors such as the Si/Al ratio and the nature and position of extra-framework cations. While natural zeolites like tuff and kaolinite are inexpensive, they exhibit limited CO_2 adsorption capacity. Natural zeolites have gained increasing attention as cost-effective alternatives to synthetic zeolites for CO_2 capture due to their abundance, low environmental impact, and intrinsic microporosity. These materials, primarily found in volcanic tuffs and sedimentary deposits, consist of a

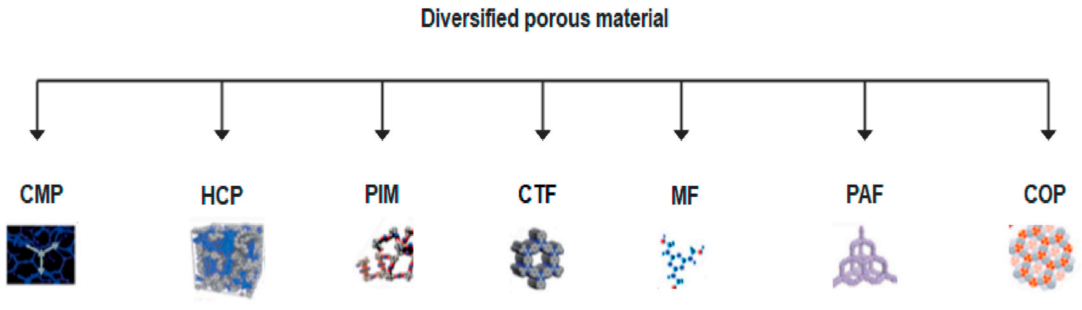


Fig. 25. Chemical structure of diversified porous material [198].

Table 17
Merits and Demerits of different classes of adsorbents [12].

Adsorbents	Advantages	Disadvantages
Zeolites	• Rapid adsorption kinetics •Adjustable pore size and surface characteristics •High surface area and porosity •Significant CO_2 adsorption capacity •Excellent thermal stability	•High synthesis costs •Limited tolerance to moisture and impurities •Low selectivity •Reduced adsorption at elevated temperatures •Presence of impurities, such as H_2O, diminishes efficiency
Activated Carbon	•Rapid kinetic mechanism •Effective desorption through PSA •Wide availability of precursors •Cost-effective •High specific surface area •Good thermal stability •Fair tolerance to moisture •Easy regeneration	•Limited CO_2 adsorption capacity •Prone to friability •Low selectivity •Pore characteristics vary across different materials •Presence of impurities reduces efficiency
Metal organic framework	•Adjustable pore size and surface properties •High surface area and porosity •Significant CO_2 adsorption capacity	•Complex and costly synthesis •Limited tolerance to moisture and impurities •Restricted thermal stability •Low selectivity •Current desorption methods (TSA or PSA) are not fully developed
Amine functionalized adsorbent	•Variety of support materials •High CO_2 adsorption capacity •Low production costs •Good regeneration capabilities •Adsorption efficiency dependent on partial pressure •Rapid kinetic mechanism	•Low thermal and oxidative stability due to amine degradation •Potential for pore blockage •By-product formation from impurities present

wide range of aluminosilicate frameworks with variable Si/Al ratios and cationic compositions. Their availability and affordability make them attractive candidates for large-scale CO_2 capture applications, particularly in regions with significant natural zeolite reserves. Table 18 shows a comparison between natural and synthetic zeolites.

