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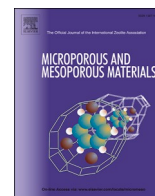
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Review

Adsorption-based CO₂ separation from gas streams: Porous adsorbents, mechanisms, and cyclic process design

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ABSTRACT

Adsorption-based CO₂ separation using porous solids is increasingly investigated for flue gas treatment, biogas and natural gas sweetening, hydrogen purification, direct air capture, and selected CO₂-containing petrochemical streams. This review focuses on adsorption-based CO₂ separation from gas streams by integrating recent findings in experimental studies, simulations and modeling works, and selected pilot and industrially relevant examples to clarify how porous adsorbents can be linked to practical cyclic CO₂ capture systems. The review is organized around a structure-mechanism-process (SMP) selection logic that links the dominant adsorption mechanism required by a given gas stream to a suitable adsorbent class and cyclic process and applies it across five representative CO₂-containing streams. Porous solids, including zeolites and metal-organic frameworks (MOFs), are emphasized as promising materials owing to their extensive surface area, adjustable pore structures, and selective adsorption capabilities. The study reviews the adsorption characteristics of popular zeolites (4A, 5A, 13X) under diverse conditions and assesses their reported performance in relation to industrial CO₂ removal requirements. Also, key parameters such as adsorption capacity, regeneration energy, and selectivity are discussed in this review. Moreover, the performance of adsorbents in key adsorption process configurations is examined, including pressure swing adsorption (PSA), vacuum swing adsorption (VSA), temperature swing adsorption (TSA), and hybrid schemes (e.g., PVSA, TVSA).

Key challenges include the absence of a practical adsorbent-selection framework, limited hydrothermal and contaminant tolerance, regeneration-energy penalties for strongly binding sorbents, shaping and mechanical robustness, and scalable synthesis. Future progress will depend on the combined optimization of adsorbent chemistry, morphology, and process configuration to achieve practical, economically viable CO₂ capture solutions. By systematically linking adsorption mechanisms, materials design, and process engineering, adsorption-based CO₂ capture holds promise for advancing from laboratory-scale studies to practical, energy-efficient industrial implementation.

1. Introduction

In recent decades, the concentration of carbon dioxide in the atmosphere has dramatically increased. This concentration has risen by more than 50% since the industrial revolution, from 280 ppm to around 430 ppm in 2025 [1,2]. An important part of this increase is attributed to anthropogenic activities such as deforestation and emissions from vehicles, power plants, and chemical processes [3].

This acceleration in CO₂ emissions is a major driver of global warming and has led to the development of diverse mitigation strategies including point-source capture, direct air capture (DAC), and negative emission technologies [4–6]. Among the available capture techniques, adsorption-based processes using solid sorbents have attracted major attention as alternative to the conventional amine and NaOH scrubbing systems [7]. In comparison, adsorption offers potentially lower regeneration energy, fewer solvent-related environmental concerns, and a

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modular process design [8,9]. Over the last two decades, there has been an explosion of research on porous adsorbents for CO₂ separation, spanning zeolites [10], activated carbons [11], metal–organic frameworks (MOFs) [12], and amine-functionalized solids [13]. Several reviews have addressed specific aspects of this field, such as low-temperature adsorption systems [1], carbon-based sorbents [14], advances in absorption and adsorption [15], porous liquids [16,17], and MOF-based CO₂ capture [18]. However, there remains a need for a review that simultaneously maps the evolution of research topics in CO₂ adsorption by porous solids, compares the performance of major adsorbent families across relevant gas mixtures and operating conditions, and links material properties to process-scale performance through rigorous cyclic process simulations. This study addresses this need by presenting an integrated perspective on CO₂ adsorption by porous solids. It presents a bibliometric analysis to map the evolution of research conducted in this field, a critical comparison of representative adsorbent families across different gas mixtures and operating conditions, and a process-scale evaluation in PSA, VSA, TSA, and hybrid configurations using rigorous cyclic simulations. The core contribution is a condition-based framework linking adsorbent class and adsorption mechanism to real operations, ultimately determining which materials are most suitable for specific separation targets and regeneration constraints. Recent surveys have critically examined adsorption processes, their energetics, and pilot-to full-scale demonstrations [19]. The present review is complementary, focusing on the material and mechanistic basis of CO₂ adsorption and on a structure-mechanism-process logic for selecting adsorbent-cycle pairings across a broad range of CO₂-containing streams, including DAC-oriented materials and CO₂/olefin purification.

2. Bibliometric analysis

To provide a quantitative overview of research activity in CO₂ adsorption by porous solids, a bibliometric analysis was carried out using the Scopus database. The search was limited to English-language research articles and reviews published between 1970 and 2025. The search term included the combinations of CO₂ adsorption, porous solid, zeolite, metal-organic framework, activated carbon, and adsorption mechanism. The resulting dataset was analyzed using VOSviewer (version

1.6.20) to construct keyword co-occurrence networks and to identify broad thematic clusters. Keyword co-occurrence networks were constructed using full counting, retaining keywords with a minimum of 12 occurrences. Before interpretation, closely related terms and abbreviations were checked to reduce duplication where possible. Because keyword co-occurrence analysis is sensitive to the search strategy and terminology used in the original publications, the clusters are interpreted here as broad indicators of research trends rather than definitive mechanistic classifications.

Fig. 1 shows the history of studies on CO₂ separation over time, presenting the number of papers published per year. While a few studies from the 1930s addressing CO₂ separation may be found, emphasis of the present study is on the more recent research, further focused on the environmental aspects. As observed, the first investigations were conducted in the 1970s, which led to a great deal of interest in the field. Although the 1970s marked the beginning of modest investigations into this critical field, a substantial increase in interest can be observed at the turn of the millennium. This rapid growth shows how the world's concern regarding CO₂ emissions is growing and highlights the urgent need for effective mitigation solutions.

When conducting an analysis of CO₂ separations in the literature, keyword-clustering matrix is a helpful tool. This approach provides an understanding of key research areas and trends in the subject. The clustering keywords matrix, which was constructed utilizing VOSviewer software, analyzes the research on CO₂ adsorption by porous solids, as illustrated in Fig. 2 and Fig. 3. This analytical tool identifies clusters of closely linked keywords in academic literature, offering helpful insights into key study areas and the evolution of the topic. Also, this network provides an efficient framework for organizing future research activities through the comprehension of the most relevant and frequently utilized terms in literature.

Fig. 2 shows the keywords clustered into four main groups, each represented by a different color. These four clusters reveal the key research directions pursued in the CO₂ capture field. The yellow cluster (I) represents the studies conducted by modelling tools on separation of CO₂, especially using MOFs and how they can be used to separate certain gases. This cluster is focused on important terms like CO₂ separation, MOFs, C₂H₆, molecular simulation, force field, C₂H₂, Grand Canonical Monte Carlo (GCMC), Zeolitic Imidazolate Frameworks (ZIF), and Cu-BTC

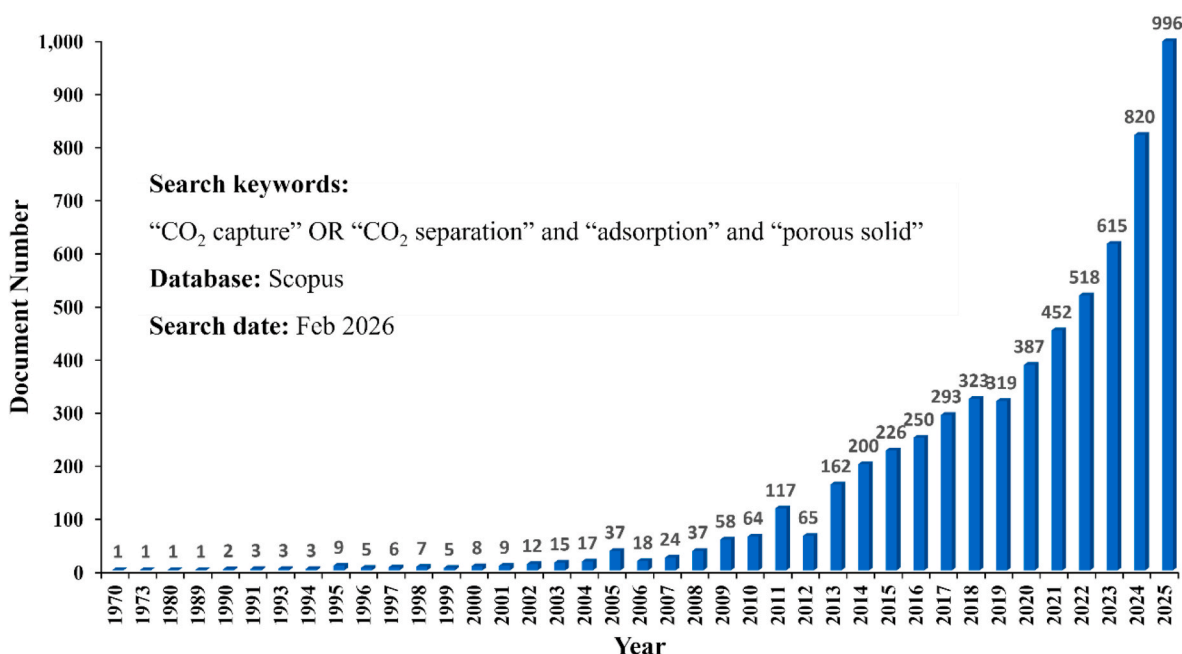


Fig. 1. Publication trend of CO₂ adsorption research per year from 1970 to 2025.

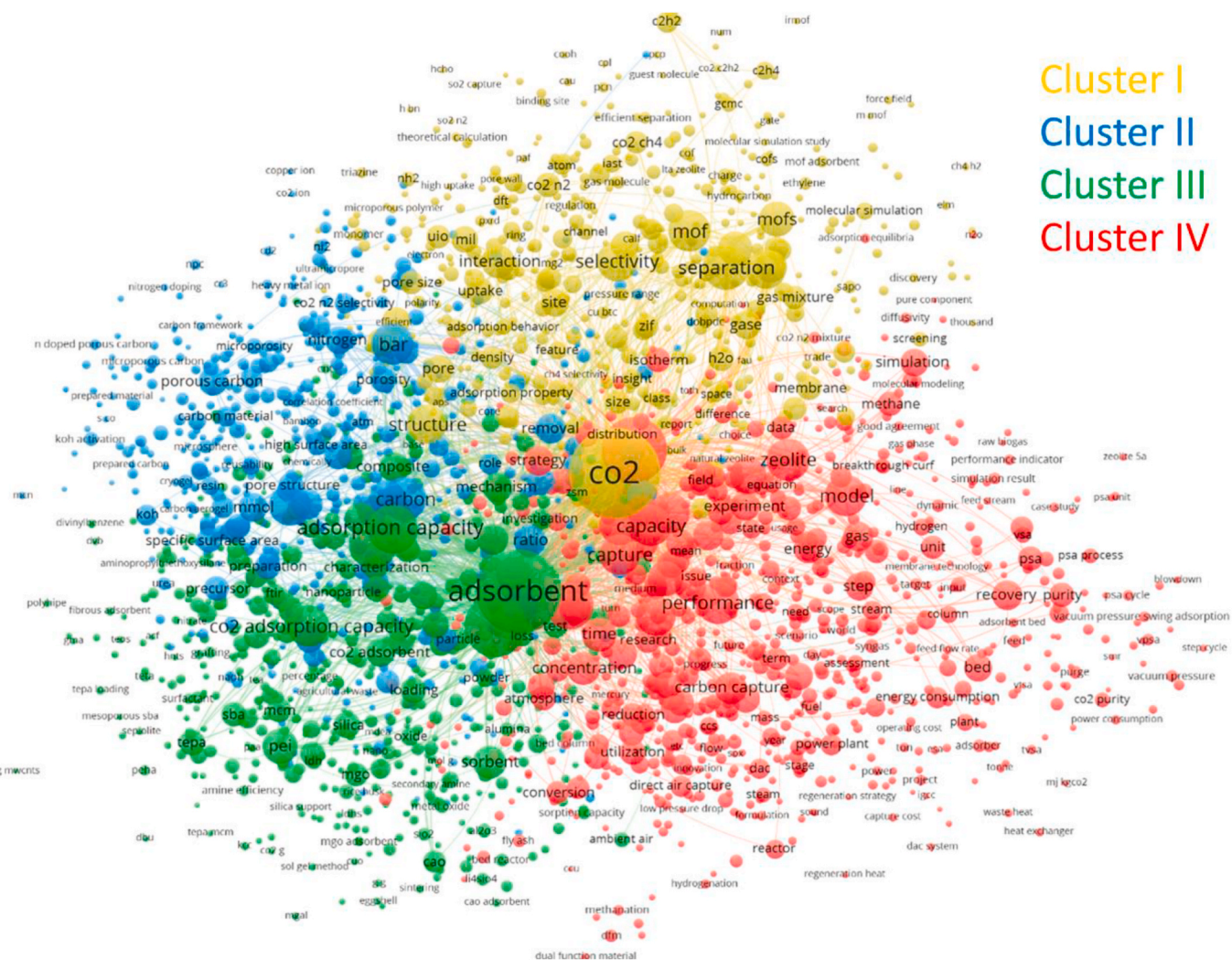


Fig. 2. Keyword clustering network of CO₂ adsorption studies from bibliometric analysis.

(HKUST-1). This combination depicts how advanced computational methods, such as molecular dynamics simulation (MD) that use specific force fields and GCMC methods, can be used to predict, understand, and improve the separation of CO₂ from other gases, especially light hydrocarbons. The repeated mention of MOFs, ZIF, and HKUST-1 demonstrates how MD can be used to test new materials capability to capture CO₂. The blue cluster (II) depicts the structural properties and detailed description of porous adsorbents. The blue cluster (II) represents studies related to porous structure, textural characterization, and adsorption-performance analysis. Keywords such as *pore structure*, *porous carbon*, *high surface area*, *porosity*, *carbon framework*, *nitrogen*, and *correlation coefficient* indicate the frequent use of adsorption characterization, isotherm fitting, and structure/performance evaluation in this area. The keyword *nitrogen* represents the widely applied nitrogen adsorption/desorption technique to achieve detailed information on pores. This cluster shows that the main goal in studies is to alter the internal structure of adsorbents in order to enhance their CO₂ capture performance. The green cluster (III) presents experimental research in material science for CO₂ capture. The core keywords include *adsorbent*, *Fourier-transform infrared spectroscopy (FTIR)*, *powder*, *nanoparticle*, *sol-gel method*, *sintering*, *sorbent*, *alumina*, *silica support*, *ZSM* (referring to ZSM zeolite family), and *composite*. These keywords emphasize the diverse methodologies employed for synthesizing and refining solid adsorbents, ranging from traditional techniques like the sol-gel method and sintering to the development of advanced composite structures. The inclusion of

characterization analysis such as FTIR indicates their importance for understanding composition and surface functionalities, while the keywords *alumina*, *silica* support, and *ZSM* are related to the exploration of various inorganic frameworks to be applied as effective support or primary adsorbents. The red cluster (IV) covers all aspects of CO₂ removal through adsorption, from improving the performance and recovery of the process to investigating different swing adsorption methods essential for application in the real world. These topics are reflected in keywords *carbon capture*, *performance*, *utilization*, *recovery*, *PSA (Pressure Swing Adsorption)*, *VSA (Vacuum Swing Adsorption)*, *TSA (Temperature Swing Adsorption)*, *energy*, *innovation*, and *DAC*. Keyword *energy* shows the emphasis on energy optimization in capture processes and the keywords *innovation* and *DAC* show the need for novel and efficient systems.

