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Recent Advances in Structured Sorbents and Honeycomb Adsorbents for CO_2 Capture: Mechanisms, Materials, and Regeneration Strategies

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ABSTRACT

This review critically evaluates recent advances in solid and structured sorbents for CO_2 capture, emphasizing the link between material properties, structured geometry, regeneration, and process performance. Representative sorbent classes typically achieve 2-6.8 mmol/g CO_2 uptake for zeolites and carbons, while selected MOFs can reach higher gravimetric capacities under favorable laboratory conditions; these values are not directly comparable due to differences in temperature, pressure, humidity, gas composition, and active-phase loading. In structured systems the principal advantage is often reduced pressure drop, improved heat and mass transfer, and higher reactor-level efficiency rather than higher intrinsic gravimetric capacity. A recent techno-economic analysis of a DAC monolith showed substantially lower fan work than a packed bed owing to an approximately two-order-of-magnitude reduction in pressure drop, although the packed bed exhibited higher reference productivity (2.4 versus 1.2 kg CO_2/ m^3h) and the modeled capture cost remained above 1500 € per tonne of CO_2 at a capture scale of 100 kt CO_2/yr. Electrified regeneration routes, including resistive/electrothermal swing adsorption, microwave, and induction heating, enable rapid and localized heating but face challenges in temperature uniformity, electrical-to-thermal efficiency, materials compatibility, and scale-up. The review argues that adsorbent selection should prioritize working capacity, impurity tolerance, regeneration energy, cyclic stability, pressure drop, volumetric productivity, and cost rather than maximum equilibrium capacity alone. Application-specific criteria are proposed for post-combustion capture, direct air capture, and biogas upgrading, together with research priorities for realistic multicomponent testing and integrated material-process optimization.

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1. Introduction

Anthropogenic carbon dioxide (CO_2) emissions, primarily from fossil fuel combustion and industrial processes, are the principal driver of current climate change. The continuous accumulation of CO_2 in the atmosphere has resulted in significant environmental challenges, including global warming, ocean acidification, and extreme weather phenomena [1]. According to [2], without effective mitigation, atmospheric CO_2 levels could surpass critical thresholds that trigger irreversible climate feedback loops [2]. As a result, technologies for CO_2 capture have become indispensable in any pathway toward net-zero emissions. Among the various CO_2 mitigation strategies, post-combustion CO_2 capture is widely recognized due to its compatibility with existing energy infrastructures. The most mature technique in this context is amine-based chemical absorption, which involves reversible reactions between CO_2 and aqueous amine solutions. This method, particularly with monoethanolamine (MEA), offers high removal efficiency under dilute CO_2 concentrations [3, 4]. However, it suffers from significant limitations. These include high energy demands for solvent regeneration often representing more than 30% of a power plant's energy output as well as solvent degradation, corrosion, and toxic byproducts that reduce its operational viability [1, 3].

Another category of separation technologies is membrane-based processes, which exploit selective permeation of CO_2 through polymeric or inorganic membranes. These systems are attractive due to their modularity, low space requirements, and potential for integration into distributed sources [5]. Nevertheless, membrane systems face critical challenges, including low selectivity at high throughput, fouling in humid environments, and limited performance at atmospheric pressure conditions prevalent in direct air capture [6, 7].

Unlike liquid amine systems, many solid adsorbents can exhibit low corrosivity and favorable cyclic stability; however, solid sorbents are not inherently immune to degradation. Humidity, acidic gases, oxidation, thermal cycling, pore blockage, and functional-group degradation can progressively reduce working capacity and selectivity. Consequently, stability must be evaluated for the specific sorbent, gas composition, and regeneration protocol rather than assumed from the adsorbent class alone.

Each class of adsorbent has distinct advantages and limitations. Activated carbons are low-cost and highly porous but generally perform better under dry conditions [8]. Their performance is strongly linked to surface area, micropore volume, and surface functionalization, which influence CO_2 uptake and selectivity. For example, KOH-activated biochars derived from biomass sources have shown promising results, with tunable surface chemistry enhancing their affinity toward CO_2 [9]. Moreover, the thermodynamics and kinetics of CO_2 adsorption on carbons can be precisely modeled, enabling predictive design for real applications [10].

On the other hand, zeolites, especially 13X, are crystalline aluminosilicates with uniform pore structures and high CO_2 selectivity due to electrostatic interactions between CO_2 and cations in the framework [11, 12]. Zeolites exhibit excellent performance under low CO_2 partial pressures, making them attractive for DAC. However, their hydrophilicity can reduce effectiveness in humid environments. Surface hydrophobization, as demonstrated by [12], significantly improves moisture resistance [12]. Furthermore, advances in 3D-printing of zeolite structures have allowed the creation of gyroid monoliths with enhanced porosity and mechanical integrity [13].

Importantly, adsorption allows process intensification and electrification. Emerging studies suggest using microwave or induction heating for regeneration, reducing energy consumption and enabling modular deployment [14-16]. These novel regeneration techniques further distinguish adsorption from thermal-intensive solvent processes. Additionally, hybrid systems combining adsorption and membranes show synergy in efficiency and operational flexibility [5].

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From a techno-economic perspective, adsorption systems offer advantages in operating cost, process modularity, and material renewability. Composite monoliths, in particular, are suited for compact capture units in decentralized settings, such as biogas purification or indoor air quality management [17,18]. Moreover, structured adsorbents demonstrate superior thermal stability and cyclic durability compared to traditional packed beds [19].

In conclusion, adsorption should not be regarded as universally superior to absorption or membranes. Its principal opportunity is the simultaneous optimization of sorbent chemistry and process architecture. Structured sorbents can reduce pressure drop and intensify heat and mass transfer, but they may introduce higher fabrication costs and, depending on geometry and kinetics, lower volumetric productivity. The relevant question is therefore not which material has the highest equilibrium capacity, but which material–structure–cycle combination minimizes the total cost and energy penalty for a defined capture duty.

The distinctive contribution of this review is an application-oriented framework that connects five levels that are often evaluated separately: (i) sorbent chemistry and adsorption mechanism, (ii) structured geometry and transport, (iii) competitive impurities and degradation, (iv) regeneration and cycle design, and (v) techno-economic and deployment constraints. Rather than ranking materials by equilibrium capacity alone, the review evaluates the material-geometry-cycle-impurity-economics chain. This framework is used to interpret why the same sorbent can appear highly competitive in a single-component laboratory test but become less attractive when humidity, SO_2/NO_x, shaping, regeneration energy, pressure drop, and manufacturing cost are considered simultaneously (Figure 1).

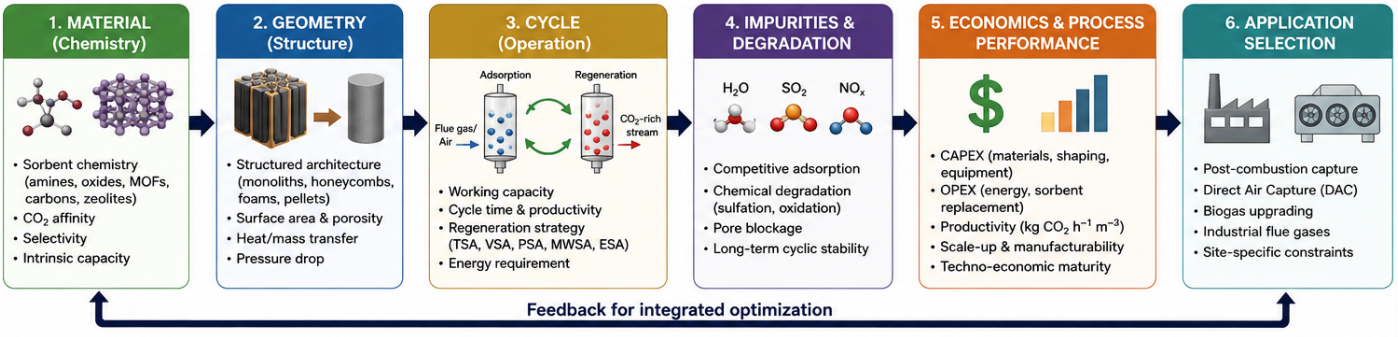


Fig. 1. Integrated material-geometry-cycle-impurity-economics framework for the selection and optimization of structured sorbents for CO_2 capture.

2. Adsorption Fundamentals and Performance Metrics

Adsorption is a surface-based separation process that plays a central role in carbon dioxide (CO_2) capture, particularly in post-combustion and direct air capture applications. A solid adsorbent selectively attracts CO_2 molecules from a gas mixture, often under mild operating conditions. To optimize adsorption systems, it is critical to understand the physical and chemical nature of adsorption, the effects of pressure and temperature, and the interplay between kinetics and equilibrium.

2.1. Physical vs. Chemical Adsorption

Adsorption mechanisms are typically classified into physisorption and chemisorption, distinguished by the type and strength of interactions between CO_2 molecules and the adsorbent surface. Physisorption relies on weak van der Waals forces and is generally reversible, requiring relatively low energy for regeneration. This mechanism predominates in materials such as activated carbon, zeolites, and metal-organic frameworks, making them well suited for pressure swing

and temperature swing processes [7, 8]. In contrast, chemisorption involves stronger covalent or ionic bonding, often occurring at functional groups or metal active sites on the sorbent surface. Although this mechanism provides higher selectivity and stability, it typically requires elevated temperatures for regeneration and is less favorable for rapid cyclic operation [2, 20].

For example, amine-modified silica materials exhibit chemisorption through direct chemical reaction with CO_2, whereas KOH-activated biochars primarily operate through physisorption facilitated by tailored pore structures [9, 21]. The fundamental distinctions between physisorption and chemisorption play a decisive role in determining the suitability of adsorbents for different CO_2 capture applications. These mechanisms differ not only in the nature of CO_2-surface interactions but also in regeneration energy requirements, reversibility, selectivity, and cyclic performance. For clarity, the main differences between physical and chemical adsorption are summarized in Table 1.

Table 1. Comparison between Physisorption and Chemisorption Mechanisms in CO_2 Capture

Feature	Physisorption	Chemisorption	Ref
Nature of interaction	Weak van der Waals forces	Strong covalent or ionic bonding	[2, 7]
Adsorption energy	Low (5-40 kJ/mol)	High (40-400 kJ/mol)	[10, 20]
Reversibility	Highly reversible	Often partially reversible	[8, 21]
Selectivity	Moderate (depends on pore size and polarity)	High (specific chemical affinity)	[7, 21]
Temperature effect	Capacity decreases significantly with temperature	May require moderate temperature for activation	[22, 23]
Regeneration energy	Low	High	[15, 16]
Suitability for cyclic processes	Excellent (PSA, VSA, TSA)	Limited due to high regeneration cost	[9, 24]
Sensitivity to moisture	Generally lower (for hydrophobic carbons)	Can be strongly affected depending on functional groups	[12, 25]
Typical materials	Activated carbon, zeolites, MOFs	Amine-functionalized silica, metal oxides, alkali-based sorbents	[8, 11]
Example in CO_2 capture	CO_2 adsorption in ultramicropores of activated carbon	Carbamate formation in amine-modified silica	[9, 21]

As presented in Table 1, physisorption is characterized by weak intermolecular forces and relatively low heats of adsorption, typically below 40 kJ/mol, which enable easy regeneration through pressure or temperature swing processes. This makes physically adsorbing materials such as activated carbons and zeolites highly suitable for cyclic industrial operations. In contrast, chemisorption involves the formation of stronger chemical bonds, often associated with adsorption enthalpies exceeding 40 kJ/mol, resulting in higher selectivity but also increased regeneration energy requirements. While chemisorption-based materials, such as amine-functionalized sorbents, demonstrate strong CO_2 affinity particularly at low partial pressures their long-term cyclic stability and energy efficiency may be limited compared to purely physisorptive systems. Therefore, the choice between physisorption and chemisorption depends strongly on process conditions, including CO_2 concentration, operating temperature, and regeneration strategy.

The fundamental differences between physical and chemical adsorption mechanisms are schematically illustrated in Figure 2. The figure highlights the nature of intermolecular interactions, bond strength, and reversibility characteristics associated with each adsorption pathway.

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As shown in Figure 2(a), physisorption occurs through weak intermolecular forces between CO_2 molecules and the internal surface of porous adsorbents, such as activated carbon or zeolites. The adsorption process is primarily governed by van der Waals interactions and pore confinement effects, resulting in low heat of adsorption and high reversibility. In contrast, Figure 2(b) illustrates chemisorption, where CO_2 reacts with surface functional groups such as amine groups to form chemical species (e.g., carbamates). This mechanism involves stronger bonding and higher adsorption enthalpy, leading to enhanced selectivity but increased regeneration energy requirements.

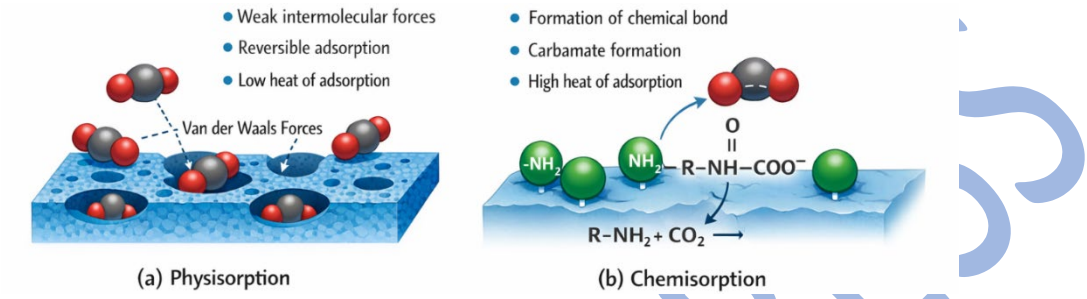


Fig. 2. Schematic illustration of CO_2 adsorption mechanisms: (a) physisorption via weak van der Waals interactions within porous structures, and (b) chemisorption through chemical bond formation between CO_2 and surface amine groups.