Despite their advantages, natural zeolites face challenges related to impurity content, variable porosity, and lower CO_2 selectivity compared to synthetic counterparts. Raw natural zeolites often contain non-zeolitic phases, such as quartz and feldspars, which reduce their adsorption efficiency. Additionally, their pore structure is typically less uniform, limiting mass transfer rates and adsorption kinetics. To address these challenges, modification strategies such as acid treatment, ion exchange, and thermal activation have been employed to enhance the adsorption performance of natural zeolites. These modifications improve surface area, porosity, and cation exchange capacity, leading to greater CO_2 uptake and selectivity. For example, acid-leached clinoptilolite has demonstrated a 50 % increase in CO_2 adsorption capacity due to improved pore accessibility and cation mobility [306]. Recent studies have shown that natural zeolites, when modified, can exhibit comparable or even superior CO_2 adsorption characteristics relative to synthetic zeolites. Research on acid-activated and metal-exchanged clinoptilolite has demonstrated CO_2 adsorption capacities of 2.5–3.8 mmol/g, comparable to some synthetic zeolites [307]. Similarly, cation-exchanged natural zeolites (e.g., Ca^{2+}- and K^+-modified tuff) have shown improvements in CO_2/N_2 selectivity, making them viable candidates for flue gas separation applications. Further research into composite formation (e.g., blending natural zeolites with activated carbon) and hybrid adsorbent systems is expected to enhance the competitiveness of natural zeolites in commercial CO_2 capture. Their low cost and widespread availability make them attractive for large-scale deployment, especially in cost-sensitive industrial sectors. The application of modified natural zeolites in VTSA and hybrid adsorption systems holds significant potential for energy-efficient CO_2 capture. As research continues to refine their properties, natural zeolites could become a sustainable and scalable solution for CO_2 sequestration. Further studies are needed to optimize modification techniques, improve stability under humid conditions, and integrate natural zeolites into industrial carbon capture systems.

Table 18
Comparison of natural and synthetic Zeolites.

Property	Natural Zeolites	Synthetic Zeolites	References
Cost	Low (abundant, easily mined)	High (complex synthesis)	[299]
Availability	Readily available worldwide	Limited by production capacity	[300]
Porosity	Variable, depends on source	Precisely controlled	[301]
Si/Al Ratio	Wide range (1–6)	Tunable (1–100)	[302]
Cation Content	Naturally occurring (Na, K, Ca, Mg)	Controlled by ion exchange	[303]
CO_2 Selectivity	Moderate (varies with purity)	High (engineered for specificity)	[304]
Regeneration	Can suffer from structural degradation	Designed for stability	[305]

Synthetic zeolites, particularly zeolite 13X, offer higher CO_2 adsorption capacity but are more costly to produce. One major disadvantage of zeolites is their high sensitivity to moisture, which compromises their CO_2 capture efficiency and necessitates a drying step for effective utilization. On the other hand, carbon-based adsorbents are characterized by ease of synthesis and regeneration, economic viability, abundance, rapid carbonation kinetics, low desorption temperatures, and stability. However, their CO_2 capture performance is limited by a low adsorption capacity and selectivity, primarily due to the weak van der Waals forces that govern this temperature-sensitive adsorption. Therefore, carbonaceous adsorbents are typically favored for use at temperatures below 60 °C.

Zeolites, while stable and possessing large surface areas, face challenges related to gas desorption and adsorbent regeneration. The CO_2 adsorption capacity of zeolites is significantly influenced by temperature, exhibiting a positive correlation with pore size; however, this capacity declines markedly when temperatures exceed 100 °C. The optimal CO_2 adsorption temperature for zeolites, MOFs, and carbon-based adsorbents is around 70 °C, which is lower than typical flue gas temperatures (90 °C). To utilize these adsorbents in industrial settings, either flue gas cooling or modification of the adsorbents to accommodate high-temperature adsorption is necessary. Flue gas cooling, being an energy-intensive process, requires careful consideration. Silica and clays exhibit rapid adsorption kinetics and a high capacity for CO_2 capture under mild conditions; however, their current stage of development restricts their applications. These adsorbents are susceptible to moisture adsorption and entail significant energy consumption, while CO_2 desorption and costly pre-treatment processes further elevate regeneration expenses. POPs, although offering improved selectivity and CO_2 uptake, are constrained by complex and expensive synthesis processes. MOs, while demonstrating high adsorption capacity, necessitate high-temperature regeneration procedures.