Fig. 3 visualizes the most frequently co-occurring high-frequency keywords in the CO₂ separation field over time. This analysis helps researchers to find new trends and possible topics for innovative future research. The most recent keywords are highlighted in yellow and light green, including MOFs, *membrane technology*, *energy consumption*, *COF*, *PCP*, and *DAC*. This trend suggests direct air capture and novel porous materials as high-potential areas for future CO₂ capture innovation. Researchers may explore novel solid sorbents to improve selectivity and overall process performance. In particular, high-performance materials could enable more efficient direct air capture, which is a rapidly growing area. It should also be noted that some emerging topics may not appear as dominant keywords in the final VOSviewer map because the co-

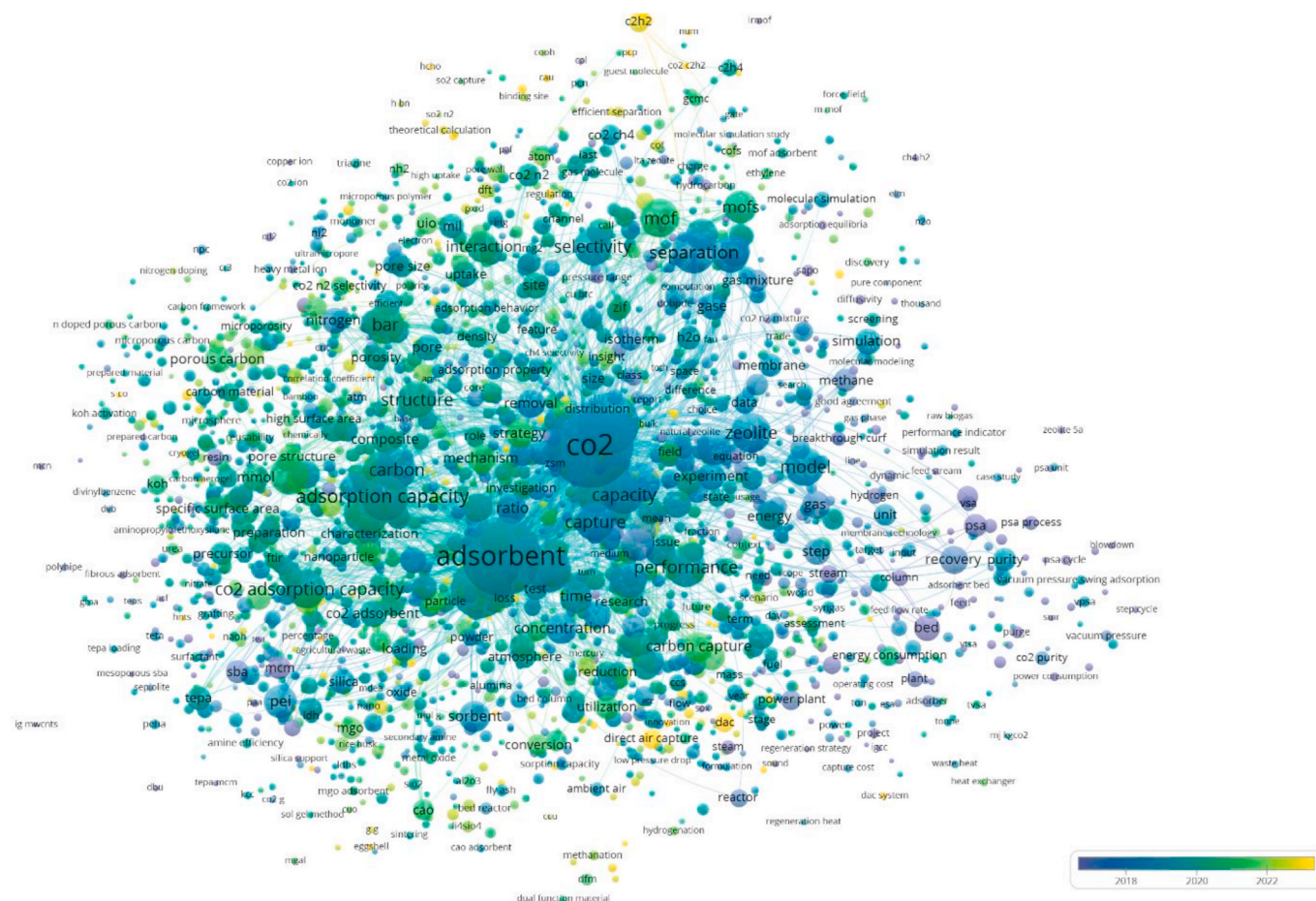


Fig. 3. The occurrence of keywords over time in the CO₂ adsorption literature.

occurrence network retains only terms above the selected frequency threshold. For example, AI-assisted adsorbent screening, machine learning, techno-economic analysis, and life-cycle assessment are increasingly important in recent CO₂ adsorption research, but they may remain below the high-frequency keyword threshold compared with established terms such as MOFs, DAC, energy consumption, and membrane technology. Although these approaches are not new in themselves, their co-occurrence with core CO₂-adsorption terms is still comparatively low. These emerging directions are nevertheless important because they shift the field from isolated material screening toward integrated material–process–system evaluation. Machine learning and high-throughput screening can accelerate adsorbent discovery, while TEA and LCA provide criteria for evaluating cost, energy demand, scalability, and environmental performance.

Beyond describing the volume and direction of research activity, the four keyword clusters identified above also help explain the structure of this review. The materials- and mechanism-oriented clusters, including the yellow cluster related to computational screening and MOF-based separation and the green cluster related to adsorbent synthesis and characterization, correspond to the adsorbent classes and structure-property discussions in Sections 4 and 5. The process-oriented red cluster, which includes PSA, VSA, TSA, DAC, performance, recovery, and energy-related terms, corresponds to the cyclic process design and comparative insights discussed in Sections 6 and 7. The blue cluster, centered on porous structure, textural characterization, and adsorption-performance analysis, links these two parts by supporting the property-performance relationships discussed throughout the review. The emerging lower-frequency topics noted above, including AI-assisted screening, techno-economic analysis, and life-cycle assessment, are also connected to the research gaps and future directions discussed later

in the manuscript. In this way, the bibliometric analysis is used to contextualize the scope of the review.

3. Research gaps in CO₂ separation

CO₂ separation, particularly through adsorption, has certainly experienced a remarkable surge in interest, driven by the critical need to mitigate climate change [20]. Adsorption can offer process advantages in selected CO₂ separation applications, particularly through cyclic regeneration, modular solid-sorbent contactors, and reduced solvent-related operational issues. These advantages depend strongly on the target gas stream, required CO₂ purity and recovery, regeneration strategy, energy source, and adsorbent lifetime. Ongoing innovation is improving the available technology in the field, from advanced material design to system optimization [21]. However, despite the rapid progress in adsorption-based CO₂ capture, several barriers still limit large-scale industrial deployment of these adsorption systems [22]. This review is therefore positioned to complement recent process- and demonstration-focused surveys [19] by providing a material- and mechanism-level selection framework.

A major area requiring further effort is the development of truly high-performance adsorbents. While MOFs and modified carbon materials show substantial promise, and machine-learning approaches are increasingly being used to accelerate materials discovery and screening [23], the main challenge is to develop a reduced portfolio of robust and tunable materials which can be selected according to the specific separation process. These materials should balance high CO₂ adsorption capacity [24] and selectivity [25], long-term cyclic stability [26], fast adsorption and desorption kinetics, and cost-effective synthesis and regeneration [27], which is a challenging objective to achieve. For

instance, some materials can deliver high CO₂ uptake yet require energy-intensive regeneration approaches, which undermines their overall environmental benefit and offsets the intended sustainability benefits. There is also a clear need for deeper understanding of CO₂ capture at the molecular scale, for both adsorbent structure and adsorption process, in order to guide the design and development of efficient materials and processes [28].

Furthermore, ensuring long-term stability of adsorbents under real industrial conditions remains a critical challenge. In practice, post-combustion flue gas is mainly composed of N₂ and O₂, with lower concentrations of CO₂, water vapor, and trace contaminants such as SO_x and NO_x; therefore, adsorbents must be evaluated under realistic humid and multicomponent gas conditions rather than under dry single-component CO₂ conditions alone [29]. This is particularly important because many promising adsorbents, especially certain MOFs, are sensitive to moisture and exhibit structural degradation and/or substantial losses in adsorption capacity under humid conditions [15,30]. Although strategies such as incorporating hydrophobic functional groups or adopting core-shell structures can improve moisture tolerance, they may reduce CO₂ uptake/selectivity or increase synthesis complexity [31,32]. Therefore, future investigations should focus on developing durable materials that remain effective over prolonged exposure to harsh operating conditions and multicomponent gas streams.

Another critical research need concerns optimizing energy utilization across the entire capture process. Conventional swing adsorption methods (e.g., PSA, VSA, and TSA) are energy-intensive due to the need for pressure and/or temperature changes in regeneration [33]. While emerging approaches such as electricity-driven regeneration [33,34] and magnetically assisted regeneration [35] are being explored to reduce energy consumption, their viability and widespread application remain to be established through further investigations, particularly with respect to long-term stability and the economic costs. Ultimately, the key challenge is to reduce regeneration energy demand without compromising capture performance or adsorbent lifetime. The synchronization of the adsorption and regeneration cycles is necessary for efficient cyclic operation in addition to reducing the intrinsic regeneration energy. Incorrectly matched cycle steps lead to unused beds, large adsorption units and large adsorbent storage space. Therefore, future process optimization should not only consider pressure and temperature levels, but also the step duration, bed utilization, productivity and regeneration-adsorption coupling [36].

Finally, the successful scale-up of CO₂ adsorption technologies from laboratory experiments to industrial deployment presents multifaceted challenges. For instance, lab-scale MOF synthesis commonly relies on solvothermal methods, which are often time-consuming, energy-intensive and low-yield, which limits their scalability and industrial production viability [37]. In addition, powdered adsorbents frequently used in laboratory experiments can face practical issues such as excessive pressure drop in fixed beds and solid loss in continuous operation, and therefore need to be shaped into pellets, monoliths, or films, which on the other hand add cost and can reduce adsorption capacity in some cases [38,39]. A further gap is the limited adoption of integrated process design with systematic evaluation of total energy demand and overall footprint. Bridging the gap between scientific advances and large-scale implementation requires rigorous techno-economic analysis, life-cycle assessment, and strong cross-disciplinary collaboration. More robust and reliable mathematical models are also needed to predict performance under varying conditions and enable effective process optimization.

4. A brief history of adsorption

4.1. General chronological history

Identifying the first scientific paper specifically addressing CO₂ adsorption on solid materials is challenging. Early studies typically

examined gas adsorption and purification in general terms, without explicitly considering CO₂ as an environmental issue that dominates the field today [40]. It is also important to recognize that the motivations for CO₂ adsorption research have evolved substantially over time. Whereas current interest is largely driven by climate-change mitigation, the role of CO₂ in climate was already recognized in the late 19th century (by Arrhenius in 1896) [41], and gained further attention in subsequent decades (Callendar's work in the 1930s) [42]. Historically, scientific and industrial interest in gas adsorption, including CO₂, was primarily oriented toward vacuum technology, gas purification (e.g., natural gas processing), and fundamental studies in physical chemistry [43,44]. In 1932, W. McBain introduced the term “molecular sieve” to describe materials such as mineral chabazite (a type of zeolite) that exhibit selective adsorption based on molecular size and shape [45].

The close temporal alignment between development of adsorption theories (Polanyi, Langmuir) and the widespread industrial application of activated carbon (e.g., in gas masks and natural gas purification) in the early 20th century illustrates a strong co-evolution between theory and practice [46,47]. Industrial challenges highlighted the need for effective gas separation and generated valuable experimental data; conversely, theoretical models provided rigorous frameworks for understanding adsorption phenomena and guiding the optimization and design of new adsorbent materials and processes. This period therefore marked a pivotal transition in which adsorption evolved from largely empirical experimentation into a science-based engineering discipline. The resulting theoretical advances provided the conceptual tools required to predict and control adsorption behavior, which is essential for industrial scale-up and technology diversification [48].

Following this period, advances in both theory and materials accelerated the field. In 1938, Brunauer et al. established a framework for quantifying specific surface area as a key parameter for adsorbent performance. Accordingly, the BET model was developed to describe multilayer adsorption, providing a more comprehensive basis for characterizing adsorbent surfaces [49]. This theoretical advancement was followed by a major industrial breakthrough with the commercialization of zeolites in the 1950s, which effectively utilized McBain's *molecular sieve* concept for large-scale gas separation [50]. In the 20th century, CO₂ capture continued to serve industrial needs, especially in Enhanced Oil Recovery (EOR), where CO₂ injection into oil fields was used to increase production from the 1970s onward [51]. This suggests that CO₂ management technologies were already available but were mainly adopted for financial reasons. In the 1990s, the Norwegian government's carbon tax created a direct financial incentive for CO₂ capture, leading to the Sleipner project in the North Sea in 1996, which was the first instance of CO₂ capture and permanent storage implemented for environmental reasons [52–54].

From the year 2000 onward, research on CO₂ capture has been shaped by the urgency to mitigate climate change, driven in large part by assessments from the Intergovernmental Panel on Climate Change (IPCC) [55]. This renewed emphasis has accelerated the development and diversification of adsorbent materials beyond conventional activated carbons and zeolites. In particular, MOFs have emerged as a prominent class of porous solids, offering exceptionally high surface areas, tunable pore structures, and high CO₂ selectivity. Meek et al. comprehensively reviewed the properties, performance and potential of MOFs, highlighting their versatility for gas separation and related applications [56]. In parallel, substantial efforts have been devoted to amine-functionalized solid adsorbents which, compared to liquid amine systems, can potentially offer lower regeneration energy and improved operability, making them more attractive for large-scale deployment [57]. This era is defined by the quest for materials that are not only effective but also economically viable for a wide range of CO₂ sources, from industrial flue gases to the atmosphere itself. Overall, this period is characterized by the pursuit of sorbents that combine high capture performance with techno-economic viability for diverse CO₂ sources, from industrial flue gas streams to the atmosphere.

The latest works are increasingly exploring innovative, multi-faceted strategies on solid adsorbents. For instance, emerging cryogenic adsorption concepts seek to harness the cold energy available from liquefied natural gas (LNG) regasification to substantially reduce the energy penalty of capturing CO₂ from highly dilute sources such as air. In parallel, the development of advanced porous solids, particularly porous organic polymers (POPs) and covalent organic frameworks (COFs) is pushing the boundaries of achievable performance by enabling tunable pore architectures and improving thermal/chemical robustness, tailored to the intended application such as DAC [58]. These recent advances highlight the transition of CO₂ adsorption research from an industrial application to a critical and dynamic field at the forefront of global environmental solutions, with growing emphasis on engineering, more efficient, selective, and application-tailored solid adsorbents for future deployment.

4.2. Adsorption mechanisms

The separation of CO₂ from gas streams using solid adsorbents is governed by the interactions between the gas molecules and the solid surface. These interactions are commonly classified as physisorption, dominated by noncovalent forces (e.g., van der Waals and electrostatic interactions), and chemisorption, which involves the formation of strong chemical bonds. The dominant mechanism determines not only capacity and selectivity, but also the energy required for regeneration, which is a key aspect of cyclic processes.

Fig. 4 organizes the main adsorption pathways along a continuous spectrum, ranging from physisorption to chemisorption. The heat (enthalpy) of adsorption is used as a practical indicator for locating adsorption processes on this spectrum. It was constructed from reported ranges for physisorption, chemisorption, π -complexation, and gate-opening adsorption mechanisms [59–61].

4.2.1. Physisorption: van der Waals interactions and electrostatics

Physisorption is a reversible process in which gas molecules stick to the surface of a solid through weak, long-range intermolecular forces which are all identified as van der Waals forces. The process is generally

exothermic, with heats of adsorption often reported at 20–50 kJ mol⁻¹, a magnitude comparable to condensation enthalpies [20]. In the absence of bond formation, the adsorbed molecule retains its chemical identity, and desorption can be achieved with a modest increase in temperature or a decrease in pressure, which underpins TSA and PSA/VSA cycles. The dispersive forces and electrostatic interactions are the two main interactions governing physisorption in CO₂ separation.

Dispersive forces, also known as London dispersion forces, are attractive forces created from temporary fluctuations in molecular electron clouds. They are the primary attractive interaction between nonpolar molecules and depend strongly on the polarizability of the gas and the available surface area of the adsorbent. Activated carbons, zeolites, and many MOFs are examples of high surface area materials that provide abundant adsorption sites, enabling these interactions [62].