2.2. Effect of Pressure

Pressure is one of the most influential factors in CO_2 adsorption. Since adsorption is driven by the chemical potential gradient, an increase in CO_2 partial pressure enhances loading on the adsorbent surface especially in systems following Langmuir or Sips isotherms.

Studies on zeolite 13X and activated carbons consistently show that CO_2 uptake rises sharply with pressure up to a saturation point [26, 27]. In pressure swing adsorption (PSA), the working capacity the difference in uptake between high and low pressures is optimized by tuning operating pressure ranges [28]. In direct air capture (DAC), where CO_2 is present at ~400 ppm, materials must operate efficiently at very low partial pressures, requiring ultra-microporous structures or chemisorption mechanisms [2, 19].

2.3. Effect of Temperature

Adsorption is generally an exothermic process; therefore, increasing temperature reduces CO_2 uptake by shifting the thermodynamic equilibrium toward desorption. Low-temperature operation favors physisorption and results in higher adsorption capacity, although regeneration typically requires external heating [20]. In temperature swing adsorption (TSA) processes, adsorbents such as zeolites or carbon molecular sieves (CMS) are heated to release the captured CO_2. For example, microwave-assisted regeneration of zeolite 13X has been shown to significantly reduce regeneration time compared to conventional convective heating methods [15].

Conversely, certain chemisorbents require moderate to elevated temperatures to facilitate CO_2 uptake, particularly amine-modified materials that rely on thermal activation of reactive surface groups [21]. Consequently, thermal management becomes a critical design factor: excessive heat diminishes adsorption capacity, whereas controlled heating is necessary for effective regeneration. Optimizing this balance enhances overall process energy efficiency and operational longevity [28, 29]. Since adsorption performance is strongly governed by thermodynamic equilibrium and operating pressure, the combined influence of temperature and pressure on CO_2 capacity, separation efficiency, and

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regeneration energy must be evaluated simultaneously. The typical operational ranges and their corresponding effects on adsorption performance are summarized in Table 2.

Table 2. Effects of Temperature and Pressure on CO_2 Adsorption

Operating Condition	Temperature Range (°C)	Pressure Range (bar)	Effect on CO_2 Capacity	Effect on Separation Efficiency	Regeneration Energy	Typical Application	Ref
Low Temperature / High Pressure	25-40	1-10	High adsorption capacity (favorable equilibrium)	High selectivity (enhanced CO_2 loading)	Low (for PSA/VSA)	PSA for flue gas, biogas upgrading	[7, 24, 27]
Low Temperature / Low Pressure	20-35	0.0004-0.2	Moderate capacity (limited by partial pressure)	High affinity materials required	Low-Moderate	Direct Air Capture (DAC)	[2, 28]
Moderate Temperature	40-80	1-5	Decreasing capacity with temperature	Slight reduction in selectivity	Moderate	Industrial adsorption cycles	[22, 30]
High Temperature (TSA Regeneration)	80-150 (physisorbents)	0.1-1	Desorption dominates	Reduced separation efficiency during adsorption step	Moderate-High	TSA processes	[15,16,23]
High Temperature (Chemisorption activation)	50-120	1	Enhanced reaction kinetics (for amines)	High selectivity at low CO_2 partial pressure	High	Amine-functionalized sorbents	[4, 6, 21]
Vacuum Regeneration (VSA)	25-60	0.05-0.2	Lower equilibrium loading during desorption	Improved working capacity	Low-Moderate	VSA systems	[2 ,7]

As shown in Table 2, lower temperatures generally enhance CO_2 adsorption capacity due to the exothermic nature of the adsorption process. High-pressure conditions further increase CO_2 loading by shifting the equilibrium toward adsorption, which is particularly beneficial in PSA systems for post-combustion or biogas upgrading applications. Conversely, increasing temperature reduces equilibrium capacity but facilitates desorption during regeneration cycles, especially in TSA systems operating between 80-150 °C for physisorbents. For chemisorption-based materials such as amine-functionalized sorbents, moderate temperatures may enhance reaction kinetics and CO_2 uptake at low partial pressures; however, regeneration typically requires higher energy input. Vacuum-assisted regeneration reduces equilibrium loading during desorption, increasing working capacity while minimizing thermal energy consumption. Therefore, optimizing the interplay between temperature and pressure is essential for maximizing separation efficiency while minimizing energy penalty.

The thermodynamic trade-off between adsorption enthalpy and regeneration energy highlights the importance of designing materials with moderate heats of adsorption, balancing strong CO_2 affinity with energy-efficient desorption.

2.4. Adsorption Kinetics

Kinetics describe how rapidly CO_2 is captured, directly determining cycle time and throughput in practical adsorption systems. The adsorption of CO_2 typically involves several sequential steps, beginning with external mass transfer from

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the bulk gas phase to the particle surface, followed by intra-particle diffusion into the pore structure, and finally surface interaction or binding at active adsorption sites. These processes are commonly described using kinetic models such as the pseudo-first-order (PFO) model, which assumes that the adsorption rate is proportional to the number of unoccupied sites, and the pseudo-second-order (PSO) model, which assumes a chemisorption-controlled mechanism where the rate depends on the square of site availability. Boyd's model is frequently applied to distinguish between film diffusion and pore diffusion as the rate-limiting step.

In activated carbon systems, the pseudo-second-order and intraparticle diffusion models often provide the best fit to experimental data, indicating that CO_2 adsorption is governed by mixed control mechanisms involving both surface interaction and pore diffusion [10,22]. Structured adsorbents, such as gyroid zeolite monoliths or honeycomb composites, demonstrate improved kinetic performance due to enhanced mass transfer and reduced diffusion resistance, resulting from their engineered channel geometries [13,26].

2.5. Adsorption Equilibrium

The equilibrium capacity of an adsorbent is dictated by its adsorption isotherm, which relates the gas-phase concentration to the amount adsorbed at constant temperature. Commonly applied models include the Langmuir isotherm, which assumes monolayer adsorption on energetically uniform sites; the Freundlich model, an empirical approach suitable for heterogeneous surfaces; the Tóth and Sips models, which combine features of both Langmuir and Freundlich to improve fitting accuracy over a wider pressure range; and the Dubinin-Radushkevich (D-R) and Dubinin-Astakhov (DA) models, which are particularly suitable for describing adsorption in microporous carbons [22]. For example, the Sips model accurately described CO_2 adsorption on KOH-activated carbon, balancing micropore filling and surface heterogeneity [9]. Accurate equilibrium modeling enables prediction of working capacity and guides process design for PSA/VSA/TSA systems [19,20].

3. Equilibrium and Kinetic Models: Use, Interpretation, and Limitations

To understand and predict the adsorption behavior of carbon dioxide on solid sorbents, two key aspects must be modeled: equilibrium (isotherms) and kinetics. Isotherms describe how much CO_2 a sorbent can hold under equilibrium at constant temperature, while kinetic models explain how fast this equilibrium is achieved. Accurate modeling of both is essential for designing efficient industrial CO_2 capture systems using porous materials such as activated carbon, zeolite 13X, and composite monoliths.

The isotherm and kinetic models are retained here as the single consolidated modeling section. Earlier descriptive repetitions of these models in Section 2 should be interpreted only as brief physical context; detailed equations, assumptions, and limitations are presented here. Model selection should be based on mechanistic relevance and experimental range rather than goodness-of-fit alone. A high R^2 value does not establish that a model correctly represents adsorption physics, particularly when mass-transfer resistance, heterogeneity, or multicomponent competition is neglected.

3.1. Adsorption Isotherm Models

3.1.1. Langmuir Isotherm

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The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface with a finite number of identical adsorption sites. It is one of the most widely used models to evaluate the maximum adsorption capacity of sorbents. This model has been successfully applied to a variety of adsorbents, including KOH-activated biochars and zeolite-carbon composites, especially under dry CO_2 conditions [9, 26]. It enables estimation of the saturation capacity (q_m) and Langmuir constant (b), which relate to affinity between CO_2 and the sorbent.

3.1.2. Freundlich Isotherm

Unlike Langmuir, the Freundlich model is empirical and assumes heterogeneous surface energy and multilayer adsorption. It fits better to experimental data when the surface is non-uniform, which is common for activated carbons with broad pore size distributions [8]. In high-pressure adsorption systems or hybrid composite adsorbents, Freundlich constants help understand how CO_2 uptake scales with pressure, particularly at low partial pressures [22].

3.1.3. Tóth Isotherm

The Tóth isotherm is a three-parameter model that modifies the Langmuir equation to better fit moderately heterogeneous surfaces. It avoids the overestimation of uptake at high pressures common in Langmuir predictions. The Tóth model has shown better fitting for CO_2 adsorption on composite materials containing zeolite 13X and CMS, where both microporous and mesoporous structures are present [18, 26].

3.1.4. Sips (Langmuir-Freundlich) Isotherm

The Sips model is a hybrid of Langmuir and Freundlich models. It is particularly useful in systems where low-pressure behavior resembles Freundlich and high-pressure behavior resembles Langmuir. This makes it highly relevant for biochar-based carbons and functionalized zeolites [9, 22]. The Sips isotherm was found to best fit CO_2 adsorption on multi-pore carbons, indicating the presence of both high-energy and low-energy adsorption sites.

3.1.5. Dubinin-Radushkevich (D–R) Isotherm

The D–R model is especially suitable for microporous adsorbents, such as activated carbon and zeolite 13X. It assumes a Gaussian energy distribution of adsorption and helps in calculating the mean free energy of adsorption (E), indicating whether adsorption is physical ($E < 8$ kJ/mol) or chemical ($E > 16$ kJ/mol) [20, 22]. This model is particularly useful for studying CO_2 sorption in high-pressure and subcritical environments typical of PSA and VSA processes.

3.2. Adsorption Kinetic Models

3.2.1. Pseudo-First-Order (PFO) Model

The PFO model assumes that the rate of adsorption is proportional to the number of unoccupied sites. It is mathematically simple and provides reasonable fits during the early stages of adsorption. However, it often underestimates the final equilibrium loading for CO_2 capture [10].

3.2.2. Pseudo-Second-Order (PSO) Model

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The PSO model assumes that adsorption follows a bimolecular reaction mechanism and is often more accurate for chemisorption-dominated or cooperative adsorption processes. Many studies report that PSO provides the best fit for CO_2 adsorption on activated carbon and biochar, especially at moderate pressures [9, 10].

3.2.3. Boyd's Film Diffusion Model

Boyd's model is used to determine whether the adsorption rate is controlled by film diffusion (external boundary layer resistance) or intraparticle diffusion. A linear Boyd plot passing through the origin indicates that pore diffusion is rate-limiting [22]. This model is especially important for structured adsorbents like honeycomb monoliths, where external film resistance is often minimized, and internal mass transfer dominates [26].

3.2.4. Intraparticle Diffusion (Weber-Morris Model)

This model considers the movement of CO_2 molecules within the pores of the adsorbent particles. It helps distinguish between:

Stage I: External surface adsorption

Stage II: Gradual intra-particle diffusion

Stage III: Equilibrium

In multi-line plots, the initial slope corresponds to film diffusion, and the second slope represents pore diffusion [10, 22].

3.3. Comparison and Limitations of Kinetic and Isotherm Models

Various kinetic and equilibrium models have been employed to interpret CO_2 adsorption behavior on porous materials, including activated carbons, zeolites, and composite sorbents. Each model is derived based on specific assumptions regarding adsorption mechanism, surface homogeneity, or diffusion control. However, their applicability varies depending on material structure and operating conditions [7, 8]. A systematic comparison of the main kinetic and isotherm models, along with their assumptions and limitations in CO_2 capture studies, is presented in Table 3**.**

Table 3. Comparison and Limitations of Common Kinetic and Isotherm Models for CO_2 Adsorption

Model	Type	Main Assumption	Strength	Limitation	Ref
Pseudo-First-Order (PFO)	Kinetic	Rate proportional to unoccupied sites	Simple, good for early stage	Underestimates equilibrium capacity	[10]
Pseudo-Second-Order (PSO)	Kinetic	Chemisorption-controlled	Good fitting accuracy	May misinterpret diffusion effects	[9, 21]
Weber–Morris	Diffusion	Intraparticle diffusion control	Identifies multi-step behavior	Cannot confirm sole rate-limiting step	[22]
Boyd Model	Diffusion	Film vs pore diffusion separation	Distinguishes diffusion mechanisms	Requires linear fitting accuracy	[22]
Langmuir	Isotherm	Monolayer, homogeneous surface	Determines maximum capacity	Unrealistic for heterogeneous surfaces	[8]

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Freundlich	Isotherm	Heterogeneous surface	Good empirical fitting	No saturation prediction	[9]
Sips	Isotherm	Hybrid Langmuir–Freundlich	Good wide-pressure fitting	More complex parameter fitting	[22]
Tóth	Isotherm	Moderate heterogeneity	Accurate high-pressure behavior	Limited mechanistic meaning	[18]
Dubinin–Radushkevich	Isotherm	Micropore filling mechanism	Calculates adsorption energy	Limited for mesoporous systems	[20]

As summarized in Table 3, kinetic models such as the pseudo-first-order (PFO) and pseudo-second-order (PSO) equations are widely applied due to their simplicity and strong fitting performance. For instance, reported that the PSO model provided a better fit for CO_2 adsorption on activated carbon compared to PFO, suggesting that surface interaction plays a dominant role [10]. Similarly, observed that the PSO model accurately described adsorption kinetics on KOH-activated biochars, although diffusion effects could not be fully excluded [9]. Diffusion-based models, including the Weber–Morris intraparticle diffusion model, help distinguish multi-step adsorption mechanisms, particularly film diffusion and pore diffusion stages [22]. However, as noted in several studies, the presence of multi-linearity in Weber-Morris plots do not necessarily confirm that intraparticle diffusion is the sole rate-controlling step.

