

Nanoparticles used for CO₂ Capture by Adsorption: a Review

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Rapid industrialization, technological advancement, and innovation have led to a significant rise in carbon emissions globally, resulting in the growing problem of climate change. With the advancement of nanotechnology, the adsorption is becoming an effective strategy to directly capture CO₂ with nanomaterials. This mini-review deals with the investigation for physical adsorption, amine-modified nanomaterials for chemisorption, and moisture-swing nanomaterials for chemisorption. The purpose is to highlight the current technologies available for a simple, environmentally safe, non-toxic, low-cost CO₂ capture. In detail, this study examines several CO₂ capture nanomaterials with an emphasis on economical and environmentally safe low to high temperature solid adsorbents.

1. Introduction

The increase in atmospheric CO₂ levels is mainly due to the burning of fossil fuels such as gasoline and diesel. Reducing CO₂ emissions is challenging due to the country's economic growth and accompanying development such as industrialization, urbanization, and transportation. Global fuel combustion released approximately 32.8 billion tons of CO₂ (Grim et al., 2020). Additionally, the increased use of personal vehicles, driven by overpopulation, is also contributing to the rise in CO₂ levels.

At the 2015 UN Climate Change Conference, participants reached an agreement to create a global framework to prevent severe climate change by limiting global warming below 2 °C and striving to keep it below 1.5 °C (Streck et al., 2016). According to the IPCC (Intergovernmental Panel on Climate Change), reducing CO₂ emissions is essential if we are to keep the concentration of carbon dioxide in the atmosphere below 450 ppm by the end of 2100 and prevent climate change from becoming irreversible.

A variety of methods have been developed for removing CO₂ from gas streams, including adsorption, absorption, cryogenics, and membranes (Mancini et al., 2022). Membrane separation stands out for its ability to produce high-purity CO₂ streams, especially for power plants. It has several advantages, such as energy efficiency and continuous operation, compared to other methods like adsorption and absorption (Momeni et al., 2019). Cryogenic separation of CO₂ involves liquid CO₂ flow under high pressure, but it is expensive due to the need for refrigeration and water removal. This method is mainly suitable for highly concentrated CO₂ streams. Adsorption is a relatively new approach to CO₂ removal. To date, adsorption, together with absorption, is the most economical way to separate CO₂ from large flows (Zeini Isfahani et al., 1994). This study focuses on enhancing the effectiveness of adsorption technology. In detail, the effect of nanoparticles on adsorption has been studied.

2. Nano particles effect for CO₂ Capture

CO₂ capture can be achieved through physical and chemical adsorption at room temperature and atmospheric pressure, and the captured CO₂ can be easily released through gas flow and heating methods. CO₂ can also be captured and released through moisture-swing adsorption by controlling moisture levels.

2.1. Nanomaterials for physical adsorption

The effectiveness of physical adsorption using nanomaterials depends largely on the exposed surface area, porosity, diffusion path, and availability of adsorption sites on the material, which result from physical interactions between nanomaterials and CO₂ molecules (Oschatz and Antonietti, 2018). After extensive scientific research, various nanomaterials with strong CO₂ adsorption capabilities have been developed, including activated carbon, zeolite, metal-organic frameworks, boron nitride, and MXene (class of two-dimensional inorganic compounds). For example, activated carbon is an inexpensive and readily available material that has a high surface area, large porosity, and good thermal and chemical stability, making it ideal for physical adsorption of CO₂ under normal conditions (Karimi et al., 2018). The porosity and surface area of activated carbon can be easily adjusted through pyrolysis and etching methods to meet the structural requirements of the adsorption process (Sreńscek-Nazzal and Kielbasa, 2019). The capacity and selectivity of activated carbon materials in terms of adsorption efficiency are limited by the weak physical interactions between CO₂ molecules and the material (Coromina et al., 2015). To enhance the efficiency of CO₂ physical adsorption, zeolite materials are utilized due to the stronger physical interactions between CO₂ molecules and the negative charges on the surface of zeolite. In addition to the high surface area and abundant porosity in the zeolite structure, the intensity and distribution of surface charge can be controlled through chemical methods, which is crucial to the CO₂ adsorption efficiency. The aluminum and silicon ratios in the material can be adjusted through different synthesis methods, and this ratio can greatly impact porosity and chemical activity. Optimizing this ratio can enhance the material's ability to capture CO₂. Zeolite material's adsorption properties can be regenerated through heating (Santori et al., 2018). A major drawback of using zeolites is their strong water sorption capacity, as they undergo a similar adsorption and desorption cycle as CO₂. This makes it difficult to use zeolites for DAC (Direct Air Capture) in humid environments.