Electrostatic interactions are also particularly important for CO₂ due to their molecular characteristics. Despite lacking a permanent dipole moment, CO₂ exhibits a significant quadrupole moment, associated with its linear distribution of positive and negative charges, along with considerable polarizability [63]. This enables strong interactions with local electric fields on the adsorbent surface. Electrostatic interactions are therefore essential for achieving high selectivity in many modern porous materials [64]. Various elements on the adsorbent surface can promote electrostatic interactions. In zeolites such as 13X, 5A, and NaY, extra-framework cations (e.g., Na⁺, K⁺, Ca²⁺) are introduced to balance the negative charge of the aluminosilicate framework. These cations produce intense local electric fields that significantly interact with the CO₂ quadrupole, which leads to selective adsorption compared to less polar molecules such as N₂ [65]. Tailoring these cations via ion exchange can modify the adsorbent characteristics. For instance, Loera et al. reported that encapsulating sulfur chromophores in zeolite A increases the effective charge of Na⁺ cations, thereby altering the CO₂ adsorption enthalpies [64]. Analogous behavior is observed in several MOFs containing open metal sites (OMS), such as Cu-BTC, Mg-MOF-74, and Cu-TDPAT. In these materials, the metal nodes are inadequately coordinated, creating exposed metal cations that act as strong Lewis acid sites. These OMS sites can bind strongly and repeatedly to the electron-rich oxygen atoms of CO₂, leading to higher adsorption affinity

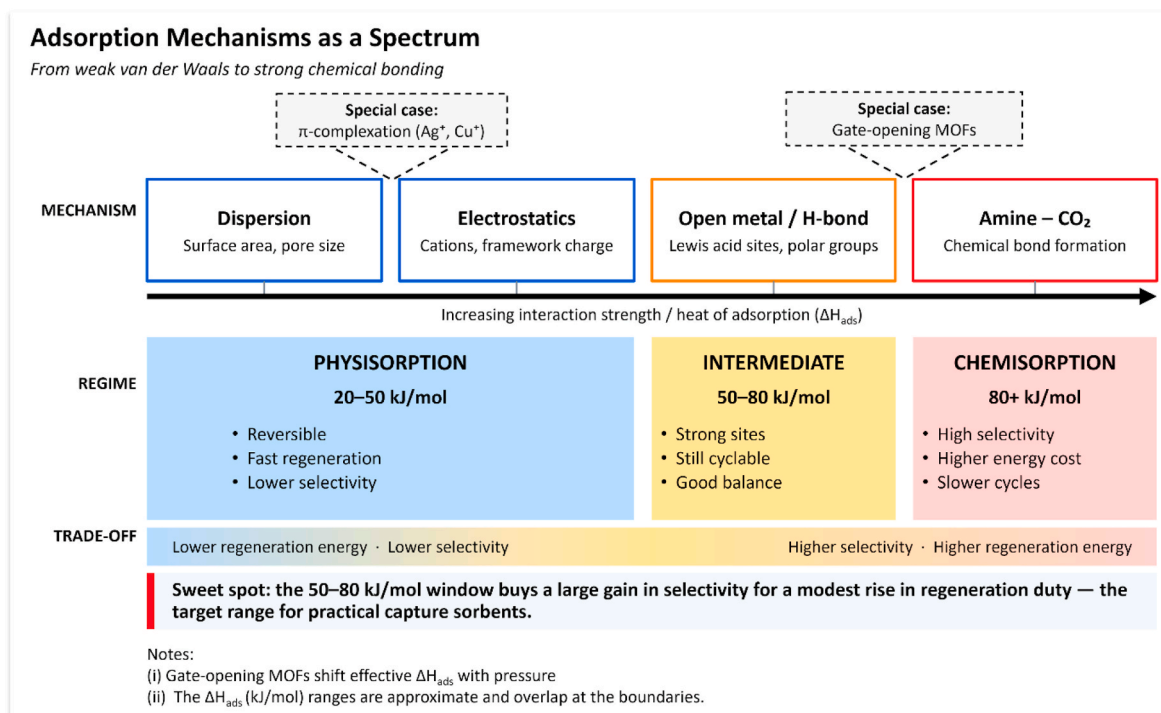


Fig. 4. Adsorption mechanism spectrum based on adsorption heat for CO₂ capture.

and improved selectivity [66].

Beyond open metal sites, MOFs can be engineered by introducing polar functional groups and Lewis basic motifs into the organic linkers. Polar groups such as $-\text{NH}_2$ and $-\text{OH}$ promote dipole–quadrupole interactions and hydrogen bonding with CO_2 . Moreover, nitrogen-rich linkers, as in Cu-TDPAT, further provide Lewis basic sites that interact favorably with the electrophilic carbon atom of CO_2 . The simultaneous presence of OMS (Lewis acidic) and Lewis basic sites within a single framework can generate synergistic adsorption behavior, leading to highly effective CO_2 capture [22,37,67]. Another contributor to physisorption-based separations is molecular sieving, where precisely designed pore apertures impose size and shape selectivity. For instance, in zeolite 5A, pores of approximately 5 Å allow CO_2 (kinetic diameter ~ 3.3 Å) to diffuse readily, while restricting the transport of larger species [68]. This concept extends to certain microporous MOFs, including ZIF-8, in which small pore windows can promote selective uptake of smaller gas molecules [67].

4.2.2. Chemisorption: covalent bonding

Chemisorption takes place by formation of chemical bonds (typically covalent) between the gas molecule and the adsorbent surface sites. This process is characterized by much higher heats of adsorption compared to physisorption (typically $> 80 \text{ kJ mol}^{-1}$) and can be irreversible under mild conditions, or require substantial energy input for regeneration [20]. In chemisorption, the adsorbed molecule no longer retains its original identity; the adsorbate converts into a distinct surface-bound species and the resulting strong and new bonds lead to high selectivity [69]. In the context of CO_2 capture, one of the most well-known examples of chemisorption is amine-functionalized solid sorbents. Primary amine groups ($-\text{NH}_2$) are commonly introduced onto high surface area supports, including porous silica and alumina. CO_2 molecules, acting as a weak Lewis acid, undergo an acid–base reaction with these basic amine sites to yield surface-bound carbamate species [70]. This reaction provides strong selectivity even at low CO_2 partial pressures, which is advantageous particularly for DAC. In this case the trade-off is the regeneration penalty, since significant energy input is needed to reverse the chemisorption step, which can raise operating costs compared with physisorption-based processes [71].

In addition to these two established mechanisms, other adsorption pathways have been explored, including π -complexation, which is a particularly effective mechanism for separating CO_2 from unsaturated hydrocarbons such as ethylene (C_2H_4) [72,73]. In π -complexation, the π electrons of molecules such as C_2H_4 or C_2H_2 interact with transition-metal cations, commonly Ag^+ or Cu^+ , incorporated into zeolites, MOFs, or related porous frameworks. This interaction creates strong and selective binding sites for unsaturated hydrocarbons and can therefore assist in the purification of CO_2 -rich or CO_2 -containing petrochemical streams [74]. According to Zhou et al., introducing Ag^+ cations into NaY zeolite through AgNO_3 modification generates highly selective π -complexation sites for olefins; ethylene binds strongly to these Ag^+ sites, facilitating its selective separation from CO_2 . *Ab initio* calculations also confirm this selectivity, with adsorption energies of $-77.5 \text{ kJ mol}^{-1}$ for C_2H_4 versus $-23.5 \text{ kJ mol}^{-1}$ for CO_2 on the Ag^+ -exchanged zeolite, both of which are stronger than the weak physisorption on the parent Na^+ sites [75]. Thus, in CO_2 -containing hydrocarbon separations, π -complexation is more appropriately described as a targeted selectivity-enhancement strategy than as a conventional CO_2 -physisorption pathway [76]. Another example is gate-opening in flexible frameworks [77–79] such as the La-PCP reported by Duan et al., which unlike rigid MOFs, possesses a flexible framework and the pore window geometry adapts dynamically upon guest molecule penetration [80]. These materials exhibit limited adsorption at low pressures; however, once a critical threshold pressure is reached, their adsorption capacity increases abruptly, producing a characteristic step-shaped isotherm [81]. This flexible framework can be extremely selective since the structural change can be caused by one

type of molecule rather than the others. This feature makes it possible to achieve sharp separations with only small changes in pressure [82,83].

4.3. Advantages and disadvantages in industry

The implementation of any CO_2 capture system requires an accurate assessment of its advantages and limitations under real industrial operating conditions. Adsorption-based systems, encompassing both physisorption and chemisorption, offer a compelling yet complex alternative to conventional solvent-based scrubbing. Their suitability, however, depends on the specific industrial application, the composition of the feed gas, and the associated economic constraints [84,85].

An advantage of solid adsorption processes is the potential for a reduced energy penalty, as the energy required for adsorbent regeneration is considerably lower than that of conventional amine scrubbing systems in some cases [86,87]. Another notable advantage is the elimination of liquid waste, which represents a significant environmental concern in NaOH-based systems [88]. As these systems primarily consume electrical energy for compression and vacuum generation, they avoid the substantial thermal energy demand associated with solvent regeneration, thereby reducing operational costs, particularly in industries where low-cost steam is not readily accessible [89]. For instance, a VPSA process employing binder-free K(23)Y zeolite for post-combustion CO_2 capture achieved a specific energy consumption of just 144 kWh per ton of CO_2 , which is a value competitive with that of considerably more complex systems [63]. Furthermore, solid sorbents offer an additional environmental benefit, as they are non-volatile and non-corrosive, thereby mitigating the issues of solvent degradation, hazardous emissions such as nitrosamines, and equipment corrosion, which are persistent challenges associated with amine-based capture technologies [69,90]. This facilitates material handling and reduces long-term maintenance costs. Furthermore, the modular design of PSA/VPSA units offers considerable operational flexibility and scalability, allowing adaptation to a range of plant capacities and more effective management of fluctuations in feed gas flow rates, which are advantages difficult to achieve with large-scale, single-train absorption columns [91].

Despite these advantages, several challenges continue to hinder the widespread industrial adoption of adsorption technologies [21]. A primary concern is the sensitivity of adsorbents to contaminants present in real industrial gas streams. Water vapor, in particular, acts as a competitive poison, occupying adsorption sites otherwise available for CO_2 on many physisorbents, which reduces overall adsorption capacity and separation performance [69,92]. Consequently, an energy-intensive dehydration step is required upstream of the main separation process, adding to both capital and operational costs. Similarly, acidic gases such as SO_x and NO_x can cause irreversible structural degradation of certain adsorbents, particularly zeolites and numerous MOFs, necessitating extensive pre-treatment of the feed gas [93,94]. Process complexity and scalability remain additional ongoing challenges. The modular configuration of industrial PSA/VPSA systems involves multiple adsorption beds, intricate valve sequencing, and pressure equalization steps, all of which increase engineering complexity [95,96]. Furthermore, the presence of a solid adsorbent bed introduces a significant pressure drop across the system, increasing the energy demand of blowers and compressors required to maintain adequate gas throughput [71].

The choice of adsorbent material is a determining step of system performance. Zeolites, such as 13X and 5A, represent the most commercially mature class of adsorbents, valued for their adequate thermal and mechanical stability, relatively low cost, and well-established performance [69,97]. Their uniform pore structure enables precise molecular sieving, and their surfaces can be further tailored through ion exchange to enhance CO_2 selectivity [65,98,99]. Here, adsorption selectivity is reported as a dimensionless ratio, as defined in the original studies. Low-silica X (LSX) zeolites, for instance, can be synthesized from industrial waste streams such as coal gangue, and have

demonstrated notable CO₂ uptake of 4.99 mmol g⁻¹ alongside a high CO₂/N₂ selectivity ratio of 376 [100]. Nevertheless, a significant limitation of zeolites is their relatively modest adsorption capacity, which continues to restrict their suitability for large-scale industrial CO₂ capture applications [101]. Their pronounced hydrophilic nature represents a further drawback, rendering them particularly susceptible to performance degradation in the presence of moisture [92].

MOFs, including ZIF-8 and Cu-TDPAT, represent the most recent generation of adsorbent materials, offering exceptionally high surface areas and tunable pore structures that can yield superior CO₂ uptake capacities and selectivity ratios [37,102]. Certain MOFs also exhibit a greater degree of hydrophobicity relative to zeolites, which improves their stability in humid gas streams. However, the principal barriers to their industrial deployment remain their comparatively limited hydrothermal and chemical stability, as well as their considerably higher synthesis costs relative to zeolites [103]. Their long-term durability under the repeated thermal and pressure cycling inherent to PSA operation also requires further investigation [81]. An additional concern is the formation of structural defects during large-scale synthesis, which can adversely affect both selectivity and adsorption capacity [104]. Amine-functionalized sorbents and modified activated alumina, by contrast, offer among the highest CO₂ selectivities due to strong chemisorptive interactions. Their limitations, however, include a high regeneration energy demand and susceptibility to thermal and oxidative degradation, both of which can lead to a gradual loss of capacity over time [105,106]. The successful industrial implementation of adsorption-based CO₂ capture ultimately depends on carefully matching the appropriate adsorbent to the specific gas stream conditions, alongside the development of cost-effective process designs that address these inherent material and operational challenges.

5. Adsorbent materials for CO₂ separations

The performance of an adsorption-based separation process depends primarily on the appropriate selection of the adsorbent material for the

specific gas mixture being processed. Industrial gas streams vary considerably in composition, pressure, temperature, and contaminant content, and this variability presents distinct separation challenges for each application [84,85]. Consequently, the development of adsorbent materials has grown increasingly complex in order to meet the demands of specific industrial applications, including natural gas upgrading, petrochemical stream purification, and CO₂ capture from power plant flue gas [15,86]. Fig. 5 represents the structures and diversity of pores for different porous solids like zeolites and MOFs, which are discussed in this section.

This section presents a review of the most recent and advanced adsorbent materials and systems developed for industrial gas separation, as summarized in Table S1. In addition, Fig. 6 illustrates the distribution of the examined adsorbent families and the range of CO₂ uptake/capacity values reported in the studies summarized in Table S1. These values are retained as originally reported in the source studies and therefore reflect different temperatures, pressures, CO₂ partial pressures, gas compositions, humidity conditions, and measurement or simulation methods. Accordingly, Fig. 6 should be interpreted as a descriptive overview of reported literature ranges rather than as a normalized performance ranking of adsorbent families.

The capacity values are not normalized to a common temperature, pressure, CO₂ partial pressure, feed composition, or humidity level, and therefore should not be interpreted as a direct ranking of adsorbent performance. For this reason, detailed operating conditions, including gas composition, temperature, pressure, and competing species where available, are provided in Table S1 to support more cautious interpretation of the reported capacities.

5.1. Zeolitic adsorbents

Crystalline aluminosilicate materials, known as zeolites, have been widely regarded as ideal candidates for industrial adsorption processes for several decades, owing to their affordability, exceptional thermal and chemical stability, and well-defined porous structure [69,109].

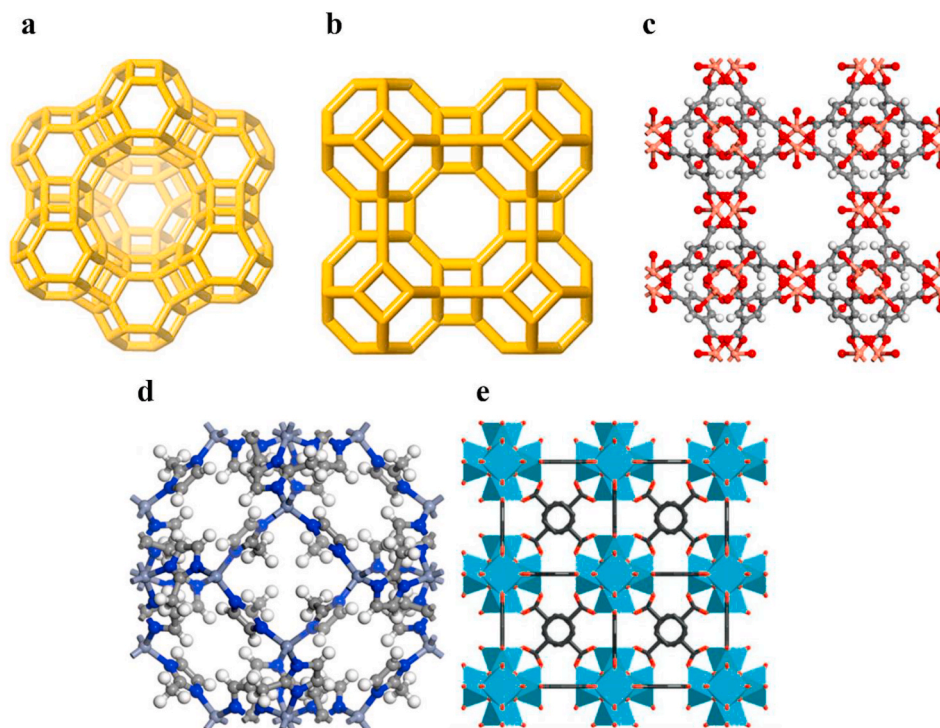


Fig. 5. Structure representation of major porous adsorbent families for CO₂ separation. Zeolites (a) FAU type, (b) LTA type [107], MOFs (c) HKUST-1, (d) ZIF-8 [16], (e) UIO-66 [108] (Reproduced with permission from ref [107], Copyright 2018, Wiley Advanced).