6. Cost implications of zeolite-based CO_2 capture systems

The economic feasibility of CO_2 capture technologies depends on multiple cost components, including synthesis, regeneration, and operational expenses. Zeolite-based adsorption systems are generally more cost-effective than solvent-based and cryogenic separation techniques, but a detailed breakdown of their costs in comparison with metal-organic frameworks (MOFs) and activated carbons provides deeper insights into their economic viability. Table 19 shows a cost breakdown of zeolite-based systems.

It can be seen from Table 19 that Zeolites offer a balance of performance and cost-effectiveness compared to other adsorbents for CO_2 capture. While MOFs have high surface areas and tunable pore structures, their high synthesis costs and lower thermal stability make them less viable for large-scale applications, with higher regeneration energy demands due to framework collapse. Activated carbons, though moderately effective, are less selective for CO_2 over N_2 and often require chemical modification, with regeneration costs comparable to synthetic zeolites but higher than natural zeolites. Between synthetic and natural zeolites, synthetic variants provide superior selectivity and tunability, but natural zeolites offer a cost-effective alternative, achieving up to 90 % of synthetic zeolites' CO_2 uptake at half the cost when modified.

7. Economic feasibility and industrial applications

The choice of adsorbent depends on the trade-off between cost, performance, and energy efficiency. Zeolite-based systems offer a balance of low-cost regeneration, long lifespan, and high recyclability, making them one of the most viable adsorbents for industrial-scale CO_2 capture. Future research should focus on optimizing low-cost synthesis methods for modified zeolites and exploring hybrid systems that combine zeolites with activated carbon or MOFs to enhance cost-effectiveness.

8. Life-cycle analysis (LCA) of zeolite-based CCS

A Life-Cycle Analysis (LCA) of zeolite-based CO_2 capture considers energy consumption, emissions, and sustainability from production to disposal. Synthetic zeolite synthesis is energy-intensive, requiring 5–10 MJ kg^{-1} due to hydrothermal and calcination processes, whereas natural zeolites require 50–70 % less energy, making them a more sustainable option. During operation, temperature swing adsorption (TSA) requires 2.5–3.2 GJ per ton of CO_2 captured, while vacuum-temperature swing adsorption (VTSA) reduces this to 1.8–2.5 GJ per ton, improving energy efficiency. The CO_2 footprint of synthetic zeolites is 0.7–1.2 kg CO_2 per kg, but this can be mitigated by using renewable energy sources for synthesis and waste-derived precursors such as fly ash. Additionally, spent zeolites modified with amines or metal oxides require proper disposal or recycling to avoid secondary environmental contamination. Future advancements should focus on low-energy green synthesis, solar-assisted regeneration, and closed-loop recycling to improve the sustainability of zeolite-based CCS. Regeneration energy requirements are a key factor in assessing the sustainability of zeolite-based CCS. Zeolites generally require 1.0–1.5 GJ/ton CO_2 captured, significantly lower than amine-based solvents, which can require up to 3.5 GJ/ton CO_2 due to solvent degradation and heat requirements [312]. Additionally, vacuum-temperature swing adsorption (VTSA) has been shown to further reduce the energy penalty by up to 30 %, making zeolites highly competitive in terms of operational efficiency [313]. The synthesis of synthetic zeolites involves hydrothermal processes that consume significant energy and generate emissions from precursor such as alumina and silica. The estimated CO_2 footprint of synthetic zeolite production is approximately 0.2–0.4 kg CO_2 per kg of zeolite [314]. In contrast, natural zeolites require minimal processing, leading to up to 70 % lower emissions materials compared to synthetic counterparts. Recent efforts to improve the sustainability of zeolite production include waste-derived precursors (e.g., fly ash-based zeolites), renewable energy integration in synthesis processes, and improved hydrothermal techniques that lower energy demands while maintaining adsorption efficiency. Table 20 shows a comparison between different adsorbents in terms of energy use and other environmental factors (see Table 21).