Regarding equilibrium models, the Langmuir model assumes monolayer adsorption on homogeneous surfaces and has been successfully applied to activated carbons and zeolite 13X [8, 27]. In contrast, the Freundlich and Sips models better describe heterogeneous surfaces, especially in biochar-derived materials [9]. Advanced three-parameter models such as Tóth and Dubinin-Radushkevich (D-R) have been shown to provide improved accuracy at high pressures and for microporous systems [20, 22]. Nevertheless, deviations often occur under multicomponent or humid conditions, highlighting the intrinsic limitations of purely empirical fitting approaches.

For clarity and practical reference, the governing mathematical expressions of the most frequently used kinetic and isotherm models in CO_2 adsorption studies are compiled in Table 4. These equations form the basis for parameter estimation and model validation in experimental investigations [7, 8].

Table 4. Governing Equations of Common Kinetic and Isotherm Models Used in CO_2 Adsorption Studies

Model	Governing Equation	Ref
Pseudo-First-Order (PFO)	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	[10, 22]
Pseudo-Second-Order (PSO)	$t/q_t = 1/(k_2 q_e^2) + t/q_e$	[9, 10]
Weber-Morris	$q_t = k_id\ t^{1/2} + C$	[22]
Boyd Model	$Bt = -0.4977 - \ln(1 - F)$	[20, 22]
Langmuir	$q_e = (q_m\ b\ C_e) / (1 + b\ C_e)$	[8, 27]
Freundlich	$q_e = K_f\ C_e^{1/n}$	[7, 9]
Sips	$q_e = (q_m\ (b\ C_e)^n) / (1 + (b\ C_e)^n)$	[9, 22]
Tóth	$q_e = (q_m\ b\ C_e) / [(1 + (b\ C_e)^t)^{1/t}]$	[18, 22]

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Dubinin-Radushkevich	$qe = qm \exp(-B\varepsilon^2)$	[20, 22]

3.4. Literature Selection and Basis for Performance Comparison

Studies used in the comparative tables were selected to represent the principal sorbent families, recent structured/honeycomb developments, and studies reporting quantitative adsorption, regeneration, stability, or process-level information relevant to CO_2 capture. Priority was given to peer-reviewed studies with clearly reported operating conditions and measurable performance indicators. Foundational studies were retained when they established widely used mechanisms or benchmark materials. Comparisons were not treated as strictly head-to-head when temperature, pressure, CO_2 partial pressure, humidity, gas composition, adsorbent form, or regeneration protocol differed. Accordingly, the reported ranges in the comparative tables are synthesis ranges rather than claims of standardized testing. To improve interpretability, the revised manuscript explicitly distinguishes equilibrium capacity from working capacity and identifies feed composition, humidity, pressure, temperature, cycle conditions, and structural form as key sources of uncertainty. A standardized benchmarking basis recommended for future studies is: CO_2 concentration and balance gas reported explicitly; controlled H_2O and acidic-gas levels; adsorption and regeneration temperatures and pressures; flow rate and sorbent geometry; cycle time; working capacity; pressure drop; and regeneration energy defined with a stated system boundary.

4. Sorbent Families and Structure–Property Relationships

The efficiency of CO_2 adsorption depends not only on process parameters, but also critically on the nature of the adsorbent. The ideal adsorbent for CO_2 capture must have high selectivity, large adsorption capacity, rapid kinetics, easy regenerability, and long-term stability. Over the past two decades, intensive research has been dedicated to developing and optimizing porous materials such as activated carbons, zeolites, and structured sorbents, each offering unique properties and trade-offs.

Across sorbent families, the reported equilibrium capacity is an incomplete basis for comparison. Carbon materials generally offer low cost and good regeneration tolerance, whereas zeolites provide strong CO_2 affinity but are vulnerable to water competition. MOFs offer exceptional tunability but may face synthesis cost, stability, and scale-up constraints. Hybrid and structured sorbents can improve transport and mechanical properties but introduce binder, shaping, and active-phase dilution effects. These trade-offs explain why the ranking of materials changes with capture duty and operating conditions.

4.1. Carbon-Based Sorbents

Activated carbon (AC) and biochar-derived materials are among the most widely used physisorbents for CO_2 capture due to their high surface area, tunable pore size distribution, low cost, and excellent regenerability These materials primarily function through physisorption, relying on van der Waals forces and pore confinement to capture CO_2. Their performance is heavily dependent on microporosity (<2 nm), especially ultramicropores (<0.7 nm), which provide strong interactions with CO_2 molecules [8, 27].

Surface functionalization, such as with nitrogen-doping or KOH activation, enhances CO_2 uptake by increasing basicity and creating high-energy adsorption sites. These modifications allow the tailoring of textural and chemical properties to match specific pressure and temperature conditions. For example, KOH-activated carbon derived from mixed sewage sludge and pine sawdust exhibited high CO_2 uptake due to a balance of microporosity and surface basic groups [9].

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While carbon adsorbents perform well under dry conditions, their capacity often drops significantly in the presence of moisture. Their hydrophobic nature can help mitigate this effect compared to more hydrophilic materials like zeolites [2].

The structural characteristics governing CO_2 adsorption in carbon-based sorbents are schematically illustrated in Figure 3, emphasizing the role of ultramicropores and surface functionalities. As shown in Figure 3, carbon-based sorbents capture CO_2 primarily through physisorption within ultramicropores (<0.7 nm), where pore confinement enhances interaction potential. Surface functional groups such as nitrogen- or oxygen-containing moieties may further increase CO_2 affinity by introducing localized polarity. The hierarchical pore structure enables rapid diffusion while maintaining high adsorption capacity, particularly under dry conditions.

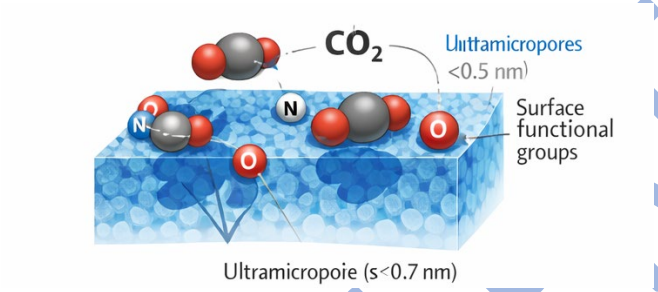


Fig. 3. Schematic representation of CO_2 adsorption in carbon-based sorbents highlighting ultramicropore filling and surface functional groups.

Carbon-based adsorbents, including activated carbons, biochars, carbon molecular sieves (CMS), and nitrogen-doped porous carbons, are widely investigated for CO_2 capture due to their tunable pore structure, chemical stability, hydrophobicity, and relatively low regeneration energy. Their adsorption performance strongly depends on micropore volume (<0.7 nm), surface functionality, and operating pressure [9, 31]. To provide a quantitative comparison of recent advances, representative studies published between 2020 and 2026 are summarized in Table 5, including adsorption conditions, adsorbent dosage, CO_2 capacity, and regeneration performance.

Table 5. Representative Studies on CO_2 Adsorption Using Carbon-Based Adsorbents

Carbon Material	T (°C)	P (bar)	Adsorbent Amount	CO_2 Capacity (mmol/g)	Regeneration / Performance	Ref
KOH-activated biochar	25	1	0.5 g	3.12	Stable over 5 cycles	[9]
Modified sludge activated carbon	25	5	0.3 g	5.21	High-pressure stability	[31]
Carbon monolith (hierarchical)	30	1	1 g	4.50	Low pressure drop; reusable	[27]
Carbon composite with zeolite	25	1	0.4 g	4.70	Microwave-assisted regeneration	[32]
Activated carbon (reviewed data)	25	1	0.5 g	2.5–4.0	Suitable for PSA	[7]

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Surface-modified activated carbon	25	1	0.5 g	3.8	Improved selectivity	[8]
Carbon–zeolite composite	25	1	0.5 g	6.35	Improved thermal conductivity	[33]

As summarized in Table 5, carbon-based adsorbents exhibit CO_2 adsorption capacities typically ranging from 2.5 to 6.35 mmol/g under ambient conditions. Activated carbons and biochar-derived materials demonstrate moderate capacities at atmospheric pressure [8, 9], primarily governed by micropore filling mechanisms. High-pressure studies reveal significantly enhanced uptake, who reported 5.21 mmol/g at 5 bar, indicating strong pressure dependence typical of physisorption-dominated systems [31]. Nitrogen doping and surface functionalization further improve CO_2 affinity through increased surface polarity.

Composite and structured carbons exhibit improved thermal management and regeneration efficiency. For instance, demonstrated effective microwave-assisted regeneration, reducing desorption time [32]. Similarly, reported enhanced effective thermal conductivity in carbon-zeolite composites, leading to improved cyclic stability [33]. Compared to zeolites, carbon-based sorbents generally offer lower sensitivity to humidity and reduced regeneration energy, making them particularly attractive for PSA and VSA applications [7]. However, their selectivity at very low CO_2 partial pressures may be inferior to strongly polar zeolitic frameworks. A comparative overview of carbon-based sorbents, highlighting their structural properties and performance metrics, is summarized in Table 6.

Table 6. Comparative Summary of Carbon-Based Adsorbents for CO_2 Capture

Carbon Type	Surface Area (m^2/g)	CO_2 Capacity (mmol/g, 25°C, 1 bar)	Humidity Resistance	Regeneration Energy	Main Advantage	Main Limitation	Ref
Activated Carbon	800-2000	2.5-4.0	High	Low	Low cost, hydrophobic	Moderate selectivity	[7, 8, 27]
KOH-Activated Biochar	1000-2500	3.0-5.0	Moderate	Low	Tunable porosity	Structural variability	[9, 12, 31]
N-doped Carbon	900-1800	3.5-4.5	Moderate	Low-Moderate	Enhanced CO_2 affinity	Complex synthesis	[8]
Carbon Monolith	700-1500	4.0-4.5	High	Low	Low pressure drop	Slightly lower density	[18, 27]
Carbon-Zeolite Composite	800-1600	4.5-6.3	Moderate	Moderate	Improved thermal management	Binder dilution effect	[26, 32, 33]

As shown in Table 6, carbon materials exhibit moderate-to-high adsorption capacities with excellent regeneration characteristics. Their hydrophobic nature makes them advantageous under humid conditions, although their selectivity at low CO_2 partial pressure remains lower than polar frameworks such as zeolites.

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4.2. Zeolites and Silica-Based Sorbents

Zeolites are crystalline aluminosilicates characterized by uniform and well-defined microporous structures, exhibiting high CO_2 selectivity, particularly at low pressures [30, 34]. various types, zeolite 13X is the most extensively used due to its relatively large pore size (~10 Å), high cation density that promotes strong electrostatic interactions with CO_2 molecules, and excellent thermal stability under cyclic adsorption-desorption conditions [23, 35]. Zeolites are highly hydrophilic, and in humid environments, water competes with CO_2 for adsorption sites, significantly reducing capacity. However, surface hydrophobization (e.g., with silane compounds) has been shown to enhance moisture resistance [12]. Recent work on 3D-printed gyroid monoliths of zeolite 13X demonstrated excellent formability, high mechanical strength, and comparable adsorption capacity to powdered forms, but with lower pressure drop and faster kinetics [13]. Zeolites exhibit good thermal stability and are compatible with TSA systems. Regeneration methods such as microwave heating have shown promising reductions in energy use and cycle time [15, 16].

The adsorption mechanism of CO_2 in zeolite and silica-based sorbents is illustrated in Figure 4, where electrostatic interactions between CO_2 molecules and exchangeable cations are highlighted. These cationic sites generate strong electrostatic fields that enhance CO_2 adsorption via quadrupole interactions. Figure 4 demonstrates the crystalline aluminosilicate framework of zeolite 13X, containing negatively charged AlO_4^- units balanced by exchangeable cations (e.g., Na^+ or Ca^{2+}). The uniform micropore structure ensures high selectivity at low partial pressures, although water molecules may compete for adsorption sites in humid environments.

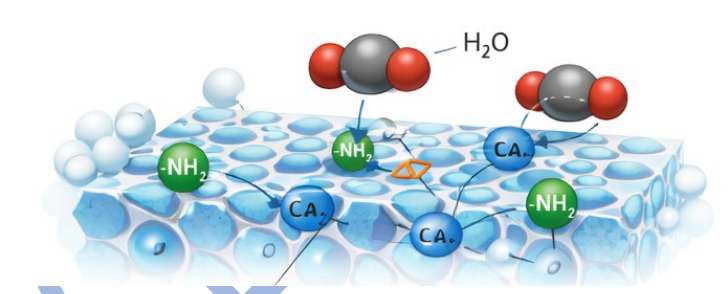


Fig. 4. Structural framework of zeolite 13X showing cationic adsorption sites and CO_2 interaction within microporous channels

Zeolites, particularly NaX (13X), CaX, and modified Y-type structures, remain among the most extensively investigated adsorbents for CO_2 capture due to their high microporosity, strong electrostatic fields, and thermal stability. Their adsorption performance strongly depends on operating temperature, pressure, and cation composition [30, 34]. To provide a systematic overview of recent experimental findings, Table 7 summarizes representative studies published between 2020 and 2026, highlighting adsorption conditions, adsorbent dosage, CO_2 capacity, and regeneration performance.

Table 7. Representative Studies on CO_2 Adsorption Using Zeolite-Based Adsorbents

Zeolite Type	T (°C)	P (bar)	Adsorbent Amount	CO_2 Capacity (mmol/g)	Regeneration / Performance	Ref
13X	35	1	0.5 g	3.38	Working capacity 2.69 mmol/g; stable TSA cycles	[30]
13X (solar-derived)	25	1	1 g	2.15	Stable at ambient conditions	[36]

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Cation-exchanged Zeolite-Y	30	1	0.3 g	2.89	Capacity decreased with T; selective over CH_4/N_2	[34]
13X	25	1	0.5 g	3.41	Comparable to geopolymer adsorbent	[14]
13X composite	25	1	0.4 g	6.35 (dry)	Capacity reduced to 2.69 mmol/g under humid conditions	[33]
13X	25	1	1 g	6.80	Stable up to 600-800 °C regeneration	[35]
13X (TSA system)	30	0.1	0.5 g	>4.0	High regeneration rate under TSA	[23]
13X in PSA	25	1-5	0.8 g	4.7	Effective for CH_4/CO_2 separation	[24]
13X	25	1	0.2 g	3.0–4.0	Successfully modeled via Langmuir & ML	[37]

As summarized in Table 7, zeolite 13X consistently demonstrates high CO_2 adsorption capacities at ambient conditions, typically ranging from 2.0 to 6.8 mmol/g depending on pressure and humidity [30, 35]. The strong electrostatic interaction between CO_2 molecules and exchangeable cations (Na^+, Ca^{2+}) enhances adsorption affinity at low partial pressures. However, increasing temperature was associated with a significant decrease in equilibrium CO_2 uptake in [34], with the uptake declining from 2.89 to 0.79 mmol/g. Similarly, humidity negatively impacts adsorption performance due to competitive adsorption, as reported by [33], who observed a drop from 6.35 to 2.69 mmol/g under moist conditions.