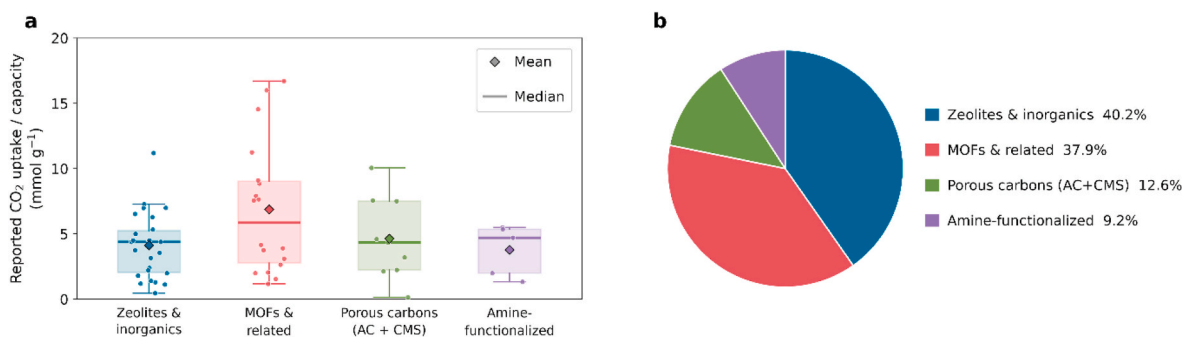


Fig. 6. Descriptive summary of Table S1 dataset across adsorbent families, showing (a) the distribution of CO₂ uptake/capacity values as reported in the original studies and (b) the distribution of adsorbent families represented in the dataset.

Their uniform, molecular-sized pores enable precise molecular sieving, while the extra-framework cations present within the structure generate strong local electric fields, rendering them highly effective for the separation of polar molecules such as CO₂ from less polar species [10,99].

5.1.1. Zeolite 13X (FAU-type)

Zeolite 13X is among the most widely studied adsorbents for CO₂ capture, featuring an FAU-type structure with a large pore aperture of approximately 7.4 Å [110]. The Na⁺ cations located within its super cages generate strong electrostatic interactions with the large quadrupole moment of CO₂, which accounts for its high adsorption affinity toward this molecule [111]. Jedli et al. conducted kinetic and equilibrium studies on commercial 13X, reporting a CO₂ adsorption capacity of approximately 5.3 mmol g⁻¹ at 298 K and 800 mmHg, considerably higher than those recorded for CH₄ and H₂, with CO₂/H₂ and CO₂/CH₄ selectivity ratios of 16.52 and 62.61 at 298 K, respectively [65]. Godini et al. carried out a techno-economic analysis of an ethylene separation unit within an Oxidative Coupling of Methane (OCM) process, demonstrating the industrial relevance of 13X for bulk CO₂ removal [112]. Nazari et al. employed Aspen Adsorption to simulate industrial-scale PSA and VSA processes using zeolite 13X as the preferred adsorbent for post-combustion CO₂ capture from flue gas, examining the influence of pressure and temperature on adsorption performance [97]. Nevertheless, as noted by Ganiyu, zeolites face significant challenges including hydrophilicity, limited selectivity in certain gas mixtures, energy-intensive regeneration, and cyclic stability concerns, all of which can compromise CO₂ capture efficiency in humid gas streams [69]. Despite these limitations, ongoing research continues to advance the performance of 13X. A variant synthesized from low-cost kaolin clay achieved an exceptional CO₂ capacity of 6.9 mmol g⁻¹, attributed to an optimized framework and cation distribution [113]. Additionally, ion exchange of the native Na⁺ cations with Li⁺ has been shown to increase capacity to 6.98 mmol g⁻¹, owing to the stronger quadrupole interaction associated with the smaller and more electropositive Li⁺ ions [114].

5.1.2. Zeolites 5A and 4A (LTA-type)

LTA-type zeolites, particularly 5A and 4A, are characterized by their small pore apertures (~5 Å and ~4 Å, respectively). Their pore dimensions are close to the kinetic diameter of CO₂ (~3.3 Å), which can induce molecular sieving effects and enhance selectivity for CO₂ over larger molecules such as CH₄ (~3.8 Å) [10]. Pakseresht et al. measured equilibrium adsorption isotherms for CO₂, CH₄, and C₂H₄ on zeolite 5A, reporting a high capacity for all three components, with CO₂ exhibiting the strongest adsorption at 3.5 mmol g⁻¹ at 303 K and 1000 kPa [63]. Zeolite 4A is particularly effective for separations involving methane, owing to its smaller pore size. Wynnyk et al. investigated high-pressure sour gas adsorption on synthesized 4A zeolite, reporting substantial CO₂ uptake of approximately 6 mmol g⁻¹ at 0 °C and 20 bar, alongside H₂S adsorption of approximately 5.2 mmol g⁻¹, but a considerably lower capacity for CH₄ of approximately 2 mmol g⁻¹, making it a promising

candidate for natural gas sweetening applications [108]. The influence of pore size and geometry was further examined by Parinyakit and Worathanakul, who simulated single- and binary-component adsorption of CO₂ and CH₄ on zeolite 4A, confirming its high selectivity for CO₂ [109]. However, LTA zeolites are inherently hydrophilic due to their low Si/Al ratio and the presence of extra-framework cations, a characteristic shared with zeolite 13X that renders their performance highly sensitive to moisture [10]. Recent structural modifications have aimed to address this limitation. Mesoporous zeolite 4A synthesized via a urea-assisted hydrothermal method demonstrated both enhanced CO₂ adsorption kinetics and reduced water uptake under humid conditions [64]. Similarly, freeze-dried mesoporous zeolite A (FDZA) exhibited improved mass transfer and structural stability, underscoring the potential of pore engineering in optimizing LTA-type zeolites for CO₂ capture and gas separation applications [110].

5.1.3. Modified and novel zeolites

Given that conventional zeolites can suffer from limitations such as moisture sensitivity, significant heat effects, and performance trade-offs across different gas mixtures, much of the recent research has focused on tuning zeolite properties to improve selectivity and working capacity while maintaining practical regeneration [115]. Tao et al. provided a comprehensive discussion of these strategies, demonstrating how cation exchange and framework modification can enhance CO₂/N₂ and CO₂/CH₄ separations by reshaping gas-cation and gas-framework interactions [99]. One particularly promising direction involves exploiting gate-opening behavior in flexible or cation-responsive frameworks. Shang et al. first demonstrated a molecular trapdoor mechanism in K-exchanged CHA zeolite (r1KCHA), whereby K⁺ cations partially block the pore windows at low temperatures but begin to oscillate with increasing temperature, selectively permitting CO₂ passage while excluding N₂, resulting in exceptionally high CO₂/N₂ selectivity at 0 °C [116]. Loera et al. investigated an alternative modification approach by encapsulating sulfur chromophores within zeolite A to alter the charge environment of the Na⁺ cations, which in turn modified the adsorption enthalpies for both CO₂ and CH₄, offering an innovative avenue for chemically tailoring the adsorbent surface [64]. The synthesis of zeolites from industrial waste streams represents a further area of active research. Liu et al. synthesized low-silica X (LSX) zeolite from low-grade coal gangue, achieving a CO₂ uptake of 4.99 mmol g⁻¹ and an IAST (Ideal Adsorbed Solution Theory) CO₂/N₂ selectivity of 376, demonstrating considerable potential for cost-effective CO₂ capture applications [100].

Moisture tolerance is another important target in zeolite modification, because water vapor can compete with CO₂ for extra-framework cation sites and sharply reduce working capacity during cyclic operation [117]. Hu et al. recently compared FAU- and MFI-type zeolites with different Si/Al ratios and cation forms under dry and humid conditions. Their results showed that conventional Al-rich, Na-containing zeolites suffer severe capacity loss in the presence of water vapor, whereas

high-silica H-form MFI zeolite showed much lower water sensitivity. After defect-healing treatment to remove hydrophilic silanol nests, MFI_H_940 healed exhibited almost unchanged CO₂ uptake under dry and humid conditions, with 0.83 mmol g⁻¹ under dry conditions and 0.84 mmol g⁻¹ at 75% relative humidity. In simulated humid PSA cycles, the same material maintained stable adsorption over repeated cycles and reached approximately 70–75% of its equilibrium capacity within 10 s, showing the importance of both hydrophobicity and fast uptake kinetics [118]. Core-shell and surface-protected zeolites provide another route for reducing water sensitivity. Bahmanzadegan et al. developed a hydrophobic zeolite 13X@ZIF-8 composite in which a ZIF-8 shell was grown on a zeolite 13X core. The composite combined the CO₂ affinity of zeolite 13X with the more hydrophobic character of ZIF-8, giving a CO₂ uptake of 1.6 mmol g⁻¹ at 25 °C and 1 bar and retaining 94.5% of its original capacity over 40 adsorption-desorption cycles. This example shows how hydrophobic shells can protect zeolite-based adsorbents from moisture while preserving cyclic CO₂ capture performance [119]. Hierarchical zeolites can also be useful when mass transfer and amine accessibility are important. Nguyen et al. synthesized hierarchical LTA zeolites with amine-functionalized mesoporous domains; the best APTMS-grafted LTA material reached 2.3 mmol g⁻¹ CO₂ uptake at 0.15 bar and 60 °C, showed 2.1 mmol g⁻¹ uptake under dynamic 15% CO₂/N₂ flow, and retained nearly constant capacity over 10 adsorption-desorption cycles. Humid CO₂ uptake was reduced to 0.81 mmol g⁻¹, but the study shows that combining zeolitic micropores with amine-functionalized mesopores can enhance CO₂ uptake and recyclability over conventional aminosilica supports [120]. These studies show that moisture-tolerant zeolite design requires balancing hydrophobicity, cation density, silanol defects, mesoporosity, amine accessibility, diffusion rate, and cyclic stability rather than optimizing dry CO₂ uptake alone. It should also be noted that this improved water tolerance is obtained at the expense of a substantially lower CO₂ working capacity than that of Al-rich zeolites such as 13X, so hydrophobicity and capacity must be traded off explicitly rather than treated as independent targets.

Kinetic and size-selective zeotype adsorbents also extend beyond carbon molecular sieves. ETS-4, an Engelhard titanosilicate molecular sieve, is a notable example because its effective pore aperture can be adjusted through dehydration, ion exchange, and thermal treatment [121]. This tunability enables molecular sieving and kinetic selectivity in mixtures where small differences in molecular size and diffusion rate are important [122]. Pillai et al. reported that NaETS-4 exhibits preferential CO₂ adsorption relative to CH₄, N₂, O₂, and Ar, while subsequent studies showed that ion exchange combined with thermal treatment can improve the thermal stability and CO₂/CH₄ size-selective adsorption performance of ETS-4. Therefore, ETS-type materials should be considered alongside CMS and trapdoor zeolites when discussing kinetic adsorbents for CO₂-containing gas separations [123].

Beyond ion exchange and cation-mediated gating mechanisms, a rapidly growing area of research involves the development of hybrid and composite zeolite structures designed to improve thermal management, electrical conductivity, mass transfer, and structural stability. Ribeiro et al., for instance, combined an activated carbon (AC) monolith with zeolite 13X for electric swing adsorption (ESA), reporting an approximately threefold increase in CO₂ capacity relative to the AC monolith alone when the zeolite fraction reached 18 wt% [124]. Regufe et al. similarly developed extruded AC/13X hybrid pellets for ESA applications, demonstrating that a 50/50 (AC/13X) composition yielded balanced adsorption performance and uniform Joule heating behavior. A 30/70 (AC/13X) composition, despite offering higher CO₂ capacity and CO₂/N₂ selectivity, failed to generate sufficient heat under the tested electrical conditions [125].

Zeolite-silica composites represent a further example of how zeolites are increasingly engineered as hierarchical micro-mesoporous systems. Zhou et al. reported micro/mesoporous 5A-MCM-41 composites achieving CO₂ uptake as high as 4.08 mmol g⁻¹ at 100 kPa and 298 K,

attributing the improvement to mesoporous channels that facilitate access to active adsorption sites and reduce diffusion limitations [126]. There is also growing interest in metal-exchanged and functionally modified zeolites targeting specific separations beyond conventional flue gas applications. For instance, Cu-exchanged 13X has been reported to enhance selectivity in CO₂-rich streams for olefin purification, achieving a capacity of 0.46 mmol C₂H₄ g⁻¹ with a demonstrated selectivity benefit after Cu exchange under PSA/TSA conditions [127]. Collectively, these studies reinforce an important principle: modified zeolites are no longer solely concerned with maximizing single-component CO₂ uptake, but rather with rationally designing the framework composition, cation chemistry, and pore texture in a manner that satisfies the actual process constraints, including thermal management, adsorption kinetics, structural stability, and regeneration strategy.

5.2. Metal-Organic Frameworks (MOFs)

MOFs have emerged as a distinct class of adsorbent materials, offering exceptionally high surface areas and considerable chemical tunability that enable the systematic engineering of pore size, pore geometry, and surface chemistry [22].

5.2.1. Benchmark MOFs: Cu-BTC and ZIF-8

Cu-BTC (HKUST-1) is still one of the most studied MOFs. Its open Cu sites facilitate CO₂ binding and promote high uptake at practical pressures. After activation, HKUST-1 loses coordinated water molecules and generates coordinatively unsaturated Cu sites (open metal sites), which strengthens the framework-CO₂ interaction and is one reason why it is repeatedly used as a benchmark sorbent [37]. Wu et al. incorporated Cu-BTC in comparative breakthrough simulations, documenting its superior separation performance and affirming its status as a benchmark material for process-level investigations [66]. However, HKUST-1 is well known for its sensitivity to moisture, and recent efforts have therefore focused on protecting its open Cu sites through coordination with species such as imidazole, acetonitrile, pyrrole, and glycine, with the aim of improving water stability while retaining CO₂ uptake [37]. Beyond the pristine form, HKUST-1 supported on magnetic sugarcane bagasse has been reported as a practical composite adsorbent, delivering a CO₂ uptake of 14.55 mmol g⁻¹ as determined by Dubinin-Astakhov fitting, and evaluated under PSA conditions for CO₂/CH₄/N₂ separation [128]. More broadly, recent research has increasingly shifted toward engineered variants of HKUST-1 that address the kinetic and stability limitations. Chang et al. reviewed several composite and hierarchical design strategies, including the growth of Cu-BTC in the presence of porous carbons, to introduce additional ultrafine pores and improve mass transfer, thereby increasing CO₂ capacity and reducing equilibration time relative to the pure Cu-BTC form [37]. Such structural tuning is of considerable practical importance, as faster adsorption kinetics and lower regeneration energy demands can be as consequential as equilibrium capacity in the context of cyclic separation processes.

Zeolitic imidazolate framework-8 (ZIF-8) is widely recognized for its exceptional molecular sieving capability. Its effective pore aperture of approximately 3.4 Å is well-suited for the separation of CO₂ from larger molecules such as CH₄ and N₂, as this dimension falls below the kinetic diameters of both CH₄ and N₂, underpinning size-selective adsorption and transport [12]. Abd et al. applied ZIF-8 in a PSA simulation for biogas upgrading, achieving a biomethane purity of 99.93% with a recovery of 96.5%, demonstrating its strong separation performance [67]. Beyond process-level studies, ZIF-8 is also widely employed as a benchmark material in molecular simulation screening. A Grand Canonical Monte Carlo (GCMC) comparison of MOF-5, UiO-66, and ZIF-8 reported a CO₂ uptake of 11.25 mmol g⁻¹ at 258 K and 20 bar (495.22 mg g⁻¹) for ZIF-8, providing a consistent reference point for evaluating candidate MOFs across a range of pressure and temperature conditions [129]. ZIF-8 has also been extensively investigated as a functional phase in composite separation systems. Jomekian et al., for

instance, incorporated ZIF-8 as a filler in Pebax-1657 mixed-matrix membranes, reporting a substantial improvement in CO₂/CH₄ separation performance [130]. Collectively, these examples illustrate why Cu-BTC and ZIF-8 continue to serve as reference materials in the MOF literature, not only as extensively characterized adsorbents but also as versatile platforms that can be systematically modified through composite formation, shaping, and hybrid configurations to better satisfy real process requirements.