Future Sustainability Strategies

To further reduce the environmental impact of zeolite-based CCS, future efforts should focus on:

I. **Utilizing industrial by-products** (e.g., fly ash) as alternative raw materials to minimize CO_2 emissions from synthesis.
II. **Enhancing VTSA and hybrid regeneration techniques** to lower energy consumption.
III. **Integrating renewable energy sources** in zeolite synthesis and regeneration to reduce fossil fuel reliance.
IV. **Developing bio-based zeolites** with biodegradable or eco-friendly precursors to further improve sustainability.

9. Integration of renewable energy in zeolite-based systems

The integration of **renewable energy sources** into zeolite-based CO_2 capture systems presents a significant opportunity to reduce their overall **carbon footprint and energy demand**. The primary areas where renewable energy can be leveraged include:

I. Renewable energy (e.g., solar, wind, and hydroelectric power) can be used to power the hydrothermal synthesis of synthetic zeolites, reducing the emissions associated with conventional fossil-fuel-based energy sources. Studies suggest that **solar-powered hydrothermal processes** could cut emissions by up to **40 %** [317]. A study by **Kumar et al.** [315] demonstrated that integrating solar energy into zeolite synthesis reduces the carbon footprint while maintaining adsorption efficiency, making it a viable strategy for sustainable CO_2 capture materials.
II. Renewable-powered **vacuum-temperature swing adsorption (VTSA)** or **solar-assisted desorption systems** can further **reduce energy consumption during regeneration.** Research indicates that **solar-thermal energy can decrease the desorption energy demand by up to 30 %**, making CO_2 capture more sustainable. In a study by **Martinez et al.** [318], solar-heated desorption was shown to improve adsorption efficiency and significantly lower energy requirements, reinforcing the potential of renewable-driven zeolite regeneration.

Table 19
Cost breakdown of zeolite-based systems.

Cost Component	Synthetic Zeolites	Natural Zeolites	MOFs	Activated Carbons	Reference
Synthesis Cost	High (\$2000–4000/ton)	Low (\$500–1000/ton)	Very High (\$5000–10,000/ton)	Moderate (\$1500–2500/ton)	[308]
Regeneration Cost	Moderate (1.0–1.5 GJ/ton CO_2)	Low (0.8–1.2 GJ/ton CO_2)	High (1.5–2.5 GJ/ton CO_2)	Moderate (1.0–1.8 GJ/ton CO_2)	Wang et al., [309, 310]
Operational Cost	Moderate (\$20–50/ton CO_2 captured)	Low (\$15–40/ton CO_2 captured)	High (\$60–120/ton CO_2 captured)	Moderate (\$30–70/ton CO_2 captured)	[310]
Lifespan & Stability	High (>10 years)	Moderate (5–10 years)	Variable (depends on framework stability)	Moderate (6–12 years)	[156,310]
Environmental Impact	Low (high recyclability)	Low (naturally occurring)	High (metal leaching issues)	Moderate (waste disposal concerns)	[311]

Table 20
Comparative between different adsorbents in terms of energy use and other key factors.

Factor	Synthetic Zeolites	Natural Zeolites	MOFs	Activated Carbons	Reference
Energy Use (GJ/ton CO_2)	1.0–1.5	0.8–1.2	1.5–2.5	1.0–1.8	[315]
CO_2 Footprint (kg CO_2/kg material)	0.2–0.4	0.05–0.1	0.5–1.2	0.3–0.6	[316]
Waste Generation	Low	Minimal	High (solvent waste)	Moderate	[156]
End-of-Life Disposal	Recyclable	Naturally occurring	Complex	Requires regeneration	[310]

Table 21
Comparative impact of renewable energy adoption.