In contrast, several studies confirm excellent thermal stability and regeneration performance of 13X, particularly under temperature swing adsorption (TSA) processes [23, 35]. High-temperature stability up to 600-800 °C enables repeated adsorption-desorption cycles without significant structural degradation. Overall, recent literature confirms that zeolite-based adsorbents remain highly competitive for post-combustion capture and PSA applications, although sensitivity to moisture and performance decline at elevated temperatures remain key challenges. The main performance indicators of zeolite-based adsorbents are comparatively presented in Table 8. Zeolite 13X demonstrates the highest CO_2 affinity due to strong electrostatic interactions with exchangeable cations. However, moisture sensitivity remains the primary operational challenge.

Table 8. Comparative Summary of Zeolite-Based Adsorbents

Zeolite Type	Si/Al Ratio	CO_2 Capacity (mmol/g, 25 °C, 1 bar)	Sensitivity to Moisture	Regeneration Temp (°C)	Selectivity	Main Limitation	Ref
13X (NaX)	1-1.5	3.0-6.8	High	120-200	Very High	Water competition	[11, 30, 35]
CaX	~1.2	3.5-5.0	High	150-250	High	Energy intensive regeneration	[11, 34]
Zeolite-Y	2-5	2.5-4.0	Moderate	120-200	High	Lower micropore volume	[25, 34]
Modified 13X	1-2	4.0-6.5	Moderate	100-180	Very High	Stability under cycling	[8, 13, 14]

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4.3. Metal-Organic Frameworks (MOFs)

Metal-Organic Frameworks (MOFs) represent a highly versatile class of crystalline porous materials composed of metal ions or clusters coordinated to organic linkers, forming extended three-dimensional networks. Their exceptionally high surface areas (often exceeding 1000-6000 m^2/g), tunable pore sizes, and adjustable chemical functionality make them among the most promising adsorbents for CO_2 capture.

Unlike conventional physisorbents such as activated carbons and zeolites, MOFs offer precise control over pore environment and adsorption energetics. CO_2 adsorption in MOFs occurs primarily through physisorption; however, the presence of open metal sites (OMS) or functionalized linkers can significantly enhance specific interactions via Lewis acid-base interactions, hydrogen bonding, or quadrupole interactions [7].

Certain MOFs, such as Mg-MOF-74, HKUST-1, and UiO-66, have demonstrated high CO_2 uptake at low and moderate pressures due to strong interactions between CO_2 molecules and exposed metal centers. Additionally, amine-functionalized MOFs introduce chemisorptive contributions, further enhancing low-pressure performance particularly relevant for direct air capture (DAC) applications. The structural architecture of MOFs and their tunable adsorption sites are schematically illustrated in Figure 5. The modular architecture and tunable adsorption environment of MOFs are illustrated in Figure 5, highlighting the role of metal nodes, organic linkers, and open metal sites in enhancing CO_2 affinity. As shown in Figure 5, MOFs consist of metal clusters connected by organic linkers to form highly ordered porous frameworks. The presence of open metal sites generates strong localized electric fields that enhance CO_2 adsorption through specific interactions. Functionalized linkers may further increase adsorption affinity by introducing polar groups capable of interacting with CO_2. This tunability enables precise control of pore size and adsorption energetics, distinguishing MOFs from conventional porous adsorbents.

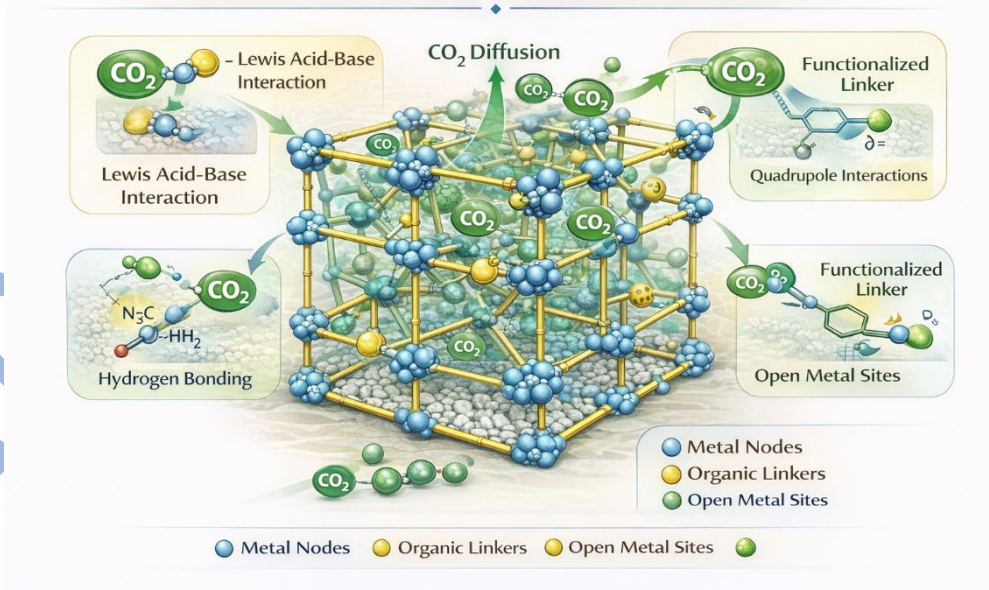


Fig. 5. Representative structure of a MOF illustrating metal nodes, organic linkers, open metal sites, and tunable CO_2 adsorption interactions**.**

Table 9. Representative Studies on CO_2 Adsorption Using MOFs

MOF Type	Surface Area (m^2/g)	T (°C)	P (bar)	CO_2 Capacity (mmol/g)	Key Findings	Ref

Mg-MOF-74	1200-1500	25	1	6-8	Strong interaction with open metal sites	[7]
Amine-functionalized MOF	1000-1800	40	1	8-10	Enhanced low-pressure uptake	[28]
Hybrid MOF-amine	900-1500	50	1	7-9	High selectivity; increased regeneration energy	[2]
UiO-66	900-1200	25	1	4-6	High structural stability	[23]
HKUST-1	1500-1800	25	1	5-7	High initial uptake; moisture sensitivity	[12]
Functionalized MOF composite	1200-2000	30	1	9-12	Improved cyclic stability	[24]
MOF-based composite monolith	1000-1600	25	1	6-8	Reduced pressure drops in structured form	[14]

As summarized in Table 9, MOFs typically exhibit CO_2 adsorption capacities ranging from 4 to 12 mmol/g at ambient conditions, surpassing many conventional physisorbents. Materials with open metal sites, such as Mg-MOF-74, demonstrate particularly strong affinity for CO_2 due to enhanced electrostatic interactions. Amine-functionalized MOFs show superior low-pressure performance, making them attractive candidates for DAC systems [28]. However, the introduction of chemisorptive functionalities increases regeneration energy requirements and may reduce long-term stability [2].

Despite their high capacity and tunability, MOFs face challenges related to hydrothermal stability, moisture sensitivity, and synthesis cost. Frameworks such as UiO-66 demonstrate improved chemical robustness, offering better resistance to humid environments [23]. Overall, MOFs offer exceptional material-level performance, although scale-up and economic feasibility remain critical considerations for industrial deployment.

Table 10. Comparative Evaluation of Representative MOFs for CO_2 Capture

MOF Type	CO_2 Capacity	Selectivity	Moisture Stability	Regeneration Energy	Industrial Readiness	Ref
Mg-MOF-74	High (6-8)	High	Moderate	Moderate	Emerging	[7, 38]
HKUST-1	Moderate–High	High	Low	Moderate	Limited	[7, 12]
UiO-66	Moderate	Moderate	High	Low-Moderate	Promising	[23, 38]
Amine-Functionalized MOF	Very High	Very High	Moderate	High	Developing	[2, 28]
MOF Composite	High	High	Improved	Moderate	High Potential	[14, 24, 38]

4.4. Functionalized and Hybrid Sorbents

Functionalized and hybrid sorbents represent an advanced class of materials designed to enhance CO_2 selectivity and low-pressure adsorption performance through chemical modification of porous supports. Unlike purely physisorptive materials such as activated carbons or zeolites, these sorbents introduce reactive surface groups most commonly amine functionalities that chemically interact with CO_2 molecules. Amine-functionalized materials, including amine-grafted silica, polyethyleneimine (PEI)-impregnated carbons, and amine-modified mesoporous supports, rely on chemisorption

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mechanisms involving carbamate or bicarbonate formation [21]. These systems are particularly effective under low CO_2 partial pressures, such as in direct air capture (DAC) applications.

The dual adsorption mechanism in functionalized and hybrid sorbents is schematically illustrated in Figure 6, highlighting the interaction between CO_2 molecules and reactive amine groups within a porous scaffold. As depicted in Figure 6, CO_2 molecules first diffuse through the porous support, where physical adsorption may occur within micropores. Simultaneously, reactive amine groups chemically bind CO_2 to form carbamate or bicarbonate species. This dual adsorption mechanism enhances CO_2 affinity at low partial pressures while maintaining reasonable diffusion rates. However, the formation of stronger chemical bonds increases regeneration energy requirements compared to purely physisorptive systems.

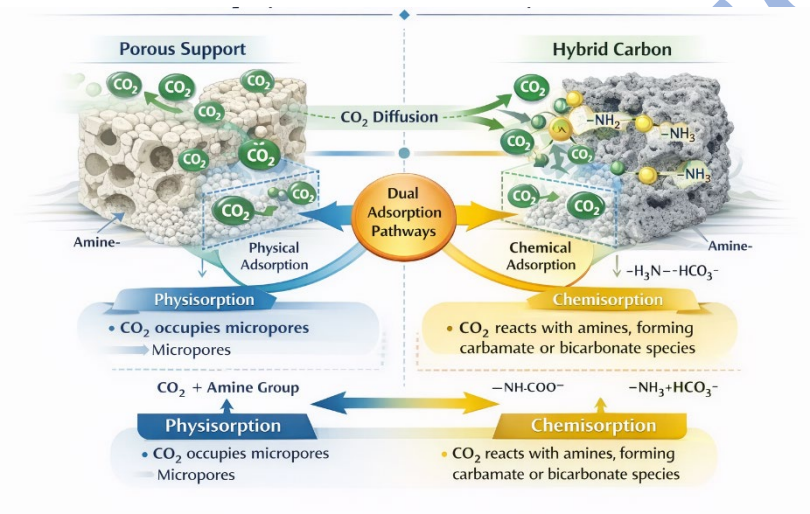


Fig. 6. Mechanism of CO_2 capture in functionalized and hybrid sorbents illustrating chemisorption via amine groups and dual adsorption pathways within porous supports.

Hybrid sorbents combine physical and chemical adsorption pathways by integrating porous scaffolds with reactive functional groups. The porous matrix ensures rapid diffusion and high surface area, while amine sites enhance CO_2 affinity and selectivity. However, these materials typically require higher regeneration energy compared to purely physisorptive systems due to stronger binding interactions [7]. Recent experimental studies on functionalized and hybrid CO_2 sorbents are summarized in Table 11.

Table 11. Representative Studies on Functionalized and Hybrid CO_2 Sorbents

Sorbent Type	Functional Group	T (°C)	P (bar)	CO_2 Capacity (mmol/g)	Regeneration Characteristics	Ref
Amine-silica composite	$-NH_2$	25	1	5.2	Thermal regeneration at 90-120 °C	[21]
PEI-impregnated biochar	PEI	30	1	4.8	Stable over 5 cycles	[9]
Amine-grafted mesoporous silica	$-NH_2$	40	1	6.5	Effective at low CO_2 partial pressure	[28]
Hybrid carbon–amine sorbent	Mixed amines	50	1	7.1	High selectivity; higher energy penalty	[2]
Electrified amine sorbent	Polyamine	60	0.4	5.8	Induction heating regeneration	[29]

Surface-modified carbon	Oxygen/N groups	25	1	3.8	Improved affinity	[8]

As shown in Table 12, functionalized and hybrid sorbents generally exhibit CO_2 adsorption capacities between 4.0 and 7.1 mmol/g under ambient conditions. Their performance is particularly advantageous at low CO_2 partial pressures, where physisorption-based materials typically show reduced uptake. Amine-grafted silica and hybrid carbon-amine systems demonstrate enhanced selectivity due to chemical bonding mechanisms [2, 21]. However, this stronger interaction increases regeneration temperature requirements, often ranging between 80-120 °C. PEI-impregnated and nitrogen-doped carbons provide a balance between capacity and regeneration energy [9]. Electrified regeneration methods, such as induction heating, further improve energy efficiency and reduce thermal gradients [29]. Despite their advantages, long-term stability and amine degradation under humid conditions remain key technical challenges.