5.2.2. Highly stable MOFs: UiO-66

UiO-66 is a zirconium-based MOF widely recognized for its exceptional thermal, chemical, and mechanical stability, making it one of the most suitable MOF candidates for industrial adsorption applications [131]. A recent comparative GCMC study examining MOF-5, ZIF-8, and UiO-66 across temperatures of 258–323 K and pressures of 0–30 bar demonstrated that UiO-66 exhibited the highest CO₂ uptake at room temperature (298 K, 1 bar) and generally dominated the low-pressure adsorption regime, with the exception of 258 K, owing to its polar pore environment. In the same study, UiO-66 achieved a CO₂ uptake of approximately 94.37 mg g⁻¹ at 298 K and 1 bar (≈ 2.14 mmol g⁻¹), reinforcing its suitability for post-combustion-relevant operating conditions. Mechanistically, this strong low-pressure affinity was attributed to CO₂ interactions with the polar Zr-O clusters within the framework, which also accounts for its tendency toward earlier pore saturation relative to larger-pore MOF structures [129].

Defect engineering represents another significant direction for enhancing UiO-66 performance. The controlled introduction of missing linkers or missing clusters can tune adsorption sites, porosity, and transport pathways while preserving the inherent stability that makes UiO-66 an attractive candidate for industrial applications [132]. This missing-linker concept has been identified in the UiO-66 literature as particularly tunable and consequential for gas adsorption, motivating extensive research into the deliberate introduction of defects to balance capacity, selectivity, and stability [129]. Beyond defect engineering, linker functionalization has been widely employed to strengthen CO₂-framework interactions while maintaining the chemical resilience of the Zr-based node. Fan et al. reported that incorporating polar or electron-withdrawing functional groups can enhance CO₂ affinity and, in many cases, improve CO₂/N₂ separation performance [133,134]. Energy-focused assessments cited in the same work indicate that UiO-66-NH₂ can outperform several alternative materials owing to its relatively large working capacity, while UiO-66-(OH)₂ and UiO-66-NO₂ have also demonstrated improved energy performance relative to pristine UiO-66-H. These trends are of particular relevance to cyclic adsorption processes, where high-performing materials are characterized not only by elevated equilibrium uptake, but also by a favorable combination of working capacity and practical regeneration energy [12]. Finally, given that real industrial gas streams frequently contain moisture, recent UiO-66 variants have increasingly been designed with humidity management as a key design consideration. Certain functionalization strategies have been shown to reduce competitive water uptake, as evidenced by UiO-66-NO₂ exhibiting lower water adsorption than unmodified UiO-66 under comparable conditions, which is beneficial for maintaining CO₂ capture performance in humid gas streams [135].

Hu et al. explored mixed-ligand strategies involving the functionalization of UiO-66 with 2-aminobenzimidazole, demonstrating that this modification reduces the Lewis acidity of the Zr-O node and increases framework hydrophobicity, thereby improving water stability for humid flue gas capture applications [136]. In a related study, Chang et al. investigated composite and ion-assisted designs, including Li⁺@PAA@UiO-66, in which the introduction of dual lithium sites was associated with enhanced CO₂/N₂ and CO₂/CH₄ selectivity, with CO₂ affinity increasing proportionally with Li⁺ concentration. Notably, CO₂/N₂ and CO₂/CH₄ selectivities were increased by approximately 20-fold and 10-fold, respectively, upon raising the LiOH concentration

from 0.05 M to 0.1 M. This material also demonstrated notable water stability, satisfactory recyclability, and the advantage of low-cost and readily available raw materials, collectively positioning it as a promising candidate for industrial CO₂ adsorption and separation applications [137].

Collectively, these examples illustrate why UiO-66 is widely regarded as a platform MOF. Its inherent structural stability, combined with multiple independent tuning strategies, including defect engineering, linker functionalization, and humidity-resistant design, provides a versatile foundation for optimizing adsorption performance toward realistic industrial operating conditions.

5.2.3. Industrially relevant stable MOFs: CALF-20 and MIL-160(Al)

Among recently developed MOFs, CALF-20 has become one of the most important examples of a practically relevant adsorbent for post-combustion CO₂ capture. CALF-20 is a zinc-based framework constructed from triazolate and oxalate linkers, and its significance lies not only in its CO₂ uptake but also in its unusual combination of hydrothermal stability, CO₂ selectivity under humid conditions, scalable synthesis, and compatibility with structured contactor designs [138,139]. Lin et al. described CALF-20 as a scalable and durable physisorbent for CO₂ capture, showing that it maintains CO₂ adsorption performance under humid flue-gas-relevant conditions and remains stable against steam, wet acid gases, and prolonged flue-gas exposure. This makes CALF-20 distinct from many early benchmark MOFs such as HKUST-1, whose open metal sites provide strong CO₂ affinity but also lead to moisture sensitivity [139].

From a process perspective, CALF-20 is particularly relevant because it has been incorporated into structured sorbent filters for rapid-cycle temperature swing adsorption. Its value therefore arises from the combined consideration of material stability, water tolerance, adsorption affinity, shaping/processability, and cyclic regenerability rather than from equilibrium CO₂ capacity alone [140]. Recent studies on CO₂/N₂ and CO₂/H₂O adsorption in CALF-20 further show why competitive water adsorption and humid-mixture behavior must be considered when evaluating MOFs for post-combustion capture. In this respect, CALF-20 represents a more industrially realistic MOF benchmark than many high-surface-area frameworks that show excellent dry-gas uptake but limited stability under practical operating conditions [141,142].

Several studies have examined CALF-20 for CO₂ capture process design. Dilipkumar et al. studied the equilibrium adsorption and transport of CO₂, N₂, and H₂O in CALF-20 using gravimetric, volumetric, and breakthrough measurements over a wide temperature and humidity range. Their work showed that the adsorption behavior could be described by the Sips–Henry model, while transport in shaped CALF-20 particles was mainly influenced by Knudsen diffusion through macropores. This is important because it shows that CALF-20 performance in cyclic processes cannot be judged only from equilibrium uptake, but also depends on diffusion and moisture transport [143]. Raganati et al. further evaluated CALF-20 prepared by a reduced-solvent mechanochemical route for TSA-based post-combustion CO₂ capture. In a fixed-bed system operated at 3–20 vol% CO₂ and 28–130 °C, the material reached a CO₂ uptake of up to 2.55 mmol g⁻¹. This showed complete regeneration and maintained stable performance over ten TSA cycles [144]. These results support the potential of mechanochemical synthesis as a more sustainable route for producing CALF-20 without losing its cyclic adsorption performance. From a process-level viewpoint, Shin et al. assessed CALF-20 and five isorecticular derivatives for biogas upgrading by combining molecular simulation, PVSA optimization, and techno-economic analysis. Among the studied materials, CALF-20 gave the most favorable economic performance, producing CH₄ with > 97% purity [145]. Taken together, these studies show that CALF-20 is now being assessed not only as a stable MOF adsorbent, but also as a material whose diffusion behavior, synthesis route, cyclic performance, and process economics are relevant to practical CO₂ separation.

MIL-160(Al) is another stable MOF that has gained attention for post-

combustion CO₂ capture and pilot-scale evaluation. Its aluminum-based framework provides good chemical robustness, and the material has been tested in pelletized form in a VPSA pilot unit for post-combustion CO₂ capture at Technology Centre Mongstad [146]. Together, CALF-20 and MIL-160(Al) illustrate the direction in which MOF-based CO₂ adsorption is moving, from maximizing surface area and single-component uptake toward moisture-tolerant, scalable, shaped, and process-compatible materials. Recent studies further show the practical direction of MIL-160(Al) research. Karimi et al. investigated shaped MIL-160(Al) for CO₂/N₂ separation under post-combustion-relevant conditions. Breakthrough experiments were first carried out at 313 K and 4.0 bar, followed by validation of a five-step PSA cycle consisting of pressurization, feed, rinse, blowdown, and purge. The subsequent industrial PSA simulation showed that shaped MIL-160(Al) could achieve approximately 67.3% CO₂ purity with 99.1% CO₂ recovery, indicating strong recovery but also showing that additional cycle optimization would be needed to reach high-purity CO₂ product specifications [147]. Bordonhos et al. extended the evaluation of MIL-160(Al) to CO₂/CH₄ separation for biogas upgrading. In that study, MIL-160(Al) was shaped into silica-containing beads without loss of adsorption performance beyond the expected dilution effect from the nonporous binder. Industrial PSA/VPSA simulations based on a two-bed, four-step Skarstrom cycle showed that VPSA gave substantially higher CH₄ recovery than PSA, approximately 82% compared with 52% [148]. These results show that MIL-160(Al) is being evaluated not only as a stable CO₂-selective MOF, but also as a shaped adsorbent for realistic PSA/VPSA operation in post-combustion capture and biogas upgrading.

5.2.4. Flexible and "Phase-change" MOFs

Beyond benchmark frameworks such as Cu-BTC and ZIF-8, and highly stable platforms such as UiO-66, flexible or phase-change MOFs represent another important and distinct class of adsorbent materials. Unlike rigid frameworks, flexible MOFs possess structurally adaptive pore systems capable of reversible changes in pore size and geometry upon exposure to guest molecules, a phenomenon commonly referred to as gate-opening or breathing behavior [149,150]. These materials characteristically exhibit step-shaped adsorption isotherms, which are particularly advantageous for swing adsorption processes, as they can deliver substantial working capacities with only modest variations in pressure or temperature [151]. A representative example in the context of post-combustion CO₂ capture is F4-MIL-140A(Ce), which was evaluated as a phase-change adsorbent by Danaci et al. The authors reported a non-hysteretic, step-shaped CO₂ isotherm that yielded improved VSA performance relative to benchmark zeolite 13X, achieving high CO₂ purity and recovery under the tested conditions, with a reported CO₂ capacity of approximately 2.65 mmol g⁻¹ [81].

Flexible MOFs have also demonstrated considerable potential beyond flue gas applications. Horike et al. showed that rare-earth porous coordination polymers (PCPs) can exhibit gate-opening behavior whose step position is tunable through variation of the metal center, enabling selective CO₂ removal from light hydrocarbon mixtures. In particular, La-PCP is explicitly described as a gate-opening framework that strongly adsorbs CO₂ at low pressure while showing negligible adsorption of C₂H₄ and C₂H₆ up to approximately 150 kPa, enabling selective CO₂ removal from CO₂/C₂H₄ and CO₂/C₂H₆ mixtures under near-ambient conditions [80]. Further studies confirm the generality and tunability of this concept. Peng et al. reported selective CO₂ capture in a stable flexible MOF through a discriminatory gate-opening effect [77], Aguado et al. demonstrated guest-induced gate-opening in a ZIF-type framework [78], and Cheng et al. showed that the gate-opening transition itself can be systematically tuned during CO₂ sorption [79]. From a process design perspective, the key objective is not only to achieve a step-shaped isotherm, but to position the step within the relevant CO₂ partial pressure window while ensuring that the structural transition remains sufficiently fast and reversible over repeated adsorption cycles.

5.3. Carbon-based adsorbents

5.3.1. Activated carbons

Activated carbons (ACs) are amorphous, highly porous materials derived from carbon-rich precursors such as coconut shells, wood, and coal [152]. Their principal advantages include low production cost, high surface area, and inherent hydrophobicity, which renders them considerably less sensitive to moisture in flue gas relative to zeolites [153]. However, their nonpolar surface chemistry results in an absence of strong, specific binding sites for CO₂, and consequently, CO₂/gas selectivity is substantially lower than that of zeolites [154]. This selectivity limitation is well illustrated by classical equilibrium comparisons. Sievers et al. reported that CO₂/N₂ selectivity on ACs was substantially lower than on molecular sieve 5A, underscoring the contribution of electrostatic CO₂-cation interactions in zeolites relative to the weaker physisorption interactions characteristic of carbon surfaces [62]. Process-level studies further illustrate the inherent trade-off between cost and robustness on one hand, and separation sharpness on the other. Zarghampoor et al. conducted a CO₂/N₂ VSA modeling study comparing AC with zeolite 13X, finding that 13X exhibited a considerably longer breakthrough time ($\times 3.5$ longer) and a marginally higher cyclic utilization of 80% relative to 74% for AC, demonstrating the performance advantage of zeolites when high separation efficiency is the primary objective [155]. Punpee et al. compared AC, zeolite 13X, and a carbon molecular sieve (CMS) within a VPSA framework under biogas upgrading conditions for CO₂/CH₄ separation, reporting dynamic CO₂ capacities of approximately 2.24 mmol g⁻¹ for CMS, 2.13 mmol g⁻¹ for AC, and 1.13 mmol g⁻¹ for 13X, with CMS exhibiting the highest dynamic adsorption capacity under the evaluated cycle conditions [156].

Beyond conventional commercial ACs, considerable research attention has been directed toward biomass-derived and surface-modified carbons as a means of improving performance toward practical process targets. Rathore et al. evaluated a biomass-based activated carbon derived from coconut shells for post-combustion CO₂/N₂ separation in a TSA simulation, reporting a product CO₂ purity exceeding 90 mol% and a CO₂ capacity of 4.6 mmol g⁻¹ [87]. A further promising direction involves modifying carbon surface chemistry to introduce CO₂-philic adsorption sites while preserving the inherent stability of the carbon framework. Mukherjee et al. synthesized activated carbon from spent coffee grounds and functionalized it using a deep eutectic solvent, reporting improved separation performance in a dynamic CO₂/N₂ mixture and demonstrating that the adsorbent retained approximately 92% of its uptake capacity over multiple adsorption-desorption cycles, supporting the premise that targeted surface functionalization can partially bridge the selectivity gap of unmodified ACs [157].

5.3.2. Carbon Molecular Sieves (CMS)

Carbon molecular sieves (CMS) is a specialized class of porous carbons characterized by narrow, well-defined micropores. In carbonaceous adsorbents, pore architecture exerts a strong influence on both adsorption capacity and diffusion behavior, such that tuning microporosity affects not only uptake capacity but also mass transfer rates and overall separation performance [153]. Unlike conventional adsorbents in which separation is predominantly governed by equilibrium selectivity, CMS frequently achieve gas separation under kinetic control, whereby the primary advantage derives from differences in diffusion rates among the constituent species during the adsorption step. In practice, the pore mouth geometry of CMS imposes additional diffusion resistance, enabling faster-diffusing species such as CO₂ to enter the micropores rapidly while slower species such as CH₄ and N₂ lag behind on the timescale of a short adsorption cycle. This kinetic selectivity mechanism is precisely why CMS are widely regarded as strong candidates for rapid-cycle PSA and VPSA processes, in which the bed is switched before full adsorption equilibrium is attained [158].

Rainone et al. conducted fixed-bed adsorption and desorption experiments for CO₂/CH₄ separation using two commercial CMS grades,

finding that while AC can exhibit higher overall capacity, CMS demonstrated considerably lower CH_4 adsorption owing to combined thermodynamic and kinetic sieving effects, resulting in higher CO_2/CH_4 separation selectivity. The authors further emphasized that intraparticle diffusion governs the adsorption dynamics, and that the optimal adsorbent choice is therefore strongly dependent on cycle kinetics and process design [159]. Park et al. measured adsorption equilibria and uptake kinetics of CO_2 , CO , and N_2 on pelletized CMS across a temperature range of 298–318 K and pressures up to 10 bar, validating their kinetic parameters through dynamic breakthrough simulations, reinforcing that CMS-driven separations generally require kinetic modeling in addition to equilibrium isotherm characterization [160]. Overall, CMS perform most effectively in rapid PSA and VPSA cycles where the process benefits from kinetic discrimination. However, as contact times increase and the bed approaches adsorption equilibrium, the kinetic advantage diminishes and materials with stronger equilibrium selectivity may become more competitive [161].