Application Area	Conventional Energy Use	Renewable Energy Potential	Reference
Zeolite Synthesis	High emissions (fossil-fuel powered)	40 % emission reduction via solar hydrothermal	[313, 317]
Regeneration (VTSA)	1.0–1.5 GJ/ton CO_2	30 % reduction with solar-assisted desorption	[312, 318]
Hybrid Systems	Fossil-fuel-dependent heat supply	Waste heat + geothermal integration for continuous operation	[320]
Electrification (PSA/TSA)	Grid-powered systems with fossil-based electricity	Full integration with solar and wind power to reduce emissions	[319]

III. Combining **waste heat recovery with renewable energy** for desorption processes can lead to **greater energy efficiency** and lower overall operational costs. Some industrial-scale CCS projects have explored the use of **geothermal energy for continuous heat supply** in adsorption-desorption cycles. **Ahmed et al. (2023)** reported that coupling geothermal energy with zeolite-based CCS reduced energy demand by 25 %, highlighting its feasibility for industrial applications.
IV. The use of renewable electricity from **solar photovoltaics (PV) and wind power** for **pressure swing adsorption (PSA) and temperature swing adsorption (TSA)** can reduce reliance on fossil fuels, significantly cutting emissions [319] found that wind-powered adsorption systems demonstrated long-term energy savings, particularly in offshore carbon capture applications.

The continued integration of renewable energy into zeolite-based CCS requires further research in:

I. **Optimizing solar-thermal desorption technologies** to improve adsorption-desorption efficiency.
II. **Scaling up industrial applications of hybrid renewable energy systems** for sustainable CCS deployment.
III. **Advancing low-emission zeolite synthesis techniques** that utilize green energy sources.
IV. **Developing electrified adsorption systems that can be directly powered by renewable electricity.**

10. Readiness of zeolite-based systems for industrial integration

Zeolite-based CO_2 capture systems have been extensively studied at the lab and pilot scale, demonstrating promising adsorption capacities, selectivity, and regeneration efficiency. However, their transition to full-scale industrial applications requires addressing key challenges related to scalability, cost-effectiveness, and integration with existing infrastructure (Zhang et al., 2023). Below are the key **advantages for industrial deployment:**

1. Zeolites exhibit high CO_2 selectivity and thermal stability, outperforming traditional amine-based solvents in harsh industrial conditions. Their ability to withstand multiple adsorption-desorption cycles without degradation enhances their viability for long-term industrial use [321].
2. Unlike amine scrubbing, which requires high-temperature regeneration (~120–150 °C), zeolites can be regenerated at much lower temperatures (~80–100 °C) or via vacuum-temperature swing adsorption (VTSA), reducing operational costs [322].
3. Zeolites are compatible with existing post-combustion CCS systems, particularly in power plants, cement manufacturing, and steel industries, where CO_2 concentrations are relatively high [319].

11. Advances in fly ash-derived and bio-based zeolites have made their production more environmentally friendly and cost-effective, reducing reliance on synthetic precursors [318]

However, there are challenges and barriers to industrial adoption:

I. While natural zeolites are abundant and inexpensive, synthetic zeolites require costly hydrothermal synthesis processes. Scaling up low-cost manufacturing and utilizing waste-derived precursors is critical to widespread adoption [323].
II. Laboratory-scale results often rely on pure CO_2 streams, whereas industrial flue gases contain humidity, SO_2, and NO_x impurities that can impact zeolite performance [324]. Functionalization strategies (e.g., amine-modified zeolites) are being explored to enhance CO_2 selectivity in realistic industrial settings.
III. VTSA and hybrid thermal desorption methods are promising but require further validation at the megaton-scale to ensure economic feasibility [320].

Several demonstration projects and industrial trials are currently evaluating the large-scale feasibility of zeolite-based CCS. Pilot plants in Europe and North America are testing zeolite adsorption for cement plants, refineries, and natural gas processing facilities (IEA, 2023). Moving forward, the key priorities include:

I. Advancing material optimization to improve adsorption-desorption kinetics and resistance to industrial contaminants.
II. Developing hybrid capture systems that combine zeolites with amine scrubbing or membrane separation for enhanced CO_2 capture performance.
III. Establishing techno-economic assessments to compare zeolite-based CCS against existing commercial technologies (e.g., amine solvents, MOFs, and solid sorbents).