Table 12. Comparative Evaluation of Functionalized and Hybrid Sorbents

Sorbent Type	Mechanism	CO_2 Capacity	Selectivity	Regeneration Energy	Humidity Tolerance	Industrial Potential	Ref
Amine-Silica	Chemisorption	High	Very High	High	Moderate	High (DAC)	[2, 6, 21]
PEI-Carbon	Hybrid	High	High	Moderate-High	Moderate	High	[7, 9]
N-Doped Carbon	Enhanced Physisorption	Moderate	Moderate	Low	High	Moderate	[8]
Alkali-Modified Sorbent	Chemical	Moderate–High	High	High	Low	Emerging	[21, 39]
Electrified Amine Sorbent	Chemisorption	High	Very High	Moderate (electrified)	Moderate	Very High	[14, 16]

4.5. Structured and Honeycomb Adsorbents

Structured and honeycomb adsorbents represent an advanced engineering strategy in CO_2 capture systems, where macroscopic geometry is optimized to enhance process efficiency rather than solely improving intrinsic adsorption capacity [21, 26]. Unlike conventional packed beds composed of randomly distributed particles, structured systems utilize engineered channel geometries such as honeycomb monoliths, gyroid structures, extruded lattices, and 3D-printed architectures to precisely control fluid dynamics and thermal transport within the adsorption unit [14, 27].

These structures typically incorporate active adsorbent phases (e.g., zeolite 13X, activated carbon, carbon molecular sieves, or hybrid composites) that are coated or integrated onto ceramic, metallic, or polymeric supports [18]. The defining feature of honeycomb and monolithic architectures is the presence of parallel flow channels, which enable uniform gas distribution, significantly reduce pressure drop, improve mass transfer rates, enhance radial heat dissipation, and provide superior mechanical stability [23, 33].

In cyclic adsorption systems such as PSA, VSA, and TSA, these structural advantages directly translate into lower compression energy requirements, faster regeneration kinetics, and improved working capacity [23, 32]. The structural and process-level differences between conventional packed beds and engineered honeycomb monolithic adsorbents are illustrated in Figure 7, emphasizing the influence of channel geometry on gas distribution, pressure drop, and thermal management during cyclic CO_2 adsorption. As shown in Figure 7, conventional packed beds consist of randomly arranged granular particles that create tortuous flow paths and heterogeneous void distributions. This configuration

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results in non-uniform gas velocity profiles, higher pressure drops, and limited radial heat transfer, which may lead to channeling and localized thermal gradients during adsorption-desorption cycles.

In contrast, structured honeycomb monolithic adsorbents feature parallel and uniformly distributed flow channels that significantly reduce pressure drop and improve flow uniformity. The engineered open-channel architecture enhances radial heat dissipation, allowing faster thermal equilibration and improved regeneration efficiency. Furthermore, the controlled geometry facilitates integration with advanced regeneration techniques such as microwave and induction heating, enabling volumetric and energy-efficient desorption. Overall, Figure 7 demonstrates that while intrinsic material adsorption capacity may be comparable between packed and structured configurations, the macroscopic structural design of honeycomb systems substantially improves process efficiency, energy consumption, and operational stability in cyclic CO_2 capture applications.

Parameter	Packed Bed (pellets/beads)	Monolith / Honeycomb (structured)	Remarks
Productivity (kg CO_2 h^{-1} m^{-3})	2.4	1.2	Higher in packed bed due to larger adsorbent inventory
Pressure drop (at same superficial velocity)	~10^2 times higher	~10^0 times (reference)	Monolith shows ~two orders of magnitude lower pressure drop
Heat transfer coefficient (W m^{-2} K^{-1})	10 – 25	50 – 250	Improved heat transfer in monolith due to open channels
Mass transfer (performance)	★★★☆☆ (Moderate)	★★★★☆ (High)	Shorter diffusion path in structured channels
Sorbent inventory per reactor volume	High	Lower	Lower inventory in monolith reduces working capacity
Manufacturing complexity	Low	High	Monolith shaping and coating are more complex
Typical applications	High-capacity post-combustion capture	Low-pressure-drop processes, DAC, mobile/compact units	Selection depends on application constraints

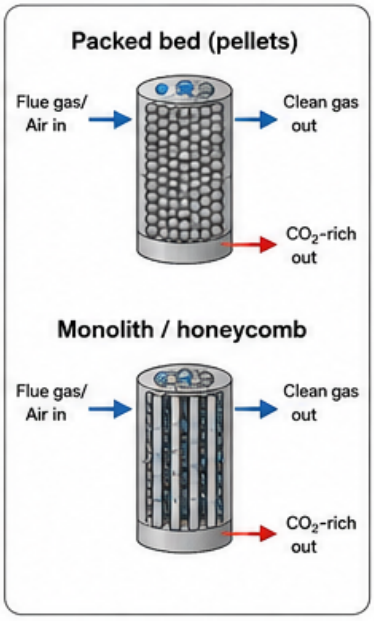


Fig. 7. Process-level comparison of packed-bed and monolithic adsorbents for cyclic CO_2 capture, highlighting productivity, pressure drop, heat and mass transfer, and manufacturing trade-offs.

Honeycomb monoliths are especially attractive for industrial-scale applications because they maintain structural integrity under repeated thermal cycling. The periodic channel geometry reduces axial dispersion and prevents channeling phenomena commonly observed in packed beds [18]. Additionally, structured adsorbents facilitate integration with electrified regeneration technologies. Microwave and induction heating can be applied more effectively in monolithic systems due to improved thermal conductivity pathways and reduced thermal gradients [23, 32].

Table 13. Representative Studies on Honeycomb and Monolithic CO_2 Adsorbents

Structure Type	Active Phase	T (°C)	P (bar)	CO_2 Capacity (mmol/g)	Process Advantage	Ref
Honeycomb monolith	13X + Activated Carbon	25	1	3.2	Very low pressure drop	[18]
Monolithic TSA reactor	13X	30	0.1	>4.0	Fast thermal regeneration	[23]
Structured pellets	13X	35	1	3.38	Stable working capacity	[30]
Honeycomb composite	Zeolite–Carbon	25	1	6.35	Improved thermal conductivity	[33]

Monolithic structured bed	13X	25	1	3.41	Long-term cyclic stability	[14]
Structured Zeolite-Y	Zeolite-Y	30	1	2.89	Enhanced CO_2/CH_4 selectivity	[34]
Microwave-assisted monolith	13X composite	25	1	4.7	Reduced desorption time	[32]

As shown in Table 13, honeycomb and monolithic adsorbents exhibit CO_2 capacities ranging from approximately 2.8 to 6.35 mmol/g under ambient conditions. Although these values are comparable to powdered sorbents, the primary benefit of structured architectures lies in improved process-level efficiency rather than higher intrinsic adsorption capacity. Honeycomb geometries significantly reduce pressure drop compared to granular packed beds, thereby lowering compressor energy requirements [18]. In TSA systems, monolithic configurations enhance radial heat transfer, leading to faster regeneration cycles and improved productivity [23].

Composite honeycomb systems integrating carbon phases improve effective thermal conductivity, reducing hotspot formation and enhancing cyclic stability [33]. Furthermore, microwave-assisted regeneration demonstrates shorter desorption times and lower energy penalties compared to conventional convective heating [32]. Thus, structured honeycomb adsorbents represent a shift from material-centered optimization to system-integrated design.

Table 14. Performance Comparison of Adsorbent Configurations

Parameter	Packed Bed	Honeycomb Monolith	Composite Honeycomb	3D-Printed Lattice	Ref
Pressure Drop	High	Very Low	Low	Low	[14, 18, 23]
Flow Uniformity	Moderate	High	High	Very High	[13, 27]
Heat Transfer Efficiency	Limited	Moderate–High	High	High	[28, 33]
CO_2 Capacity	High	Moderate–High	High	Moderate	[26, 30]
Regeneration Compatibility	Conventional heating	TSA / Microwave	Electrified regeneration	Advanced systems	[16, 29, 32]
Scalability	Moderate	High	Very High	Emerging	[14, 17, 18]

While structured adsorbents may exhibit slightly reduced gravimetric adsorption capacity due to binder dilution or lower active phase fraction, their superior fluid dynamic behavior and thermal management significantly enhance system productivity and energy efficiency. In large-scale PSA and TSA units, pressure drop reduction can result in substantial operational cost savings. Moreover, structured systems are particularly suitable for modular direct air capture (DAC) units and indoor air purification technologies, where compact design and flow uniformity are critical. Nevertheless, fabrication cost, mechanical durability under long-term cycling, and optimization of coating thickness remain technical challenges requiring further research.

5. Critical Assessment of Carbon-Based Sorbents

Activated carbon (AC) remains one of the most prominent solid sorbents for CO_2 capture, due to its wide availability, high surface area, tunable pore structure, and favorable regeneration properties. Unlike chemically reactive materials, activated carbon captures CO_2 primarily through physisorption, making it ideal for pressure or temperature swing cycles. This section explores how specific surface area (SSA), microporosity, temperature, surface chemistry modification, and regeneration conditions affect CO_2 uptake in carbonaceous adsorbents.

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5.1. Specific Surface Area (SSA) and CO_2 Uptake

SSA is a key parameter for gas adsorption. Higher SSA generally provides more active sites for CO_2 interaction. However, not all surface area is equally effective only pores that match the size and energy characteristics of CO_2 molecules contribute significantly to adsorption. ACs with SSA >1000 m^2/g showed significantly improved CO_2 capacities under dry conditions [8]. However, the effective surface area, particularly in the micropore range (<2 nm), is more important than total SSA [27]. Thus, ultramicropores (<0.7 nm) play a dominant role in CO_2 capture, as they maximize interaction strength through pore confinement [9]. Excess mesoporosity, on the other hand, may increase SSA without meaningfully enhancing uptake.

5.2. Role of Microporosity and Pore Size Distribution

The adsorption performance of activated carbons (ACs) is strongly governed by their microporous structure and pore size distribution, particularly under low-pressure conditions such as post-combustion capture and direct air capture (DAC). Activated carbons derived from biochar or industrial waste streams can be engineered to exhibit a high volume of micropores, which play a dominant role in CO_2 uptake at ambient pressure. The enhanced adsorption capacity arises from the overlapping adsorption potential fields within narrow pores, which significantly strengthen CO_2-surface interactions.

KOH-activated carbon prepared from sewage sludge and pine sawdust achieved a high micropore volume of approximately 0.5 cm^3/g, resulting in CO_2 uptake values up to 4.8 mmol/g at 1 bar [9]. The chemical activation process not only increased total surface area but also generated ultramicropores that are particularly effective for CO_2 adsorption. Similarly, confirmed that micropore filling is the dominant adsorption mechanism at low temperatures, and that optimizing pore entrance size facilitates improved diffusion of CO_2 molecules into internal adsorption sites [31].

The effectiveness of microporosity is closely related to pore size distribution. Narrow micropores, especially those centered near the kinetic diameter of CO_2 (~0.33 nm), generate stronger adsorption potential fields due to spatial confinement effects. This confinement enhances physisorption strength at ambient conditions, leading to higher adsorption capacity and improved selectivity relative to larger mesopores. However, excessively narrow pores may limit diffusion kinetics, indicating that an optimal balance between ultramicropore volume and accessible pore entrances is essential for maximizing overall adsorption performance.

5.3. Effect of Temperature on CO_2 Adsorption

As an exothermic process, CO_2 adsorption on activated carbon (AC) is thermodynamically favored at lower temperatures and decreases progressively with increasing temperature. At ambient conditions (25-30 °C), adsorption capacity typically reaches its maximum, as the equilibrium shifts toward adsorption and intermolecular interactions between CO_2 and the carbon surface are strongest. However, as temperature rises, the equilibrium shifts toward desorption, resulting in a noticeable decline in uptake capacity.

Experimental evidence supports this thermodynamic behavior. [22] reported that increasing the temperature from 25°C to 70 °C led to approximately a 40% reduction in CO_2 adsorption capacity on South African coal-derived activated carbon [22]. Similarly, in dynamic breakthrough experiments, observed earlier breakthrough times at elevated temperatures, indicating weaker adsorption interactions and reduced residence time of CO_2 within micropores [28].

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These findings highlight an important operational trade-off in temperature swing adsorption (TSA) systems employing activated carbon. While lower temperatures maximize capture capacity, higher temperatures are required for efficient desorption and regeneration. Therefore, process optimization must carefully balance adsorption efficiency during the capture phase with the thermal energy input required for regeneration, ensuring both high working capacity and overall energy efficiency.

5.4. Surface Chemistry and Functionalization

Although activated carbons (ACs) primarily operate through physisorption mechanisms, surface chemistry modification can substantially enhance their CO_2 adsorption performance. Tailoring the chemical functionality of the carbon surface introduces basic or polar groups that strengthen CO_2-surface interactions beyond purely van der Waals forces. One of the most common modification strategies is chemical activation using alkaline agents such as KOH or NaOH, which not only increases microporosity but also generates basic surface sites that improve CO_2 affinity [9]. The resulting ultramicroporous structure enhances pore confinement effects, while the introduced basic functionalities promote stronger quadrupole interactions with CO_2 molecules.

Nitrogen doping represents another effective approach to improving adsorption performance. The incorporation of nitrogen-containing groups introduces electron-donating functionalities that increase surface basicity and enhance CO_2-surface electrostatic interactions [8]. Depending on the nitrogen configuration (e.g., pyridinic, pyrrolic, or graphitic nitrogen), adsorption affinity and selectivity can be significantly improved, particularly at low CO_2 partial pressures.

Oxidative surface treatments further modify carbon materials by introducing oxygen-containing functional groups such as hydroxyl and carboxyl moieties. These polar groups can enhance CO_2 binding, especially under humid conditions where hydrogen bonding interactions may contribute to adsorption [2]. However, excessive oxidation may reduce micropore volume or alter surface hydrophobicity, potentially affecting overall adsorption capacity.

Moreover, functional groups introduced through surface modification can serve as anchoring sites for additional active components such as metal oxides or amines. While this hybridization strategy can markedly increase CO_2 selectivity and low-pressure uptake, it shifts the adsorption mechanism partially toward chemisorption. Consequently, regeneration energy requirements increase due to stronger CO_2 binding interactions, potentially reducing the energetic advantage typically associated with physisorptive carbon materials.