5.4. Amine-functionalized sorbents

The prospect of combining the high selectivity of chemisorption with the practical advantages of solid materials has motivated the development of amine-functionalized sorbents. In these materials, amine groups ($-\text{NH}_2$) are grafted onto the surface of a porous support such as silica or zeolite, enabling CO_2 capture through stronger and more specific interactions than those achievable with conventional physisorbents [162]. McDonald et al. demonstrated that diamine-appended metal-organic frameworks can significantly enhance CO_2 uptake at very low partial pressures through cooperative adsorption. Specifically, mmen- $\text{Mg}_2(\text{-dobpdc})$ achieved an uptake of approximately 2.0 mmol g^{-1} at $\sim 390 \text{ ppm CO}_2$, considerably exceeding the capacity of the parent framework, and remains a promising candidate for DAC applications [163]. Supported polyethylenimine (PEI) sorbents represent a further well-established class of materials widely used as benchmarks for DAC and dilute-stream capture; however, long-term stability remains a significant limitation. Guta et al. reported that a 45 wt% PEI/ $\gamma\text{-Al}_2\text{O}_3$ sorbent is susceptible to accelerated oxidative degradation in the simultaneous presence of CO_2 and O_2 , with capacity losses becoming particularly pronounced under humid operating conditions, which is a common realistic challenge limiting the long-term deployment of amine-functionalized sorbents in practical flue gas and ambient air capture campaigns [105].

Recent studies have increasingly focused on low-cost supports, structured contactors, and low-temperature regeneration DAC technologies. Fricke et al. developed 3D-printed activated carbon monoliths functionalized with 3-aminopropyltriethoxysilane (APTES). This approach achieved a CO_2 uptake of 0.25 mmol g^{-1} at 0.04 kPa CO_2 , which is directly relevant to atmospheric CO_2 capture. The chemisorbed CO_2 was assigned to ammonium carbamate formation and could be desorbed at 75°C , suggesting the potential of amine-functionalized carbon monoliths as scalable DAC contactors [164]. Roh et al. introduced aminosilane-grafted cellulose fiber sorbents prepared through solvent-tuned grafting, where the optimized toluene–water system reached an amine loading of $1.63 \text{ mmol N g}^{-1}$. CO_2 uptake was 0.27 mmol g^{-1} at 420 ppm CO_2 and showed stable performance over 20 adsorption–desorption cycles. This study highlights cellulose fibers as an abundant, low-cost platform for DAC sorbents, especially when amine loading and pore preservation are balanced [165]. Han et al. further showed that epoxide functionalization of amines can improve cyclic working capacity at low desorption temperatures. In particular, butylene-oxide-modified PEI300 and TREN sorbents showed strong cyclic performance at desorption temperatures as low as 45°C and 40°C , respectively, while maintaining stability under oxygen-rich and humid conditions [166]. These examples show that DAC adsorbent development is shifting from simple amine loading toward structured, low-cost, and cyclically stable sorbents that can operate at low CO_2 partial

pressure and moderate regeneration temperature.

Rahim et al. evaluated amine-functionalized silica nanocapsules (SiNC series) and reported a notable variation in CO_2 capacities depending on formulation, with SiNC-A4 achieving 7.03 mmol g^{-1} as listed in Table S1, illustrating the substantial influence of support architecture and amine environment on overall performance [167]. Beyond individual material examples, recent research has consistently demonstrated that performance is rarely determined by amine loading alone; the dispersion quality and accessibility of amine sites during repeated cycling can be equally decisive factors. Tao et al. investigated TETA-loaded polymer resins and found that amine–support compatibility strongly influenced both uptake capacity and cyclic stability, with certain resin supports enabling a CO_2 capacity of approximately 4.2 mmol g^{-1} at 35°C with only modest capacity loss over repeated adsorption cycles [162]. Overall, amine-functionalized sorbents remain among the most effective materials for low-partial-pressure CO_2 capture; however, their full potential is achieved only when uptake capacity, regeneration energy demand, and long-term chemical stability are considered collectively rather than optimized in isolation.

5.5. Hybrid solid–solvent adsorption systems

Hybrid platforms such as supported liquid membranes (SLMs), porous liquids, and mixed-matrix membranes (MMMs) aim to integrate the advantages of porous adsorbents, liquid solvents, and polymeric membranes into a single CO_2 -selective system [17]. In SLMs, a selective liquid phase, typically an amine solution, ionic liquid, or deep eutectic solvent, is immobilized within a porous support matrix. This configuration can, in principle, deliver high CO_2 selectivity with a minimal solvent inventory and reduced solvent loss relative to conventional absorption processes; however, long-term stability challenges, including solvent leakage, pore wetting, and chemical and thermal degradation, remain significant obstacles under realistic operating pressure and temperature gradients [168].

Porous liquids and MMMs represent two additional approaches to embedding adsorbent functionality within fluid or polymeric media. Type II and III porous liquids disperse rigid porous particles, such as MOFs or porous organic cages, in size-excluded carrier liquids, seeking to combine the CO_2 affinity characteristic of solid adsorbents with the processability of liquid systems [16]. MMMs, by contrast, incorporate porous fillers such as zeolites, activated carbons, or MOFs into a polymer matrix to overcome the permeability–selectivity trade-off inherent to neat polymers [169]. Although many hybrid materials demonstrate improved CO_2 selectivity or permeability under laboratory conditions, challenges related to viscosity control, interfacial compatibility, defect formation, mechanical robustness, and large-scale fabrication continue to limit their industrial maturity relative to established packed-bed adsorption processes [170,171].

6. Adsorption process configurations

The recovery and reuse of adsorbents in industrial processes is critical, and the selection of an appropriate adsorbent is therefore inherently linked to the design of the cyclic adsorption process employed [172]. The configurations most extensively studied include TSA, PSA, VSA, and various hybrid systems, each of which presents distinct energy demands and is suited to different industrial applications [173,174]. In practical applications, the choice of adsorption cycle is strongly connected to the feed gas composition and operational conditions, such as pressure and temperature; therefore, post-combustion flue gas, natural gas upgrading, hydrogen purification, and DAC cannot be evaluated using the same process assumptions.

An additional distinction is whether CO_2 behaves as the strongly adsorbed component or the weakly adsorbed component in the target separation. In post-combustion CO_2/N_2 capture, biogas and natural gas sweetening, H_2 purification, and DAC, CO_2 is generally the more

strongly adsorbed component and is recovered during regeneration steps such as blowdown, evacuation, heating, steam-assisted desorption, or hybrid desorption. In these cases, the weakly adsorbed component, such as N_2 , CH_4 , or H_2 , is typically recovered during the adsorption step. By contrast, in some CO_2 -containing petrochemical purification streams, particularly when olefin-selective Ag^+/Cu^+ sites or π -complexation adsorbents are used, CO_2 may behave as the weakly adsorbed component while the unsaturated hydrocarbon is preferentially retained. This distinction directly determines product-collection strategy, purge direction, pressure-equalization steps, regeneration severity, and the overall cycle configuration.

Adsorption should not be presented as a universally superior alternative to absorption, membrane separation, or cryogenic separation; rather, its relevance depends strongly on feed composition, operating pressure and temperature, humidity, contaminants, and regeneration strategy [175]. For many dilute post-combustion flue-gas applications, aqueous amine absorption remains the main commercial benchmark because of its high CO_2 recovery and mature process integration [176]. Membrane systems offer compact and continuous operation, but low CO_2 partial pressure in flue gas often requires multistage designs, recycle, vacuum, or compression to reach high recovery and purity [177, 178]. Cryogenic separation is generally more suitable for high-pressure or CO_2 -rich streams and for applications requiring CO_2 liquefaction, but it is usually energy-intensive for dilute gas streams. In this context, adsorption can be attractive when solid sorbents are incorporated into structured beds, monoliths, laminates, or filters that reduce pressure drop and enable cyclic operation through pressure, vacuum, temperature, steam, or hybrid regeneration [179]. However, adsorption performance must be evaluated using process-level indicators such as working capacity, selectivity under realistic gas mixtures, CO_2 purity, recovery, regeneration energy, pressure drop, water tolerance, sorbent lifetime, and environmental impact, rather than equilibrium uptake alone [180]. Reported energy requirements illustrate why adsorption is context-dependent rather than universally superior: for 90% post-combustion capture, aqueous-amine (MEA) regeneration typically requires about 3.5–4.0 GJ tCO_2^{-1} of low-grade thermal energy, whereas optimized vacuum- and temperature-vacuum-swing adsorption cycles have reported roughly 1.5–3 GJ tCO_2^{-1} , part of which is supplied as electrical (vacuum) work. These figures are not directly comparable, because thermal and electrical energy differ thermodynamically and because energy demand, product purity, and recovery are coupled along process Pareto fronts; under dilute, humid flue-gas conditions the adsorption energy penalty can approach or exceed that of amine scrubbing, which is why absorption remains the benchmark for such streams [19]. With respect to environmental impact, solid-sorbent adsorption can avoid volatile-amine emissions, solvent degradation, and reclaim waste associated with aqueous-amine scrubbing; however, a complete comparison requires life-cycle assessment that also accounts for sorbent manufacturing, shaping, and end-of-life disposal.

In addition to equilibrium adsorption properties, adsorption kinetics and breakthrough dynamics are central to practical PSA and VSA design. In fixed-bed operation, the useful capacity of an adsorbent is not determined only by its equilibrium CO_2 uptake, but also by the rate at which CO_2 and competing gases move through the external gas film, macropores, mesopores, and micropores of the shaped adsorbent particle [181,182]. When intraparticle diffusion is slow, the mass-transfer zone becomes broader, the breakthrough front becomes less sharp, and CO_2 can appear at the bed outlet before the equilibrium capacity of the bed is fully used. This lowers bed utilization, productivity, and cyclic working capacity [160]. Desorption kinetics are equally important because slow diffusion out of the particle can lead to incomplete regeneration, especially in short PSA/VSA cycles, causing capacity loss in the following adsorption step [183]. In diffusion-controlled separation processes, such as those using carbon molecular sieves or size-selective zeotypes, the separation is intentionally based on differences in uptake rate rather than only on equilibrium selectivity.

Therefore, cycle time, particle size, pellet/monolith geometry, purge flow, vacuum level, and pressure-equalization steps must be optimized together with adsorption equilibrium [184,185]. Recent studies on CALF-20, CMS, and shaped MIL-160(Al) illustrate this point: CALF-20 transport studies showed the importance of Knudsen diffusion and moisture transport in shaped particles, CMS studies demonstrated kinetic CO_2/CH_4 and CO_2/N_2 discrimination, and MIL-160(Al) PSA/VPSA models used breakthrough data and linear-driving-force-type kinetic descriptions to connect material behavior with process performance [143,147,160]. Thus, breakthrough experiments under realistic multi-component conditions are essential for translating adsorbent properties into practical cycle metrics such as breakthrough time, bed utilization, purity, recovery, productivity, and energy demand.

6.1. Temperature swing adsorption

In Temperature Swing Adsorption (TSA), CO_2 is adsorbed at ambient temperature, and the bed is regenerated through the application of heat. This configuration is particularly well-suited to adsorbents with high heats of adsorption, such as chemisorption-based materials including amine-functionalized sorbents. The principal limitation is the thermal energy requirement, arising primarily from the sensible heat associated with heating the adsorbent, support, and process hardware, although TSA can achieve high product purity in applications where strongly bound species must be removed.

Several studies illustrate these trade-offs. A comparative study examining activated carbon, zeolite 13X, and Mg-MOF-74 reported that Mg-MOF-74 yielded the lowest total energy consumption and the highest CO_2 separation exergy efficiency of approximately 22%, while activated carbon exhibited the highest energy demand under the tested TSA conditions. This comparison demonstrates that TSA performance is governed not only by adsorption capacity, but also by how the cycle distributes energy between sensible heating and the separation work itself [186]. TSA has also been applied to more targeted purification tasks requiring strong and specific molecular interactions. Chen et al. conducted a TSA case study using $AgNO_3/NaY$ for a $CO_2/C_2H_4/N_2$ mixture, reporting deep removal of ethylene from CO_2 to below 1 ppmv through strong Ag^+ -olefin π -complexation. The same study reported bed regeneration in air or CO_2 at 240–260 °C and near-complete recovery of adsorption capacity following regeneration, with a re-adsorption capacity of approximately 17.7 mL g^{-1} compared to an initial value of approximately 17.8 mL g^{-1} , demonstrating that TSA can be effective even when separation relies on specific chemical binding rather than weak physisorption alone [187].

6.2. Pressure swing adsorption

Pressure Swing Adsorption (PSA) is among the most well-established and industrially promising configurations for gas separation. It operates across medium to high pressure ranges, with adsorption occurring at elevated pressure and regeneration achieved through a rapid pressure reduction. PSA is particularly well-suited to physisorbents such as zeolites and most MOFs, where adsorption is reversible with changes in pressure, and process studies have demonstrated its flexibility across a wide range of gas mixtures [188]. However, this configuration requires feed gas pressurization prior to adsorption, can incur considerable energy consumption for gas compression, and may exhibit incomplete regeneration under certain operating conditions [28]. Jedli et al. investigated CO_2/CH_4 separation on zeolite 13X through combined kinetic and equilibrium studies, demonstrating that 13X exhibits significant selectivity for both CO_2/CH_4 and CO_2/H_2 separations under practically relevant conditions [65]. Abd et al. integrated experimental adsorption data with Aspen Adsorption modeling for CO_2 capture from landfill biogas using ZIF-8, reporting PSA operating conditions that achieved enhanced CH_4 purity and recovery, and demonstrating that appropriate cycle design can compensate for moderate equilibrium

selectivity in certain adsorbent materials [67]. Rahim et al. further demonstrated that amine-functionalized solids can also be operated within PSA-type schemes when regeneration conditions are carefully selected. Their investigation of the SiNC-A series under PSA conditions showed that the higher-loading formulation, SiNC-A4, retained strong performance over repeated adsorption–desorption cycling, maintaining approximately 90% of its removal capacity after five cycles at a regeneration temperature of approximately 110 °C, a result of practical relevance when assessing cyclic stability rather than single-cycle uptake alone [167].

6.3. Vacuum swing adsorption (VSA)

Vacuum Swing Adsorption (VSA) can be regarded as a variant of PSA in which the desorption step is conducted at sub-atmospheric pressure. This configuration is particularly well-suited to post-combustion CO₂ capture from flue gas streams, which are typically at near-atmospheric pressure, thereby avoiding the energy cost associated with compressing the entire feed stream [91]. Adsorption takes place at ambient pressure, while regeneration is carried out under vacuum conditions. Although VSA is especially attractive for large-scale, low-pressure separations on account of this feed compression advantage, its principal limitation lies in the energy intensity of deep vacuum regeneration, where electricity demand for vacuum pumping can become a dominant contributor to the overall capture cost [28]. Zarghampoor et al. modeled CO₂ capture from CO₂/N₂ mixtures using VSA and compared the performance of activated carbon and zeolite 13X, reporting that 13X achieved a considerably longer breakthrough time and higher cyclic utilization under the tested conditions, which is one reason zeolites remain widely used as benchmark adsorbents in VSA studies [155].

6.4. Hybrid and emerging techniques

Hybrid regeneration strategies have emerged as a practical means of overcoming the inherent limitations of purely pressure- or temperature-driven regeneration methods, with the primary objective of optimizing separation performance while reducing overall energy demand [189]. Temperature-Vacuum Swing Adsorption (TVSA), investigated by Deschamps et al. in the context of DAC, combines a moderate temperature increase with vacuum application to achieve more energy-efficient adsorbent regeneration [70]. On the emerging side, Mapstone et al. investigated supercapacitive swing adsorption (SSA), in which capture and release are governed by electrical polarization protocols rather than conventional pressure or temperature swings, illustrating the broader trend toward alternative regeneration strategies [190]. At the industrial scale, economically viable CO₂ capture increasingly relies on combined and integrated process configurations. In practice, regeneration cycles may incorporate sequential steps, beginning with a PSA stage to achieve bulk desorption, followed by a TSA step to ensure complete adsorbent

recovery and readiness for the subsequent adsorption cycle. Table 1 summarizes the operating domains in which the major adsorbent families are most typically applied across common CO₂-containing feed streams and cyclic process configurations and is intended as a process-oriented guide for matching adsorbent selection to realistic operating conditions.