12. Leveraging policy incentives such as carbon credits and industrial decarbonization targets to encourage commercial adoption

12.1. Opportunities and challenges

This article analyzes recent advancements in CO_2 capture materials, focusing on the efficacy of synthetic materials in CO_2 adsorption. Porous materials are essential for CO_2 capture via adsorption. This study seeks to deliver a thorough analysis of how the physicochemical and structural characteristics of different porous materials influence CO_2 adsorption and selectivity. Zeolites, a category of porous materials, are examined in depth, emphasizing techniques to improve their CO_2 collection efficiency. The CO_2 adsorption capability of porous materials mostly relies on their surface architecture and chemical characteristics. The total specific surface area, total pore volume, and mesoporous characteristics can be modified through modifying the structure of the porous material. A greater surface area enhances CO_2 uptake; however, a more crucial factor is the ratio of active pores that facilitate bonding. The pore characteristics of the surface structure influence the trapping mechanism at gas-solid interactions.

The selection of the sorbent is an essential step in integrating existing power production utilities with CO_2 capture technologies. This framework posits that primary scientific challenges revolve around the development of novel materials with superior CO_2 capture capabilities through environmentally friendly and easily expandable synthesis approaches; specifically, their chemical and physical characteristics should be regulated at the molecular level, facilitated by a more profound comprehension of structure/function relationships [27,325,326].

The fundamental characteristics of the molecule of CO_2 include a diminutive dynamic size (about 3.3 Å) and distinct electric quadrupole properties relative to various other gases; CO_2 exhibits greater molecular polarizability [219]. The CO_2 volumetric content of the gas source post-combustion typically remains around 15 %, with a total pressure of approximately 1 atm, while additional constituents include N_2, H_2O, among others. The adsorption and removal of the gases from this source are particularly challenging due to moderate total pressure, high volumetric flow rate, and low CO_2 concentration (partial pressure). Sufficient micropores, elevated specific surface area, and customizable surface chemistry are suitable adsorbent attributes for aligning with the dynamic size and polarization of CO_2 molecules. The porous adsorbents exhibits exceptional chemical and thermal stability in an inert environment. It offers significant benefits in the separation of intricate gas sources, which is a crucial factor.

This review indicates that CO_2 adsorption on various sorbents is significantly affected by temperature, pressure, and moisture content. The CO_2 adsorption capabilities provided by these physisorbents markedly reduce at elevated temperatures. The existence of water vapor, an unavoidable element in flue gas, may adversely impact the efficacy of these sorbents and diminish the availability of the active surface area. Moreover, additional pollutants in flue gas, like SOx and NOx, adversely affect the CO_2 adsorption capability. Metalorganic frameworks (MOFs) will probably have significant adsorption capability as sorbents for post-combustion CO_2 capture; nevertheless, more study is necessary to ensure their applicability under flue gas situations. The efficacy of these sorbents for CO_2 adsorption is additionally limited by the CO_2/N_2 selectivity.

Limitations exist in the application of such adsorbent materials for substantial CO_2 adsorption. These include limited manufacturing rates of adsorbent substances, inadequate long-term durability and stability across multiple adsorption-desorption cycles, the high expense of adsorption systems, elevated volumetric flow rates of the feed gas, significant accommodation requirements for adsorbates throughout the adsorption process, extended durations required for switching gas flow paths between adsorption and regeneration, substantial capture costs in post-combustion scenarios, challenges associated with large CO_2 separation, and a significant amount of water (approximately 7 %) and impurities in flue gas [15,327].

Additionally, solvents containing nitrogen (N) and/or oxygen (O) functional groups are thought to improve the surface characteristics of the zeolite, thereby promoting the interaction between the zeolite surfaces and CO_2 molecules, which leads to an enhanced adsorption capacity [52,53,176,184]. It is essential to select the solvent used in the process with care, as it may necessitate a considerable quantity of chemicals. This can lead to increased costs and may pose environmental concerns due to the high toxicity levels associated with certain chemicals [36,54,266,325,328,329].