5.5. Regeneration Temperature and Energy

One of the key advantages of activated carbon (AC) is its relatively low regeneration energy, as CO_2 adsorption occurs predominantly through physisorption mechanisms. Because the interaction between CO_2 molecules and the carbon surface is governed mainly by van der Waals forces and pore confinement effects, desorption can typically be achieved at moderate temperatures ranging from 80 °C to 150 °C. This comparatively low thermal requirement makes AC particularly attractive for cyclic processes such as PSA, VSA, and moderate-temperature TSA systems.

Experimental investigations further support the energetic benefits of AC regeneration. Microwave-assisted regeneration in AC-packed beds resulted in significantly faster desorption kinetics and lower overall energy consumption compared with conventional convective heating [16]. The volumetric and selective nature of microwave heating reduces thermal gradients and shortens cycle times, thereby improving process efficiency. In addition, heat-transfer modeling of fluidized-bed adsorption systems demonstrated the feasibility of rapid regeneration cycles, attributed to the moderate

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thermal conductivity and relatively low heat capacity of activated carbon [28]. These thermal properties facilitate efficient heat distribution within the bed and enable faster heating and cooling transitions during cyclic operation. However, excessive regeneration temperatures (>200 °C) can damage surface functionalities or reduce micropore volume over time, thereby reducing performance. Regeneration energy is a critical parameter in evaluating the industrial feasibility of solid adsorbents for CO_2 capture. The temperature required for desorption, the heat capacity of the adsorbent, and the adsorption enthalpy collectively determine overall process energy demand.

Regeneration of Activated Carbon (AC)

One of the primary advantages of activated carbon (AC) is its relatively low regeneration energy, as CO_2 adsorption occurs predominantly via physisorption. Desorption typically requires temperatures in the range of 80-150 °C, depending on pressure conditions and pore structure. Microwave regeneration in AC-packed beds resulted in significantly faster desorption kinetics and reduced energy consumption compared with conventional convective heating [16]. Similarly, thermal management studies of fluidized-bed systems have confirmed that rapid regeneration cycles are feasible due to the moderate thermal conductivity and relatively low heat capacity of AC [28]. However, excessive regeneration temperatures (>200°C) may degrade surface functional groups or reduce micropore volume over repeated cycles, leading to gradual performance decline.

Regeneration of Zeolites

In contrast to AC, zeolites particularly 13X exhibit stronger electrostatic interactions with CO_2 due to cation quadrupole interactions. As a result, higher regeneration temperatures are typically required, generally in the range of 120-250 °C for complete desorption under TSA conditions. Zeolites also possess higher heats of adsorption compared to carbon materials, increasing the thermal energy requirement. Furthermore, their hydrophilic nature introduces additional regeneration penalties under humid conditions, as water molecules strongly bind to adsorption sites and require substantial energy for removal [30]. Nevertheless, zeolites demonstrate excellent thermal stability and can withstand repeated high-temperature cycles (up to 600-800 °C in some cases) without significant structural degradation [35].

Regeneration of MOFs

Metal-Organic Frameworks (MOFs) exhibit regeneration behavior that depends strongly on framework chemistry and adsorption mechanism. For purely physisorptive MOFs, regeneration temperatures are typically 100-200 °C. However, MOFs with open metal sites or chemisorptive functionalization may require higher desorption temperatures due to stronger CO_2 binding interactions. Amine-functionalized MOFs, in particular, may require regeneration temperatures of 120-250 °C, similar to chemisorbent systems. A key limitation is hydrothermal stability: some MOFs (e.g., HKUST-1) may undergo structural degradation under repeated high-temperature or humid regeneration conditions. More robust frameworks such as UiO-66 demonstrate improved thermal and chemical stability [12].

Table 15. Comparison of Regeneration Temperature and Energy Requirements

Adsorbent Type	Adsorption Mechanism	Typical Regeneration Temperature	Heat of Adsorption	Moisture Sensitivity	Regeneration Energy Demand	Thermal Stability	Ref

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Activated Carbon	Physisorption	80-150 °C	Low	Moderate-Low	Low	Moderate	[8, 16, 28]
Zeolite 13X	Electrostatic Physisorption	120-250 °C	Moderate–High	High	Moderate-High	Very High	[23, 30, 35]
MOFs (Physisorptive)	Physisorption	100-200 °C	Moderate	Moderate	Moderate	Moderate	[7, 23, 38]
MOFs (Functionalized)	Physisorption + Chemisorption	120-250 °C	High	Moderate-High	High	Framework-dependent	[2, 8, 28]

As shown in Table 15, activated carbon generally requires the lowest regeneration temperature and energy due to its physisorption-dominated mechanism and relatively weak CO_2 binding interactions. This makes AC particularly attractive for PSA and VSA applications where rapid cycling is required. Zeolites, although offering higher selectivity and affinity, require greater regeneration energy because of stronger electrostatic interactions and water competition effects. However, their superior thermal stability allows operation under harsh cyclic conditions.

MOFs occupy an intermediate position. While some MOFs exhibit regeneration behavior similar to zeolites, their structural stability under humid and high-temperature conditions varies significantly depending on framework chemistry. Functionalized MOFs may incur regeneration energy penalties comparable to chemisorbent systems. Overall, the trade-off between adsorption strength and regeneration energy remains a central design consideration in CO_2 capture processes. Materials with high adsorption enthalpy often require higher regeneration energy, highlighting the importance of balancing capacity and process efficiency.

6. CO_2 Adsorption on Zeolites: Structure, Ion Exchange, and Water Sensitivity

Zeolites are a class of crystalline aluminosilicates known for their uniform microporosity, high thermal stability, and selective gas adsorption properties. Among available solid adsorbents, zeolites particularly type 13X and beta are widely studied for CO_2 capture, especially under post-combustion or indoor air conditions. Their performance depends significantly on cation type, pore geometry, surface polarity, and resistance to humidity.

6.1. Role of Cation Exchange

Zeolite frameworks contain negatively charged AlO_4^- tetrahedra that are balanced by exchangeable cations such as Na^+, K^+, and Ca^{2+}. These cations play a crucial role in CO_2 adsorption, as they act as high-energy electrostatic adsorption sites, influence the quadrupole interaction between CO_2 molecules and the framework, and modulate overall adsorption affinity and capacity. Na^+ and Ca^{2+}exchanged zeolites, particularly NaX and CaA, exhibit strong interactions with CO_2 due to localized electrostatic fields within their microporous structures [11]. Similarly, ion-exchange modification of 13X zeolite enabled tuning of both selectivity and regeneration behavior [15]. [25] further showed that post-functionalization of beta zeolites allows precise control over cation positioning within micropores, thereby influencing adsorption capacity as well as water tolerance [25]. The type of cation directly affects adsorption enthalpy; smaller cations such as Li^+ generate stronger electrostatic fields, which can increase CO_2 capacity but may reduce regenerability due to stronger binding interactions.

6.2. Pore Size and Structural Characteristics

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The pore aperture and cage structure of zeolites play a decisive role in determining the accessibility of CO_2 molecules, diffusional limitations within the framework, and the potential for competitive adsorption with other species such as H_2O or N_2. Structural characteristics strongly influence separation performance and operational suitability under varying process conditions. Zeolite 13X, which possesses a FAU topology with a relatively large pore size of approximately 10 Å, exhibits high CO_2 uptake at low pressure due to its open supercage structure and high cation density. In contrast, beta zeolite, characterized by medium-sized pores of around 6.6 Å, can be better suited for humid environments when appropriately tuned through cation exchange or surface modification. Frameworks such as mordenite and CHA-type zeolites feature tighter pore structures that enhance molecular sieving and selectivity; however, their smaller pore apertures generally limit total adsorption capacity [17, 40]. Overall, zeolite frameworks with moderate pore sizes in the range of 7–10 Å and accessible cage structures support rapid CO_2 diffusion and strong adsorption interactions, making them particularly suitable for vacuum and pressure swing adsorption (PSA/VSA) systems.

6.3. Hydrophilicity vs. Hydrophobicity

Zeolites are inherently hydrophilic due to the polar nature of the aluminosilicate framework and the presence of exposed exchangeable cations. This characteristic facilitates the adsorption of water molecules, which reduces the availability of active CO_2 adsorption sites, competes for the same cationic centers, and inhibits mass transfer by partially blocking micropores. In humid flue gases or ambient air conditions, moisture can significantly decrease CO_2 adsorption capacity and slow adsorption kinetics [11]. Water molecules are typically adsorbed preferentially before CO_2, displacing weakly physisorbed CO_2 species and occupying electrostatic sites that would otherwise contribute to selective CO_2 capture.

6.4. Improving Hydrophobicity and Moisture Resistance

To mitigate the adverse effects of humidity, researchers have developed various hydrophobization strategies aimed at reducing water adsorption while maintaining CO_2 capture performance. Surface modification is one of the most widely explored approaches. For instance, zeolite 13X was modified using octadecyltrimethoxysilane (ODTMS), forming a hydrophobic surface layer that reduced water uptake while retaining CO_2 adsorption capacity and improving selectivity under humid conditions [12]. Similarly, post-synthetic treatments were applied to beta zeolites to adjust wall polarity, resulting in enhanced CO_2/H_2O selectivity [25].

In addition to surface chemistry modification, structural engineering has also been employed to address moisture sensitivity. 3D-printed gyroid monoliths incorporating zeolite 13X improved resistance to water condensation by promoting convective flow and minimizing stagnant zones within the structure [13]. Hydrophobic modifications may also alter the dominant adsorption mechanism, shifting it from cation-dominated physisorption toward hydrophobic pore-filling behavior, which can enhance CO_2 selectivity over water within specific temperature and pressure ranges.

7. Structured and Honeycomb Adsorbents: From Geometry to Process Design

Traditional fixed beds composed of powdered or granular adsorbents suffer from high pressure drop, non-uniform flow distribution, and poor heat and mass transfer, particularly in large-scale applications. To overcome these limitations, structured adsorbents, notably monolithic or honeycomb materials, have emerged as a next-generation platform for

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intensified CO_2 capture systems. These adsorbents are engineered to combine the high capacity and selectivity of microporous materials with the flow and thermal advantages of macroscopic, structured geometries.

The process value of a honeycomb or monolithic structure is governed by the interaction between channel geometry, superficial velocity, mass-transfer resistance, heat transfer, and pressure drop. A structured sorbent should therefore be evaluated at reactor level using volumetric productivity and cycle time in addition to gravimetric capacity. Increasing channel size can reduce pressure drop but may increase external mass-transfer resistance; increasing solid loading can improve capacity per reactor volume but may increase heat-transfer limitations. The optimum geometry is consequently application-specific.

7.1. Structural Features of Monolithic Adsorbents

Monoliths are three-dimensional porous bodies characterized by a periodic arrangement of parallel channels, typically in square, hexagonal, or gyroid configurations, and are often fabricated using ceramic, polymeric, or composite frameworks. The internal surfaces of these channels are coated or impregnated with adsorptive materials such as zeolite 13X, activated carbon, or carbon molecular sieves [13, 26]. The open-cell geometry of honeycomb structures maximizes gas-solid contact area, provides short diffusion pathways, and enables uniform flow distribution throughout the adsorption unit. Furthermore, hierarchical pore structures combining micro-, meso-, and macropores can be incorporated to facilitate multiscale mass transport, thereby significantly enhancing adsorption and desorption kinetics [17].

7.2. Enhanced Mass Transfer and Kinetics

One of the main performance advantages of monolithic adsorbents lies in their high mass transfer rates, which directly influence breakthrough behavior and cycle times in pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and temperature swing adsorption (TSA) systems demonstrated that hybrid monoliths composed of activated carbon, zeolite 13X, and carbon molecular sieves exhibited superior CO_2 uptake and faster adsorption kinetics compared to equivalent powder mixtures [26]. Similarly, confirmed that structured sorbents, owing to improved internal convection and lower thermal resistance, outperform conventional packed beds during dynamic capture-regeneration cycles [28]. The enhanced mass transfer characteristics reduce axial dispersion and enable more complete utilization of the active phase even at short contact times, which is particularly critical for compact or mobile carbon capture systems.

7.3. Low Pressure Drop and Energy Efficiency

In contrast to granular or pelletized beds, monolithic structures provide laminar flow pathways, negligible bed channeling, and extremely low pressure drop, resulting in more stable and predictable fluid dynamics during operation. These advantages have been experimentally validated in multiple studies. For example, 3D-printed gyroid zeolite monoliths achieved CO_2 capture performance comparable to powdered forms while reducing pressure drop by more than 80% [13]. Similarly, the open cellular geometry of mordenite-based monoliths enabled efficient gas handling even at high volumetric flow rates, facilitating their application in direct air capture (DAC) systems [17]. By minimizing pressure losses, structured adsorbents significantly reduce blower and compressor energy requirements, making them particularly well suited for energy-sensitive operations such as DAC and biogas upgrading.

7.4. Comparison with Powdered Adsorbents

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To quantify the advantages of structured monoliths, Table 16 compares key performance metrics of monolithic vs. powdered CO_2 adsorbents, based on material behavior, system integration, and energy demand. While powdered adsorbents may offer higher raw surface area per gram, monoliths translate more of their material into usable performance per unit volume, which is more relevant for modular and portable systems.

Table 16. Comparative Summary: Monolithic vs. Powder Adsorbents

Feature	Powder Adsorbents	Monolithic Adsorbents
Structure	Random packed particles	Regular structured channels
Pressure Drop	High	Very low
Mass Transfer	Limited by tortuous paths	Enhanced by open channels
Mechanical Strength	Fragile under compression	High durability
Regeneration	Slow, heterogeneous	Fast, uniform
Industrial Integration	Challenging (fluidization, pressure loss)	Compact and modular

7.5. Industrial Applications and Scalability

Recent process modeling illustrates this trade-off quantitatively. A 2025 techno-economic study of a structured DAC adsorber reported a reference productivity of 1.2 kg CO_2/ m^3h for a monolith versus 2.4 kg CO_2/m^3h for a packed bed, while the monolith reduced pressure drop and associated fan work by approximately two orders of magnitude. The same study reported capture costs above 1500 € per tonne CO_2 for the modeled 100 kt CO_2/yr case. These results demonstrate that low pressure drop does not automatically translate into lower total capture cost; reactor productivity, sorbent inventory, fabrication cost, and regeneration requirements must be optimized simultaneously [39].