6.5. Industrial and pilot-scale relevance of adsorption cycles

Although many adsorption studies remain at the laboratory or simulation scale, several industrially relevant examples show how solid-sorbent CO₂ capture is being translated into practical cyclic processes [86].

For post-combustion and industrial flue-gas streams, structured solid-sorbent systems such as rapid temperature-swing adsorption have been developed to capture CO₂ from diluted gas streams containing mainly N₂, O₂, CO₂, and diluted water vapor [191]. In these systems, the adsorbent is not used as a loose powder but is commonly shaped or immobilized into structured beds, filters, or contactors to reduce pressure drop and improve heat and mass transfer [192]. In a real-world industrial example, Svante developed a rapid-cycle temperature swing adsorption (RC-TSA) process using structured CALF-20 MOF sorbent filters for cement flue gas capture in the CO₂MENT project with LafargeHolcim, Total, and CCP. The project targeted cement flue gas containing about 15–16% CO₂, 10–12% O₂, and NO_x/SO_x impurities, included installation of a 1 tCO₂ day^{−1} VeloxoTherm™ field-testing unit at Lafarge's Richmond cement plant, and demonstrated CALF-20 process stability in a 0.1 tCO₂ day^{−1} PDU for 2300 h (>120,000 cycles) under simulated cement kiln flue gas, achieving 95% CO₂ product purity, 10.2 tCO₂ day^{−1} productivity, a 52 s cycle time, and a steam ratio of 1.9 ± 0.3 kg steam kg^{−1} CO₂ [193]. Another pilot-scale example is the MOF4AIR demonstration at Technology Centre Mongstad (TCM), where MIL-160(Al) was loaded as 17.5 kg of pelletized MOF in each of three VPSA columns and operated in a 3-bed, 6-step cycle for post-combustion CO₂ capture; the system achieved approximately 90% CO₂ recovery and 95% CO₂ purity [146].

For biogas and natural gas sweetening, PSA and VPSA systems are already used commercially to remove CO₂ from CH₄-rich streams and produce biomethane suitable for grid injection or fuel use. For biogas upgrading, Kottittitum et al. simulated and validated a commercial REBiofuel six-step PSA process using CMS-3K for a 55–45% CH₄/CO₂ feed at more than 5000 Nm³ h^{−1}; the model closely matched the real plant performance, giving 92.08% simulated CH₄ purity compared with 92.10% measured purity at 6.5 bar and 250 s adsorption time [194]. For high-CO₂ natural gas sweetening, Tao et al. tested a PSA demonstration skid at the CO₂CRC Otway site using Sorbead WS by BASF (an amorphous aluminosilicate gel used as a high-capacity adsorbent and protective pre-layer in gas sweetening) and natural gas containing 30–50% CO₂; two months of operation achieved 66% CO₂ recovery but only

Table 1

Process-oriented map linking applications, adsorbent classes, dominant mechanisms, and typical cycle configurations.

Application/Feed	Role of CO ₂	Typical adsorbent class	Dominant mechanism	Typical cycle(s)	Main constraint
Post-combustion flue gas (CO ₂ /N ₂ , humid)	Strongly adsorbed	Zeolite (13X, LTA) Hydrophobic MOFs (MIL-160, CALF-20)	Electrostatics ↔ physisorption (+ water competition)	VSA/PVSA (+ dehydration if needed)	Humidity/contaminants; energy for vacuum
Biogas/Natural gas sweetening (CO ₂ /CH ₄)	Strongly adsorbed impurity	CMS, activated carbon, Zeolites (such as ETS-4)	Physisorption + kinetic selectivity (CMS)	PSA/VPSA	Selectivity vs CH ₄ ; pressure drop
H ₂ purification (CO ₂ /H ₂ /CO/CH ₄ /N ₂)	Strongly adsorbed impurity	Zeolites (5A, 13X) Selected MOFs	Physisorption (strong CO ₂ affinity sites)	PSA (multi-step)	High-pressure operation; cycle complexity
CO ₂ -containing olefin purification streams (CO ₂ /C ₂ H ₄ , CO ₂ /C ₂ H ₆)	Case-dependent; CO ₂ may be the light component when olefin-selective sites are used	π-complexation sorbents (Ag ⁺ /Cu ⁺ sites), selected MOFs	Specific binding (π-complexation) + sieving	PSA/TSA or hybrid	Target selectivity; regeneration conditions
Direct air capture (~400 ppm CO ₂)	Strongly adsorbed trace component	Amine-functionalized solids (diamine MOFs, PEI supports)	Chemisorption (cooperative insertion)	TSA/TVSA/VTSA	Regeneration energy; oxidative aging

about 80% CH₄ purity because desorption was limited to 5–7 bar, while validated simulations predicted that reducing the desorption pressure to 1 bar could increase CH₄ purity to above 98% [195].

Hydrogen purification is one of the most mature industrial applications of adsorption-based separation, with Honeywell UOP reporting more than 1000 Polybed™ PSA systems installed in over 70 countries [196,197] and Air Products reporting more than 200 hydrogen PSA units installed worldwide [198,199]; in these systems, CO₂, CO, CH₄, N₂, and H₂O are selectively adsorbed while high-purity H₂ is recovered as the light product.

For CO₂-containing olefin-related streams, adsorption is better viewed as a targeted purification or process-intensification strategy rather than as a replacement for conventional olefin/paraffin separation. Miniplant-scale studies using zeolite 13X have demonstrated ethylene adsorption separation downstream of oxidative coupling of methane at 1–5 bar, while process-scale economic analysis for a 1 Mt year⁻¹ ethylene plant showed that integrating an adsorption unit could reduce the energy input and energy cost of the cryogenic ethylene-purification section by 75% and 89%, respectively [112,127].

For DAC, Climeworks provides one of the best industrial examples of adsorption-based CO₂ removal from ambient air. Its process uses alkaline-functionalized solid adsorbents, with CO₂ adsorption from untreated air followed by temperature-vacuum swing desorption at 80–120 °C to release concentrated CO₂. The first commercial Climeworks DAC plant in Hinwil, Switzerland, was reported to capture 900 tCO₂ year⁻¹ and deliver the CO₂ to a nearby greenhouse, while the Climeworks-CarbFix project in Iceland combined DAC with basalt mineralization and used geothermal water heat at around 120 °C for sorbent regeneration. The modular collector design, in which six collectors fit into a standard 40 ft container and each collector has a nominal annual capacity of about 50 tCO₂, illustrates how solid-sorbent DAC is being scaled through repeated adsorption/desorption units rather than through a single large packed bed [200,201]. In parallel, emerging companies such as Carbyon are developing thin-film or membrane-like DAC contactors, where amine-functionalized layers are deposited on structured supports to increase surface area and reduce pressure drop [202]; however, this route should currently be presented as an emerging process-intensification strategy rather than a fully demonstrated industrial DAC process [203].

7. Comparative insights and adsorbent–process synergies

The performance of CO₂ separation by adsorption cannot be evaluated solely on the basis of adsorbent selection or process configuration in isolation; rather, it is the combination of gas mixture composition, adsorbent properties, and process design that collectively determines practical viability. Table S1 illustrates this interdependence across a range of adsorbents, gas mixtures, and operating conditions. A further process-level criterion is whether CO₂ is the adsorbed product, the adsorbed impurity, or the weakly adsorbed product, since this determines whether CO₂ is collected during adsorption or during regeneration and strongly influences the preferred PSA, VSA, TSA, or hybrid cycle design.

From a practical selection viewpoint, the first decision is not the adsorbent family, but the separation target. For post-combustion CO₂/N₂ capture, the low CO₂ partial pressure and the presence of water vapor mean that CO₂ affinity, water tolerance, regeneration energy, and vacuum requirement must be considered together; therefore, zeolites, CALF-20, MIL-160(Al), and other stable hydrophobic adsorbents are most relevant when integrated with VSA or PVSA-type cycles. For CO₂/CH₄ separations in biogas or natural gas upgrading, the main objective is usually to remove CO₂ while minimizing CH₄ loss, so kinetic selectivity, hydrophobicity, pressure drop, and CH₄ recovery become more important than maximum single-component CO₂ uptake. In this case, CMS, activated carbons, ETS-type zeotypes, and selected hydrophobic adsorbents are more appropriate for PSA or VPSA configurations. For H₂

purification, CO₂ is normally treated as a strongly adsorbed impurity, and mature multi-step PSA cycles using zeolites or related physisorbents remain the most relevant configuration. DAC is different because CO₂ is present only at trace concentration; therefore, strong chemisorptive binding on amine-functionalized solids is usually needed, although this must be balanced against regeneration energy and oxidative or hydrothermal aging. For CO₂-containing olefin purification, the suitable adsorbent depends on whether CO₂ is the strong or weakly adsorbed component, and π -complexation or gate-opening materials may be useful when selective retention of the hydrocarbon is required.

As with Fig. 6 and Table S1, the process-relevant metrics reported across different studies are not obtained under matched operating conditions and comparing them directly can be misleading. To make this explicit, Table 2 summarizes representative process-relevant data for selected adsorbents discussed in this review, including reported uptake or working capacity where available, water tolerance, cyclic stability, regeneration method, and the specific operating conditions under which each value was obtained. Because temperature, pressure, CO₂ partial pressure, humidity, feed composition, and cycle configuration differ substantially between studies, the entries in Table 2 should be interpreted as condition-specific benchmarks rather than as a normalized ranking of adsorbent performance.

Zeolite 13X serves as the standard benchmark for post-combustion CO₂ separations, valued for its high selectivity and widespread application in VSA and PVSA processes. Nevertheless, its pronounced hydrophilicity remains a significant limitation in humid gas streams. Under such conditions, moisture-tolerant frameworks such as CALF-20 and MIL-160(Al) (Section 5.2.3), other hydrophobic MOFs including UiO-66 derivatives, or amine-functionalized supports are more appropriate, with the cycle selected accordingly - VSA/PVSA where vacuum regeneration is feasible, or TSA/VTSA where thermal or steam-assisted regeneration is preferred, since moisture tolerance and cyclic regenerability are of greater practical importance than equilibrium CO₂ uptake alone. For CO₂/CH₄ separations, CMS and activated carbons generally outperform zeolites, particularly when paired with PSA or VPSA configurations, as their hydrophobicity and favorable adsorption kinetics make them well-suited to industrial deployment. Although their intrinsic selectivities are lower than those of crystalline adsorbents, their superior stability under process conditions often offsets this limitation.

For light hydrocarbons containing CO₂, particularly those involving unsaturated hydrocarbons such as C₂H₄, including C₂H₄/C₂H₆ mixtures, conventional zeolites are generally inadequate. In such cases, Ag⁺/Cu⁺ modified zeolites, specialized MOFs, including Cu-BTC and ZIF-8, and flexible frameworks such as F4-MIL-140A(Ce), are more appropriate candidates, although the limited moisture stability of Cu-BTC and ZIF-8 must be taken into account when water vapor is present (Section 5.2.1), as they exploit mechanisms such as π -complexation or gate-opening behavior to achieve high separation selectivity. The integration of these materials with PSA or hybrid cyclic processes can yield separation performance that substantially exceeds that of conventional adsorbents. These mechanisms are especially relevant when CO₂ must be separated from, or purified in the presence of, olefinic components under petrochemical process conditions.

DAC represents the most demanding separation application owing to the ultra-dilute concentration of CO₂ in ambient air. Under such conditions, the use of chemisorbents, particularly amine-functionalized materials, is essential to achieve adequate adsorption rates at low partial pressures. These materials are typically paired with energy-intensive regeneration configurations such as TSA or TVSA, which are required to overcome the strong chemical bonds formed during the chemisorption process.

Overall, no universally superior adsorbent–process combination exists. The optimal pairing is instead strongly dependent on the target gas mixture composition, the relevant concentration range, and the prevailing operating conditions, underscoring the importance of an integrated materials and process design approach.

Table 2

Representative process-relevant metrics for selected adsorbents under their reported operating conditions.

Adsorbent/ system	Application context	Reported performance metric	Water/humidity relevance	Cyclic stability	Regeneration/ cycle	Ref.
Defect-healed high-silica MFI	Humid post combustion CO ₂ capture	0.83 mmol g ⁻¹ dry and 0.84 mmol g ⁻¹ at 75% RH	Negligible capacity loss at 75% RH	Stable in simulated humid PSA cycles; ~70–75% equilibrium capacity reached within 10 s	Humid PSA-type cycling	[118]
Zeolite 13X@ZIF- 8 core-shell composite	CO ₂ capture using hydrophobic zeolite@MOF composite	1.6 mmol g ⁻¹ at 25 °C and 1 bar	Hydrophobic ZIF-8 shell designed to reduce water sensitivity	94.5% capacity retained after 40 adsorption-desorption cycles	Thermal regeneration	[119]
APTMS-grafted hierarchical LTA	CO ₂ capture using amine-functionalized hierarchical zeolite	2.3 mmol g ⁻¹ at 0.15 bar and 60 °C; 2.1 mmol g ⁻¹ under 15% CO ₂ /N ₂ flow	Humid uptake decreased to 0.81 mmol g ₁	Nearly constant capacity over 10 dry cycles	Thermal regeneration	[120]
CALF-20	TSA-based post- combustion CO ₂ capture	Up to 2.55 mmol g ⁻¹ at 3–20 vol% CO ₂ and 28–130 °C	Humidity not isolated as the main variable in this study	Complete regeneration and stable performance over 10 TSA cycles	TSA	[144]
Structured CALF- 20 filters	Cement flue gas capture, RC-TSA pilot/ PDU	95% CO ₂ purity; 10.2 t _{CO2} m ⁻³ day ⁻¹ productivity; 52 s cycle time	Tested under simulated cement kiln flue gas containing moisture and impurities	>120,000 cycles over 2300 h	Steam-assisted rapid TSA	[193]
Pelletized MIL- 160(Al)	Post-combustion CO ₂ capture, TCM pilot	Around 90% CO ₂ recovery and ~95% CO ₂ purity reported after process tuning	Tested under pilot flue- gas conditions	Demonstrated cyclic VPSA operation in three columns	3-bed, 6-step VPSA	[146]
Shaped MIL-160 (Al)	CO ₂ /N ₂ post- combustion PSA simulation/validation	67.3% CO ₂ purity and 99.1% CO ₂ recovery at 313 K and 4.0 bar	Humidity not the main focus	Five-step PSA cycle validated	PSA	[147]
mmen- Mg ₂ (dobpdc)	DAC-relevant low- partial-pressure CO ₂ capture	~2.0 mmol g ⁻¹ at ~390 ppm CO ₂	Not primarily evaluated under humid air in the cited comparison	Not the main focus in this cited entry	TSA/ chemisorption- based regeneration	[163]
45 wt% PEI/ γ-Al ₂ O ₃	DAC/dilute CO ₂ capture	Capacity loss under oxidative conditions rather than benchmark uptake emphasized	Degradation accelerated in the simultaneous presence of CO ₂ , O ₂ , and H ₂ O	Long-term stability limited under oxidative/humid conditions	Thermal regeneration	[105]
Epoxide-modified PEI300/TREN	DAC at low desorption temperature	Strong cyclic working capacity at desorption temperatures as low as 45 and 40 °C	Stable under O ₂ -rich and humid conditions	Maintained cyclic performance under low-temperature desorption	Low-temperature thermal desorption	[166]

8. Challenges and opportunities

Adsorption-based CO₂ capture has demonstrated considerable potential for progression from laboratory research to pilot-scale implementation. However, the path toward widespread and economically viable industrial deployment remains characterized by a number of persistent challenges alongside emerging opportunities. Addressing these challenges requires a comprehensive and interdisciplinary strategy that integrates materials science, chemical engineering, and advanced computational methods. This section outlines the principal challenges currently facing the field and identifies the key opportunities that are driving future innovation.