Accordingly, subsequent research should focus on the following aspects:

1. The majority of published studies focus on simulated CO_2 capture in flue gas streams, which may differ from real gas compositions. The flue gas stream comprises not only CO_2 but also water and acid gases. Therefore, it is essential to engineer materials that exhibit high selectivity for CO_2 while maintaining significant tolerance to any additional constituents present.
2. Adsorbents must demonstrate high recyclability while maintaining substantial CO_2 adsorption capacity over numerous operational cycles. It is essential to consider that flue gas comprises various gases, which is critical to performance.
3. The future development of carbon dioxide adsorbents must integrate both physical and chemical adsorption mechanisms to ensure effective capture while maintaining cost efficiency and performance. Adding amino acids to common adsorption materials, like zeolite-based materials, is also necessary to change their functionality.
4. Before initiating experimental studies aimed at enhancing the fabrication of existing synthetic and novel materials, it is essential to perform computational simulations. This step is necessary to address identified problems and deficiencies before executing practical investigations. This significantly aids in minimizing the waste of resources during experiments. The application of theoretical modeling facilitates the optimization of conditions, the thermodynamic behavior of the reaction, and the duration of the research process.
5. From an industrial perspective, the primary consideration is the cost, which encompasses the total expenses associated with the production of adsorbents, the manufacturing of CO_2 capture devices, the regeneration of adsorbents, and the recovery processes. Although zeolite demonstrates superior performance, it lacks cost-effectiveness. Cost considerations frequently hinder the advancement of offering novel materials. Additional advancements in research and design are required to reduce costs while maintaining CO_2 capture efficiency.

13. Conclusions

Enhancing cost-effective methodologies for post-combustion CO_2 capture from flue gas emissions of fossil fuel power plants is crucial for addressing the issue of global warming. Solid sorbents represent a promising alternative for CO_2 capture from flue gas among various process technologies. Their potential is significant due to several advantageous characteristics, including low energy requirements for regeneration, cost-effectiveness, applicability to dilute gas mixtures, high CO_2 carrying capacity, operational flexibility across a wide range of temperatures and pressures, accelerated reaction rates, and minimal pressure drop. This review article analyzes the recent advancements in adsorption-based post-combustion CO_2 capture, based on ongoing research activities. It provides a comprehensive overview of state-of-the-art research and application-focused knowledge regarding solid sorbents, with a particular emphasis on zeolite-based sorbents, both modified and unmodified. It is essential to note that, despite the maturity of adsorption-based separation technology in various large-scale industrial applications, its implementation in actual post-combustion CO_2 capture processes continues to present multiple challenges concerning the sorbent materials, the gas−solid contact system, and the regeneration mode.

This review presents and discusses the CO_2 adsorption performances of various categories of solid sorbents, based on key assessment parameters such as equilibrium adsorption capacity and multi-cyclic stability, while highlighting their advantages and drawbacks. A comprehensive review of various functional groups and functionalization techniques has been conducted, revealing promising outcomes from the studies analyzed. In addition to adsorption performance, it is essential to evaluate cost factors when choosing adsorbents and materials containing N-functional groups, particularly for large-scale applications. Consequently, low-cost materials that are readily available in nature, including zeolite and amino acids, exhibit significant potential for future applications. This review discusses various regeneration modes, including temperature, pressure, and hybrid swings, with a focus on strategies to minimize the energy demand.

At this stage, from the perspective of this article review, many significant key characteristics are not available. These include kinetic data for adsorption and desorption, mass transfer and diffusional effects, the effects of flue gas contaminants, particle characteristics, and other physicochemical properties of candidate sorbents. There is limited availability of process design and economic analysis due to insufficient data regarding the performance of solid sorbents across different device configurations. The analysis indicates that sorbents alone are not adequate for offering a comprehensive solution. The effectiveness of a solid sorbent capture system is significantly dependent on the adsorption reactor, the process of regeneration, and the overall integration of the capture system, particularly the thermal integration with the power plant.

Finally, the system modeling, optimization, and techno-economic analysis required to assess the possible improvement in solid sorbent capture technologies will become more accurate and dependable as more scientific data on these sorbents becomes readily available.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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