The unique features of monolithic adsorbents make them highly suitable for industrial deployment, particularly in applications where space is limited, energy efficiency is critical, and rapid cycling is required. In direct air capture (DAC) systems, monoliths fabricated from mordenite zeolites with hierarchical porosity have demonstrated strong potential under low CO_2 concentrations (~400 ppm), providing scalable and regenerable platforms for decentralized carbon capture [17]. In indoor CO_2 control applications, modified zeolite 13X monoliths with hydrophobic surface coatings are being investigated for air purification in confined environments, where stable performance under moderate humidity is essential [12]. For flue gas treatment, composite honeycomb monoliths incorporating carbon and zeolite phases have been evaluated in post-combustion capture systems due to their thermal durability and rapid regeneration characteristics [26]. Furthermore, advances in 3D printing and extrusion technologies allow precise control over monolith geometry, material distribution, and mechanical integrity, thereby facilitating efficient scale-up from laboratory prototypes to commercial adsorption modules [13].

8. Competitive Gases, SO_2 Poisoning, and Sorbent Degradation

In practical CO_2 capture scenarios ranging from post-combustion streams to direct air capture (DAC) carbon dioxide is rarely present in isolation. The presence of co-existing gases such as N_2, CH_4, SO_2, and H_2O vapor introduces complex competitive adsorption dynamics that significantly alter the performance, selectivity, and stability of porous adsorbents. The selectivity of a material under these multicomponent conditions is governed by adsorption energetics, molecular competition, kinetic constraints, and framework hydrophilicity.

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8.1. Humidity and Water Vapor: Competitive Adsorption and Pore Blocking

Water vapor remains the most disruptive co-component in CO_2 adsorption processes, particularly in hydrophilic frameworks such as unmodified zeolites and certain carbon-based adsorbents. Due to its strong polarity and small kinetic diameter (2.65 Å), H_2O can readily access and occupy cationic adsorption sites, especially in materials like zeolite 13X [11]. Consequently, water molecules displace CO_2 from high-energy adsorption sites, induce swelling or partial blockage of hydrophilic pores, and reduce overall accessibility within the pore network. As a result, the effective CO_2 adsorption capacity decreases in a non-linear manner depending on relative humidity levels [8]. Surface modification strategies, including silanization and functionalization with hydrophobic moieties such as octadecyltrimethoxysilane (ODTMS), have been developed to mitigate these effects. [12] demonstrated that hydrophobized 13X retained approximately 70% of its dry CO_2 capacity at 60% relative humidity, whereas the unmodified counterpart exhibited a capacity loss exceeding 80% [12].

8.2. Nitrogen (N_2): Inert Diluent or Competitive Adsorbate?

In flue gas or ambient air, N_2 is typically the dominant background component. Although nitrogen possesses a negligible quadrupole moment and exhibits weak physisorption interactions with most adsorbent surfaces, its high partial pressure approximately 70–80% in air leads to a dilution of the CO_2 partial pressure, thereby reducing the thermodynamic driving force for adsorption. In materials with low intrinsic selectivity, N_2 may also occupy pore space competitively, further limiting effective CO_2 uptake. Khastkhodaei et al. reported that hybrid monoliths composed of carbon, zeolite, and carbon molecular sieves maintained high CO_2/N_2 selectivity values exceeding 30 at low pressures, underscoring the importance of adsorbent selectivity coefficients in mixed-gas systems [26]. In post-combustion capture applications, adsorbent selectivity must therefore be sufficiently high to compensate for the thermodynamic penalty associated with low CO_2 partial pressures, typically around 0.15 atm relative to N_2.

8.3. Methane (CH_4): Competitive in Biogas Upgrading

In biogas systems, CH_4 is the main component and must be separated from CO_2. Despite its larger molecular size and lower polarizability than CO_2, CH_4 competes for adsorption sites in certain nonpolar or weakly polar adsorbents. Kong et al. demonstrated that hierarchically porous zeolite monoliths exhibited CO_2/CH_4 selectivity >50, attributed to favorable electrostatic interactions with CO_2 [17]. The pore size and charge density of the framework, as well as cation placement, strongly determine CO_2-CH_4 separation efficiency. Activated carbons and CMS tend to show lower selectivity, unless tuned via narrow ultramicropores (~0.3–0.5 nm), which exclude CH_4 kinetically.

8.4. Sulfur Dioxide (SO_2): Reactive Poisoning and Irreversibility

SO_2 should be treated as both a competitive adsorbate and a chemically reactive contaminant. In low-Si/Al zeolites such as 13X, strong interactions with cationic and basic sites can lead to preferential uptake and progressive site passivation. Recent experimental evidence indicates that prolonged SO_2 exposure can reduce surface area, pore volume, and crystallinity, with sulfur-containing species remaining after thermal regeneration. This provides a mechanistic pathway from contaminant exposure to irreversible loss of CO_2 capacity: SO_2 adsorption → occupation/passivation of active sites → formation of sulfur-containing surface species → textural and structural deterioration → reduced CO_2 working

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capacity. The magnitude of degradation depends on SO_2 partial pressure, exposure time, humidity, temperature, and the specific adsorbent formulation [35].

SO_2 is a strongly adsorbing acidic gas that presents a dual threat:

1. Preferential adsorption over CO_2 due to higher polarizability and stronger interaction with basic sites.
2. Chemical reactivity that can irreversibly alter or deactivate adsorption sites, particularly amine-functionalized or basic-modified surfaces.

Amornsin et al. studied zeolite 13X under simulated flue gas conditions and showed that SO_2 exposure led to a permanent loss in CO_2 capacity, even after thermal regeneration [15]. This irreversible degradation is driven by sulfation of cationic sites and framework oxidation.

For materials designed for flue gas applications, SO_2 pre-removal or the use of SO_2-resistant coatings is necessary. Monolithic adsorbents with hydrophobic coatings or hierarchical porosity have shown improved tolerance, likely due to limited SO_2 diffusion into deeper adsorption sites [17].

In multicomponent systems, adsorbent selectivity and stability are governed not only by intrinsic textural and chemical properties but also by their response to competitive adsorbates like H_2O, N_2, CH_4, and SO_2. Strategies such as framework hydrophobization, hierarchical structuring, and cation engineering offer promising pathways to maintain high CO_2 uptake under realistic operating environments.

8.5. Nitrogen Oxides (NO_x) and Combined Acid-Gas Effects

For post-combustion applications, impurity tolerance should be evaluated after pretreatment and under residual contaminant concentrations representative of the intended process. Reporting only dry, single-component CO_2 uptake can substantially overestimate field performance.

NO and NO_2 are less consistently studied than SO_2, but their presence can become important when adsorption is applied to combustion-derived flue gas. Depending on surface chemistry, NO_2 can interact strongly with basic or amine-containing sites and may promote oxidation or formation of strongly retained surface species. The resulting effects can include competitive occupation of active sites, changes in surface functionality, and additional irreversible capacity loss. Importantly, NO_x effects should not be generalized across all sorbents because the magnitude and reversibility depend on NO_x speciation, concentration, humidity, temperature, and adsorbent chemistry. Combined $SO_2/NO_x/H_2O$ exposure is therefore a more realistic durability test than single-contaminant screening.

8.6. Chemical and Physical Degradation Mechanisms

Sorbent degradation can occur through several coupled pathways. For amine-functionalized materials, oxidative attack, thermal decomposition, volatilization or loss of the active amine phase, and irreversible reaction with acidic contaminants can reduce the number of accessible reactive sites. For zeolites, water-induced competition, cation redistribution, dealumination under severe conditions, and acidic-gas exposure can alter adsorption sites and pore accessibility. For carbonaceous sorbents, oxidation and deposition of strongly adsorbed species can modify surface chemistry and pore structure. In structured materials, degradation of binders, cracking, attrition, or loss of contact between the active phase and the support can additionally increase mass-transfer resistance or pressure drop. Long-term testing should therefore report both adsorption capacity retention and structural/mechanical integrity.

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9. Regeneration and Electrified Adsorption Cycles

Efficient regeneration is a cornerstone of sustainable CO_2 adsorption systems. The reusability of solid sorbents, particularly in cyclic processes such as Pressure Swing Adsorption (PSA), Temperature Swing Adsorption (TSA), and Vacuum Swing Adsorption (VSA), critically depends on the ease, cost, and durability of the regeneration method. Emerging techniques like microwave and induction heating offer promising alternatives to conventional thermal methods, especially in the context of energy optimization and process intensification.

9.1. Temperature Swing Adsorption (TSA)

Temperature swing adsorption (TSA) involves the desorption of CO_2 by increasing the temperature, typically within the range of 80-150 °C for physisorbents such as activated carbon or zeolites. The applied thermal energy overcomes the adsorption enthalpy, thereby releasing the captured CO_2 from the adsorbent surface. Abd et al. emphasized that activated carbons are particularly suitable for TSA processes due to their relatively low adsorption enthalpy and favorable thermal conductivity, which allow regeneration at comparatively moderate temperatures [183]. However, prolonged thermal cycling may lead to degradation of surface functionalities, especially in amine-impregnated or chemically modified adsorbents, potentially reducing long-term performance stability [7]. Although TSA is thermodynamically straightforward, it is generally slower than pressure-based processes, as regeneration is often limited by heat transfer into the adsorbent bed, particularly in dense pellets or powdered configurations.

9.2. Vacuum Swing Adsorption (VSA) and Pressure Swing Adsorption (PSA)

These methods regenerate the adsorbent by either reducing pressure, as in vacuum swing adsorption (VSA), or increasing pressure, as in pressure swing adsorption (PSA), to induce CO_2 desorption. They are widely implemented in modular capture systems and flue gas treatment processes, particularly in applications where energy or time constraints make temperature swing adsorption (TSA) less feasible. Khastkhodaei et al. reported that monolithic adsorbents composed of zeolite 13X, activated carbon, and carbon molecular sieves exhibited rapid desorption under mild vacuum conditions (~0.1 bar), with minimal performance degradation over multiple adsorption-desorption cycles [26]. In addition, Goel and Rabha modeled VSA performance in fluidized bed reactors and highlighted the influence of pore structure and particle size on optimizing desorption rate and cycle duration [28]. PSA and VSA methods are especially effective for low-heat-capacity physisorbents; however, they may not achieve complete regeneration when strongly chemisorbed species are present.

9.3. Microwave-Assisted Regeneration

Microwave regeneration provides volumetric and selective heating of the adsorbent bed, substantially enhancing regeneration rates and overall energy efficiency. The dielectric loss factor of materials such as zeolite 13X and carbon-based sorbents enables rapid internal heating with minimal thermal gradients, allowing efficient desorption of CO_2. Boylu et al. demonstrated effective CO_2 desorption from activated carbon beds using microwave pulses, achieving shorter cycle times and lower energy consumption compared to conventional oven heating [16]. Similarly, Amornsin et al. reported that microwave-regenerated zeolite 13X maintained both structural integrity and adsorption capacity over repeated cycles, even in the presence of residual humidity [15]. This approach is particularly promising for distributed carbon capture systems where rapid and energy-efficient regeneration is essential. However, successful implementation

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requires careful reactor design and uniform electromagnetic field distribution to prevent localized overheating and hot spot formation.

9.4. Electrical/Electrothermal Swing Adsorption (ESA/eTSA)

Electrical or electrothermal swing adsorption uses electrical energy to generate heat directly or indirectly within the sorbent bed, most commonly through resistive/Joule heating. Conductive sorbents can be heated directly, while electrically conductive inserts, fibers, foams, or coatings can provide indirect heating for otherwise non-conductive sorbents. Compared with externally heated TSA, the principal process opportunity is rapid and localized heat generation, potentially shortening desorption and cooling steps and enabling modular operation. Recent reviews identify Joule heating as one of the more mature electrified heating routes, while also highlighting persistent challenges in temperature uniformity, electrical-to-thermal conversion efficiency, rapid cycling, and scale-up. ESA should therefore be distinguished from microwave and induction heating: all are electrified regeneration approaches, but they differ in the mechanism by which electrical energy is converted into heat and in their requirements for material conductivity or electromagnetic response [40,41].

Emerging technologies such as induction heating utilize alternating magnetic fields to rapidly heat magnetic or electrically conductive sorbents, including hybrid monoliths and metal-functionalized frameworks [30] proposed the use of electrically responsive monolithic structures to enable precise and localized heating, thereby reducing energy losses and enhancing process intensification [29]. This approach allows instantaneous temperature control, facilitates modular system integration, and is compatible with renewable electricity sources, making it particularly attractive for electrified CO_2 capture plants. However, successful implementation requires careful material design to ensure compatibility with magnetic heating mechanisms, and the long-term effects of repeated thermal shocks on sorbent stability remain areas that require further investigation.

9.5. Regeneration Stability and Cyclic Performance

A critical consideration for any regeneration method is material stability under cyclic operating conditions. Adsorbents must maintain high cyclic CO_2 capacity, mechanical integrity, and resistance to pore collapse or functional group degradation to ensure long-term process viability. Studies by Kim et al. and Amornsin et al. indicate that hydrophobically modified zeolites preserve their adsorption performance over 20-50 regeneration cycles, whereas unmodified counterparts experience gradual capacity decline due to water-induced cation migration and associated structural alterations.

The regeneration methods reviewed here cannot be ranked by a single energy number because the reported studies use different boundaries and often report either heat supplied or electrical input rather than total cycle energy. TSA is mature and straightforward but carries sensible-heating and heat-loss penalties. VSA/PSA can reduce thermal demand but shifts the burden toward vacuum or compression work and is sensitive to working capacity at low pressure. Microwave and induction heating can reduce thermal inertia and enable rapid, localized heating, but electrical-to-thermal efficiency and temperature uniformity become decisive. ESA/eTSA offers direct electrical heating and strong compatibility with electrified operation, but conductive pathways, heat distribution, durability, and scale-up must be demonstrated. Meaningful comparison therefore requires the same basis: energy per mole of CO_2 captured, working capacity, productivity, cycle time, heat/electricity losses, and system boundary.