8.1. Limitations

Despite considerable advances in the development of high-capacity and high-selectivity adsorbents, the path to industrial viability remains obstructed by several critical challenges. Beyond the well-documented issues of moisture sensitivity, contaminant poisoning, and high regeneration energy demand, further limitations emerge during the transition from controlled laboratory synthesis to large-scale dynamic industrial operation. Among the most significant of these is ensuring the batch-to-batch reproducibility of material properties and structural characteristics. The synthesis of advanced adsorbents is frequently a complex procedure requiring precise process control, and as a result, material performance can vary considerably at industrial scale even in the absence of any apparent changes to the synthesis protocol. This inconsistency represents a major barrier to industrial adoption, which demands predictable and reliable adsorbent performance across production batches [21].

This challenge is further compounded for next-generation materials such as MOFs, which, despite exhibiting exceptional performance at the

laboratory scale, have yet to demonstrate fully proven mechanical and chemical stability under the prolonged thermal and pressure cycling characteristic of industrial operation [204]. The influence of structural defects presents an additional concern. Given that pore size and geometry are primary determinants of adsorption selectivity, particularly in physisorption-based separations, even minor structural imperfections can have a disproportionately large impact on separation performance. Furthermore, CO₂ concentration in industrial flue gas streams is not constant but subject to fluctuations arising from variations in process load. Such variability poses a significant operational challenge for adsorption systems, which are typically optimized for fixed feed conditions and therefore require robust control strategies to maintain separation performance within acceptable limits under dynamic operating conditions [16].

A further significant challenge lies in the divergence between the powdered adsorbent forms commonly investigated in academic research and the structured forms required for industrial deployment. While powders are favored in laboratory studies for their favorable mass transfer characteristics, industrial PSA and VPSA systems require materials to be shaped into pellets or other macroscopic forms to reduce pressure drop across large adsorption columns [205,206]. This shaping requirement introduces an inherent trade-off, whereby smaller pellets enhance intraparticle mass transfer but increase bed pressure drop, while larger pellets reduce pressure drop at the expense of slower gas diffusion kinetics.

Another practical issue is that most adsorbents reported in the literature are first evaluated as powders, whereas industrial adsorption beds require pellets, beads, monoliths, coated structures, or other shaped forms. This transition can change material performance substantially. Binders and additives used during pelletization, extrusion, 3D printing, or monolith formation may dilute the active adsorbent phase, partially block micropores, or introduce extra diffusion resistance, so the

CO₂ uptake of the shaped body is often lower than that of the original powder [38,39,206]. At the same time, the shaped adsorbent must be mechanically robust enough to tolerate repeated pressure, vacuum, heating, cooling, and purge steps without excessive attrition or loss of capacity. These issues are particularly important for MOFs and amine-functionalized sorbents, where framework degradation, amine loss, or pore blocking can occur during long-term cycling [21,105]. For this reason, industrial adsorbent screening should include not only equilibrium capacity and selectivity, but also pressure drop, pellet or monolith density, mass-transfer resistance, crush strength, attrition resistance, cyclic capacity retention, and reproducibility at scale. Structured contactors such as monoliths, laminates, fibers, and sorbent-coated filters are promising because they can reduce pressure drop and improve heat and mass transfer, but their cost, durability, and scalability still need to be demonstrated under realistic gas compositions and regeneration conditions [193,205].

Collectively, the limitations associated with scalability, long-term stability, material shaping, and dynamic operational responsiveness contribute to elevated capture costs and underscore the considerable gap that remains between current laboratory-scale achievements and the requirements of large-scale industrial deployment.

8.2. Opportunities for future advancement

The persistent challenges facing adsorption-based CO₂ capture are simultaneously defining the most promising directions for future innovation. The field is progressively moving beyond the pursuit of maximum equilibrium capacity toward the targeted design of material properties that satisfy the demands of real-world separation performance.

A primary opportunity in this regard lies in the rational design of advanced adsorbent materials. Within the domain of porous solids, the focus is shifting from the discovery of materials with exceptionally high surface areas toward the simultaneous achievement of high selectivity, exceptional stability, and targeted chemical functionality. These advances have given rise to emerging material classes such as covalent organic frameworks (COFs), porous organic polymers (POPs), and functionalized MOFs, all of which are demonstrating considerable promise and are attracting rapidly growing research interest [207]. A further promising direction is the continued development of flexible and phase-change MOFs, which exhibit step-shaped adsorption isotherms particularly well-suited to swing adsorption processes. These materials offer the potential for highly efficient cyclic separation with substantial working capacities achievable at minimal energy input, a characteristic of considerable importance for economic viability [208,209]. For zeolites, opportunities lie in both the sophisticated modification of existing frameworks through defect engineering and targeted functionalization, and in the pursuit of sustainable synthesis routes aligned with circular economy principles.

A further significant opportunity lies in the integration of simulation, modeling, and data-driven approaches, including machine learning (ML) and high-throughput computational screening, to accelerate the discovery and development of novel adsorbent materials. Recent studies have demonstrated that ML models can rapidly screen large databases of hypothetical structures to predict adsorption performance, identifying promising candidates for experimental synthesis and validation [210, 211]. Complementary tools such as Aspen Adsorption simulations and molecular dynamics (MD) modeling can be employed to predict optimal adsorbents for targeted separations, offering the potential for substantial reductions in both development time and associated costs.

Another important opportunity is the co-design of adsorbent chemistry and contactor architecture. Instead of optimizing powders first and shaping them later, future studies should develop adsorbents directly in process-compatible forms such as pellets, monoliths, fibers, laminates, or structured filters [212,213]. This approach would allow adsorption capacity, diffusion kinetics, pressure drop, heat transfer, mechanical

robustness, and regeneration strategy to be optimized simultaneously, which is essential for moving promising porous materials toward industrial adsorption units [214,215].

Finally, considerable opportunities remain in the domain of process and system innovation. While emerging technologies such as porous liquids, mixed-matrix membranes (MMMs), and advanced supported liquid membranes (SLMs) are attracting growing research interest for CO₂ capture applications, these platforms remain insufficiently mature for industrial deployment relative to established adsorption-based processes.

9. Toward predictive and data-driven frameworks for adsorption-based CO₂ capture

Despite the substantial body of experimental and computational work on CO₂ adsorption, no unified framework yet exists that systematically connects adsorbent structure, adsorption mechanism, and process configuration. Most studies concentrate on a single level, whether materials characterization, equilibrium isotherm analysis, or cyclic process modeling, which makes it difficult to compare adsorbents on a common basis or to translate laboratory-scale performance into process-level metrics such as product purity, recovery, and specific energy consumption.

A useful means of organizing existing knowledge is to view adsorption-based CO₂ capture through a structure–mechanism–process (SMP) lens. At the structural level, properties such as micropore volume, pore size distribution, framework charge density, and surface functionality determine the intrinsic adsorption potential of a material. These structural features favor distinct adsorption mechanisms: physisorption governed by dispersion and electrostatic interactions in carbons, zeolites, and many MOFs; chemisorption in amine-functionalized solids; and hybrid behavior in materials that combine strong specific binding sites with a porous scaffold. At the process level, these mechanisms are then exploited in different ways depending on the cyclic configuration employed. Physisorbents with moderate heats of adsorption are well-matched to PSA and VSA cycles, while strongly chemisorbing materials are more compatible with TSA or TVSA schemes. Considered together, these three levels make clear that adsorbent materials cannot be meaningfully ranked in isolation from the process configurations in which they are intended to operate.

Fig. 7 presents the SMP framework introduced in Section 9, together with its application to five representative CO₂-containing gas streams discussed throughout this review. For each stream, the dominant separation constraint (humidity, competing-molecule selectivity, operating pressure, or CO₂ partial pressure) determines the capture mechanism, which in turn dictates the adsorbent structure and cyclic process best suited to it. Within this SMP framework, one of the central design considerations is the trade-off between selectivity and regeneration energy. Materials that bind CO₂ strongly, typically through chemisorption, can achieve high selectivity and maintain substantial uptake even at low CO₂ partial pressures. However, stronger binding invariably implies a higher energy demand for CO₂ release and restoration capacity. Physisorbents, by contrast, interact weakly with CO₂ and are consequently easier to regenerate, but generally offer lower selectivity, particularly for dilute feed streams. Available data for zeolites, activated carbons, MOFs, and amine-based sorbents collectively suggest the existence of an operating window of intermediate interaction strength within which both acceptable selectivity and manageable regeneration energy demands can be achieved. Expressing this trade-off through concise material descriptors, such as the isosteric heat of adsorption, working capacity, and selectivity, can provide practical screening criteria without requiring full process simulation at every stage of material evaluation.

In practical terms, the SMP framework is applied in this review as a stepwise screening logic for adsorption-based CO₂ separation. The first step is to define the gas stream, including CO₂ partial pressure, major

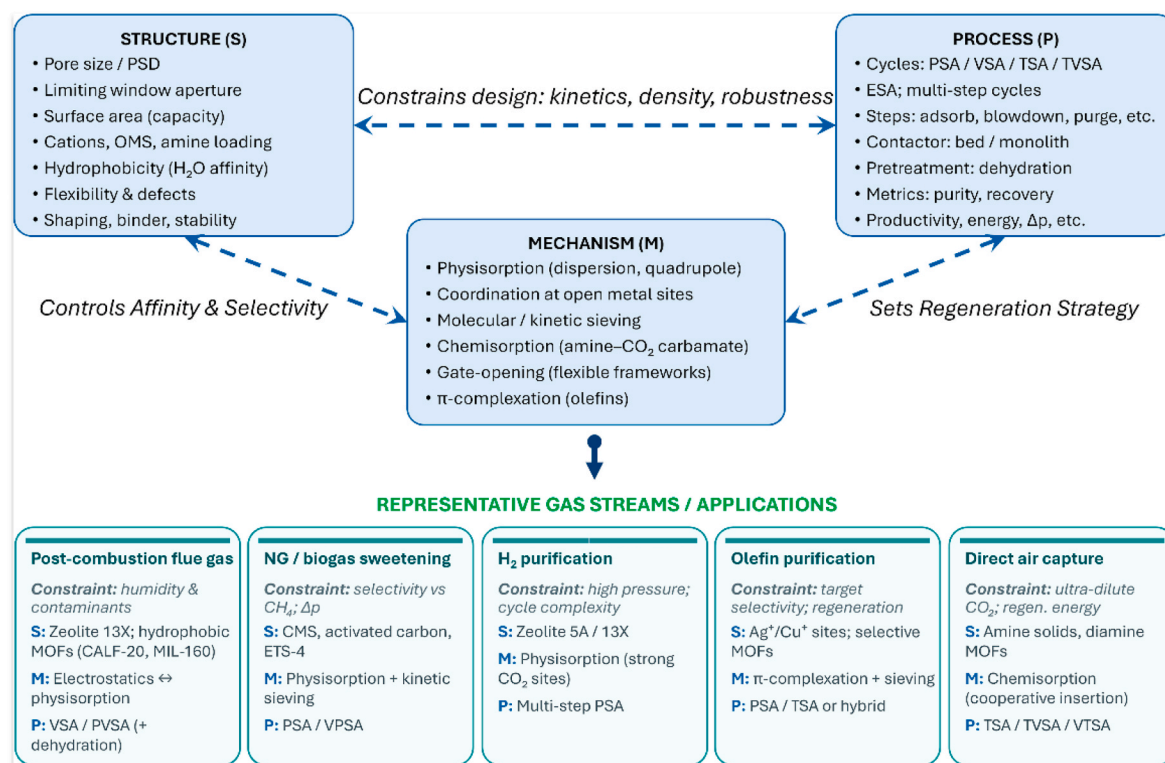


Fig. 7. Structure-Mechanism-Process (SMP) selection framework and application-specific decision guide, showing how the dominant constraint of five representative CO_2 -containing gas streams determines adsorbent structure, capture mechanism, and cyclic process design.

competing gases, humidity, contaminants, operating pressure, and whether CO_2 is the strong or weakly adsorbed component. The second step is to identify the dominant adsorption mechanism required for that separation, such as electrostatic physisorption for CO_2/N_2 capture, kinetic selectivity for CO_2/CH_4 separation, chemisorption for DAC, or π -complexation/gate-opening behavior for CO_2 -containing hydrocarbon purification. The third step is to match this mechanism with an adsorbent class and a realistic cyclic process, considering whether regeneration should be achieved mainly by pressure reduction, vacuum, heating, steam-assisted desorption, or a hybrid strategy. Finally, the selected material-process pair should be assessed using working capacity, purity, recovery, productivity, regeneration energy, water tolerance, adsorption/desorption kinetics, shaping feasibility, and cyclic stability. This logic is the basis for the process-oriented map in Table 1 and avoids ranking adsorbents only by single-component CO_2 uptake.

Beyond the framework applied here, the following outlook identifies where this logic could be extended in future work. Looking ahead, the increasing availability of detailed isotherm databases, force-field parameterizations, and process models creates the foundation for more integrated, data-driven approaches to adsorbent selection and process design. In a future digital twin of an adsorption unit, cyclic processes modeled using tools such as Aspen Adsorption could be continuously updated with real plant data, including temperatures, pressures, gas compositions, and cycle histories. Machine learning models trained on combined simulation and experimental datasets could then be employed to detect performance deterioration, predict the effects of adsorbent aging, and propose adjusted operating conditions, such as modified step times, pressure levels, or purge ratios, to recover product purity and reduce energy consumption. Such predictive and adaptive frameworks would transform adsorption-based separation from a largely static design problem into a continuously optimized and intelligent separation technology, while also facilitating the identification of the most promising material-process combinations for specific CO_2 capture applications.

10. Conclusion

This review has examined adsorption-based CO_2 separation through a Structure-Mechanism-Process perspective. Rather than ranking adsorbents only by equilibrium CO_2 uptake, the review emphasizes that adsorbent selection must begin with the target gas stream, the role of CO_2 in the separation, the dominant adsorption mechanism, and the cyclic regeneration strategy. This approach provides a practical framework for comparing porous adsorbents across post-combustion capture, biogas and natural gas sweetening, hydrogen purification, CO_2 -containing olefin streams, and direct air capture.

A consistent finding emerging from the literature is that no single adsorbent or process configuration is universally optimal. For post-combustion capture, zeolites remain attractive owing to their mechanical robustness, wide availability, and strong CO_2 selectivity. However, their affinity for water represents a significant limitation in humid flue gas streams, where co-adsorbed moisture can suppress CO_2 uptake and reduce working capacity. MOFs, by contrast, enable precise tuning of pore environments and can achieve high adsorption capacities; however, large-scale manufacturing, stability under realistic operating conditions, and production cost remain key obstacles to their industrial adoption. Activated carbons and carbon molecular sieves offer inherent hydrophobicity and favorable adsorption kinetics but generally exhibit lower intrinsic selectivity. Amine-functionalized sorbents are essential for ultra-dilute CO_2 streams such as those encountered in DAC applications, at the cost of higher regeneration energy demand and susceptibility to chemical degradation.

The integration of material properties with cyclic process performance is critical for realistic system evaluation. Studies employing Aspen Adsorption and related modeling tools demonstrate that specific energy consumption, productivity, and purity-recovery trade-offs cannot be reliably inferred from equilibrium isotherms alone. Rather, they depend sensitively on cycle design, bed configuration, adsorbent shaping, and feed variability. Future progress will therefore depend on

the combined optimization of adsorbent chemistry, morphology, and process configuration.

Overall, the future development of adsorption-based CO₂ separation will depend on matching adsorbent chemistry, pore structure, shaping strategy, and cyclic process design within the correct operating window. Stable hydrophobic adsorbents, flexible and phase-change MOFs, structured sorbents, and AI-assisted screening can all contribute to this goal, but their value must be judged by using process-level metrics such as working capacity, purity, recovery, productivity, regeneration energy, water tolerance, kinetics, and cyclic stability. This material–process matching perspective is the main message of the present review.

CRediT authorship contribution statement

Hamed Faramarzi: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Saber Niazi:** Conceptualization, Methodology, Validation, Visualization, Writing – review & editing. **Mariachiara Zanetti:** Supervision, Writing – review & editing. **Deborah Panepinto:** Supervision, Writing – review & editing. **Antonio Nieto-Márquez:** Methodology, Project administration, Supervision, Validation, Writing – review & editing.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors used ChatGPT (OpenAI) and Claude (Anthropic) for language editing and proof-reading, and to assist in creating some graphical elements for the graphical abstract. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Declaration of competing interests

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2026.114363>.

Data availability

Data will be made available on request.

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