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10. Comparative Performance, Techno-Economics, and Application-Based Selection

The effective deployment of CO_2 adsorption technologies depends not only on uptake capacity but also on regeneration efficiency, operational costs, and material durability over repeated cycles. These performance indicators are strongly interdependent and must be carefully balanced to satisfy the techno-economic requirements of practical applications such as post-combustion capture, direct air capture (DAC), and biogas upgrading. A comprehensive evaluation therefore requires consideration of gravimetric and volumetric CO_2 capacity under relevant operating conditions, the energy demand associated with thermal or vacuum regeneration, the estimated material and process cost per unit of CO_2 captured, and cyclic stability under varying moisture, temperature, and pressure conditions. Table 17 presents a comparative summary of the main classes of CO_2 adsorbents reviewed in this work.

Table 17. Master comparison of representative CO_2 sorbent classes under reported literature conditions

Adsorbent Type	CO_2 Capacity (mmol/g)	Regeneration Energy (kJ/mol)	Cost Level	Cycling Stability	Ref
Activated Carbon (AC)	2.5 - 4.0	20 - 40	Low	High (50+ cycles)	[7, 8]
Zeolite 13X	3.5 - 5.0	30 - 50	Low-Moderate	Moderate (degrades with humidity)	[11, 12]
Functionalized Zeolite	2.8 - 4.2	35 - 60	Moderate	Improved (hydrophobized)	[12, 25]
Carbon Molecular Sieve (CMS)	2.0 - 3.5	25 - 45	Moderate	High	[26]
Monolithic Composite (Zeolite + AC + CMS)	3.0 - 4.5	25 - 40	Moderate-High	Excellent (low degradation)	[13, 17]
Amine-Impregnated Sorbents	2.0 - 4.0	60 - 90	High	Variable (degrades chemically)	[6, 7]
MOFs (for comparison)	4.0 - 6.0	50 - 80	Very High	Often poor (sensitive to moisture)	[38]

Values are literature-reported ranges obtained under non-identical conditions and therefore should not be interpreted as standardized head-to-head measurements. Direct ranking by capacity or regeneration energy is inappropriate unless temperature, pressure, CO_2 partial pressure, humidity, gas composition, sorbent form, cycle definition, and energy boundary are matched.

10.1. Process-Level Performance Metrics and Techno-Economic Trade-offs

For structured adsorbents, material-level capacity must be translated into process-level metrics. The key indicators are working capacity (the loading difference between adsorption and regeneration states), volumetric productivity, pressure drop, heat-transfer rate, cycle time, sorbent inventory, electricity or thermal demand, and sorbent replacement rate. CAPEX is influenced by the reactor, vacuum/compression equipment, heat-transfer system, electrical heating hardware, and the cost of shaping the sorbent. OPEX is driven primarily by regeneration energy, pressure management, gas handling, maintenance, and replacement. A monolith may therefore justify a higher manufacturing cost if its lower pressure drops, improved heat transfer, or compactness reduces total process cost. Conversely, a monolith with poor active-phase loading or slow mass transfer may lose its theoretical process advantage [39,42].

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10.2. Performance Trade-offs and Practical Implications

While zeolites (particularly 13X) offer high CO_2 uptake, their sensitivity to humidity necessitates surface modification or environmental control. In contrast, activated carbons, though slightly lower in capacity, are cost-effective and highly regenerable via low-temperature TSA or VSA. Composite monolithic adsorbents, such as those based on hybrid zeolite-carbon structures, balance performance with mechanical and thermal resilience. These structures also exhibit lower pressure drop and enhanced regeneration efficiency, particularly in microwave or vacuum-driven systems [13, 26]. Amine-functionalized sorbents, while offering strong CO_2 affinity under ambient conditions, require high regeneration energy and are prone to oxidative or thermal degradation, limiting their long-term applicability without chemical stabilization.

10.3. Application-Based Sorbent Selection Framework

Sorbent selection should begin with the capture duty rather than with the highest reported equilibrium capacity. For post-combustion flue gas, humidity and acidic contaminants make water/impurity tolerance and moderate regeneration energy central criteria; hydrophobically modified zeolites and carbon-zeolite structured composites are therefore attractive candidates when their cyclic stability is demonstrated under realistic gas mixtures. For DAC, high affinity at very low CO_2 partial pressure, low heat of regeneration, rapid kinetics, and tolerance to variable humidity become dominant criteria. For biogas upgrading, CO_2/CH_4 selectivity, pressure-swing working capacity, and fast mass transfer are more important. For compact or decentralized systems, pressure drop, volumetric productivity, and modular electrified regeneration may dominate material-level capacity. This application-first framework prevents the common error of ranking sorbents using a single metric measured under incompatible laboratory conditions.

10.4. Toward Sorbent Selection for Scalable Deployment

The selection of a sorbent is highly application-specific. In post-combustion flue gas treatment, where humidity levels are significant and the partial pressure of CO_2 is moderate (approximately 0.15 bar), hydrophobically modified zeolites or composite monoliths provide a balanced combination of adsorption performance and economic feasibility [12, 17]. In direct air capture (DAC) systems, where CO_2 concentration is substantially lower, adsorbents must exhibit high affinity at low partial pressures while maintaining low regeneration energy requirements. In this context, microwave-regenerated structured sorbents demonstrate considerable potential [15]. For biogas upgrading applications, carbon molecular sieves (CMS) or tailored zeolites with precisely controlled pore structures enable selective separation of CO_2 from CH_4. Overall, the future of CO_2 adsorption technologies is likely to focus on structured and hybrid sorbents that combine high adsorption capacity, low regeneration energy demand, and long-term durability, supported by modular design and scalable fabrication strategies.

Technology readiness is heterogeneous within each material family and should therefore be treated as an indicative deployment descriptor rather than a universal property. Established activated-carbon and zeolite processes have the highest practical maturity because their manufacture, shaping, regeneration, and industrial use are already demonstrated. Structured carbon/zeolite composites occupy an intermediate maturity range because the underlying materials are established but monolithic fabrication and cycle integration remain application-dependent. Amine-functionalized sorbents have demonstrated process-relevant performance but still face durability, oxidative stability, and replacement-cost challenges. MOFs generally remain at lower deployment maturity because reproducible large-scale synthesis,

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shaping, solvent/precursor consumption, and long-duration operation under realistic feeds require further validation. The decisive scale-up question is therefore not material capacity alone, but whether the material can be manufactured reproducibly and integrated into a stable, economical adsorption cycle.

Table 18. Application-oriented framework for selecting structured CO_2 sorbents.

Application	Typical CO_2 environment	Dominant constraint	Priority sorbent attributes	Preferred process options	Key validation metric
Post-combustion	~10-15% CO_2; H_2O/SOx/NOx	Humidity and impurities	Impurity tolerance; moderate affinity; cyclic stability	TSA/VSA/eTSA; structured beds	Working capacity after multicomponent cycling
Direct air capture	~400 ppm CO_2; variable humidity	Low partial pressure and energy	High low-pressure affinity; fast kinetics; low regeneration energy	TVSA/eTSA; monoliths	kg CO_2/ m^3 h and kWh/ t CO_2
Biogas upgrading	High CO_2; CH_4-rich feed	CO_2/CH_4 selectivity	Selective microporosity; fast diffusion	PSA/VSA	CH_4 recovery and CO_2 purity
Compact/decentralized	Variable	Footprint and pressure drop	Low ΔP; high volumetric productivity; modular regeneration	Structured/electrified cycles	Total cost and energy per tonne CO_2

11. Specific Research Gaps and Future Research Priorities

The most important research gap is the absence of comparable, long-duration tests under realistic multicomponent feeds. Future studies should report at least 100-1000 cycles where feasible, with controlled H_2O and SO_2/NOx exposure, and should quantify both working-capacity retention and structural/mechanical changes. A second gap is the lack of standardized process-level reporting: studies should report volumetric productivity, pressure drop, regeneration energy on a clearly defined system boundary, and sorbent inventory rather than equilibrium capacity alone. A third gap concerns structured materials, for which channel geometry, binder fraction, active-phase loading, and manufacturing reproducibility should be reported together with reactor-level performance.

A second priority is to deconvolute regeneration energy into sensible heating, desorption enthalpy, heat losses, vacuum/compression work, and auxiliary electrical consumption. This is particularly important for microwave, induction, and electrothermal regeneration, where electrical-to-thermal efficiency and temperature uniformity can dominate the process energy penalty. Future studies should report both thermal and electrical energy on a common basis and should compare electrified cycles with conventional TSA under matched working-capacity and productivity constraints [40,41].

A third priority is standardized benchmarking. At minimum, future reports should specify feed composition, humidity, adsorption and regeneration pressures, temperature, flow rate, particle or channel dimensions, binder content, cycle time, working capacity, pressure drop, and regeneration-energy boundary. Such reporting would enable meaningful comparison between powders, pellets, monoliths, and 3D-printed structures.

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For structured sorbents, the central scale-up question is the material–geometry–reactor interface. Research should quantify how shaping changes active-phase utilization, heat and mass transfer, mechanical strength, pressure drop, and volumetric productivity. The economic consequence of manufacturing complexity should be evaluated simultaneously with the process benefit of reduced pressure drop. The literature now supports the view that material discovery and reactor design should be optimized together rather than sequentially [39,42].

For DAC, future work should move beyond single-material capacity demonstrations toward integrated cycle and techno-economic validation under realistic humidity and temperature swings. Electrified regeneration is promising for coupling capture with renewable electricity, but scale-up requires quantitative evidence on heating uniformity, electrical efficiency, cycle durability, and system cost. These priorities are especially relevant for honeycomb and monolithic configurations, where the process advantage is expected to arise from low pressure drop and compactness rather than from a higher intrinsic equilibrium capacity.

Overall, future research should be organized around four measurable deliverables: (i) realistic multicomponent cyclic stability, (ii) standardized process-level benchmarking, (iii) integrated material-geometry-cycle optimization, and (iv) transparent techno-economic and life-cycle assessment. These deliverables would convert the field from material-level screening toward evidence-based process design.

Techno-economic feasibility should be complemented by life-cycle assessment (LCA), because low regeneration energy does not necessarily imply low environmental impact. LCA should include sorbent synthesis, solvent or precursor consumption, shaping, replacement frequency, regeneration energy source, and end-of-life treatment. For DAC, integration with renewable electricity can reduce operational emissions from electrified regeneration, but the benefit depends on renewable availability, capacity factor, storage requirements, and the embodied impacts of electrical heating hardware. Future DAC studies should therefore report both capture performance and the carbon intensity of the electricity and heat supplied to the cycle.

The evidence reviewed does not support a universal “best” sorbent. Instead, the preferred material is the one that satisfies the complete capture duty at the process level. The most critical near-term priorities are: (1) realistic multicomponent cycling with $H_2O/SO_2/NO_x$; (2) standardized reporting of working capacity, productivity, pressure drop, and regeneration energy; (3) shaped-sorbent scale-up with quantified binder and manufacturing penalties; (4) matched material-cycle-reactor optimization; (5) transparent techno-economic and life-cycle assessment; and (6) pilot-scale validation of electrified regeneration. These priorities provide a practical route from material discovery to deployment.

12. Conclusions

This review shows that no solid sorbent can be selected independently of the capture duty. Equilibrium capacity is useful for screening, but practical selection must simultaneously consider working capacity, low-pressure affinity, impurity tolerance, regeneration energy, cyclic stability, pressure drop, volumetric productivity, manufacturing cost, and process maturity.

For post-combustion capture, hydrophobic or modified zeolites and carbon–zeolite structured sorbents are promising when validated under humid, SO_2-containing feeds. For DAC, high low-pressure affinity and low-energy regeneration are dominant requirements, making amine-functionalized and electrified structured systems attractive candidates. For biogas upgrading, CO_2/CH_4 selectivity and fast pressure-swing kinetics are more important than maximum gravimetric

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capacity. Honeycomb structures are particularly attractive where pressure drop and compactness constrain the process, but their fabrication cost and possible active-phase dilution must be included in the economic assessment.

Electrified regeneration broadens the process-design space. ESA/eTSA, microwave, and induction heating can reduce thermal inertia and support modular operation, but their value should be demonstrated using common system boundaries for electrical energy, heat losses, cycle time, and working capacity. Recent techno-economic evidence shows that a monolith can reduce pressure-drop-related energy demand dramatically while still suffering a productivity penalty relative to a packed bed; therefore, structural optimization must be coupled to cycle and economic optimization rather than treated as a purely geometric improvement [39-41].

The most actionable research priorities are to establish long-duration multicomponent cycling protocols, report standardized process-level metrics, quantify degradation mechanisms under SO_2 and humidity, develop scalable structured-sorbent manufacturing routes, and perform integrated techno-economic and life-cycle assessments. The next generation of studies should therefore report material, geometry, and process data together so that laboratory performance can be translated into reactor-scale design decisions.

Finally, future research should prioritize the development of multifunctional, structurally integrated sorbents, resilient to real-world gas conditions and adaptable to electrified, modular systems. The integration of material development with process optimization and life-cycle assessment will be essential to accelerate the deployment of adsorption-based CO_2 capture technologies as part of global decarbonization efforts.

Symbols used Abbreviations

Abbreviation	Full Form
AC	Activated Carbon
CMS	Carbon Molecular Sieve
DAC	Direct Air Capture
MOF	Metal–Organic Framework
PSA	Pressure Swing Adsorption
VSA	Vacuum Swing Adsorption
TSA	Temperature Swing Adsorption
ESA/eTSA	electrical/electrothermal swing adsorption
SSA	Specific Surface Area
PFO	pseudo-first-order
PSO	pseudo-second-order
D–R	Dubinin–Radushkevich
DA	Dubinin–Astakhov
CFD	computational fluid dynamics
LCA	life-cycle assessment
CAPEX	capital expenditure
OPEX	operating expenditure
XPS	X-ray photoelectron spectroscopy

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