MOFs (Metal Organic Frameworks) have gained significant attention and have been widely used in various fields due to their versatility. MOFs are inorganic-organic hybrid crystalline materials formed through the self-assembly of inorganic metal cations or clusters and organic ligands. With their diverse composition, customizable pore size, high surface area, and tunable internal structures and properties, MOFs have become a promising alternative to traditional liquid and solid carbon capture sorbents. ZIF-8, a well-known type of MOFs, is a suitable candidate for CO₂ adsorption due to its high nitrogen content, large surface area, and porous structure (Liu et al., 2014). ZIF-8 is famous for its chemical and thermal stability and can accumulate CO₂ either in its molecular cage or in interspatial areas. The CO₂ sorption capacity of ZIF-8 nanoparticles (ca. 30 nm in size) material was reported to be around 29 mg/g at atmospheric pressure and room temperature, with high-content nitrogen atoms providing basic sites for CO₂ adsorption with higher capacity and selectivity.

Conjugated microporous polymers (CMPs) with optimized pore size distribution and high surface area are synthesized (Liu et al., 2014), resulting in a CO₂ sorption capacity of 76.5 mg/g, 2.6 times higher than that of pure ZIF-8 materials. The CO₂ adsorption enhancement is attributed to the pore enrichment effect of the nanomaterials.

A bioinspired MOFs (Bien et al., 2018) are developed with nucleophilic Zn-OH groups for trace CO₂ adsorption at mild temperatures. A Zn benzotriazolate metal-organic framework has been subjected to a mild CH₃CO₂⁻/HCO₃⁻ ligand exchange procedure followed by thermal activation to generate nucleophilic Zn-OH groups that resemble the active site of α -carbonic anhydrase. The post synthetically modified MOF exhibits excellent performance for trace CO₂ capture and can be regenerated at mild temperatures. IR spectroscopic data and density functional theory (DFT) calculations reveal that intercluster hydrogen bonding interactions augment a Zn-OH/Zn-O₂COH fixation mechanism (Cai et al., 2020).

Sun et al. (2013) report a study of the adsorption of CO₂ on boron nitride (BN) nanosheets and nanotubes (NTs) with different charge states. The results show that the process of CO₂ capture/release can be simply controlled by switching on/off the charges carried by BN nanomaterials. CO₂ molecules form weak interactions with uncharged BN nanomaterials and are weakly adsorbed (Sun et al., 2013b). The study shows that introducing excess electrons to BN nanomaterials results in strong adsorption of CO₂ molecules, making these nanomaterials highly effective adsorbents. The negatively charged BN nanosorbents selectively capture CO₂ from its mixtures with CH₄ and/or H₂. Removing the electrons causes the CO₂ molecules to spontaneously desorb. BN nanomaterials are therefore excellent for controlling, highly selective, and reversible CO₂ capture and release.

Owuor et al. (2017) developed a 3D BN composite foam chemically connected with poly(vinyl alcohol) materials, which showed high CO₂ uptake due to its improved porosity, surface area, and mechanical properties. Creating interconnections between inert nanosheets can remarkably enhance their mechanical properties. However, controlled design of such interconnections remains a fundamental problem for many applications of hexagonal-BN foams.

Li et al. (2017) reports that MXene is a promising candidate for CO₂ physical adsorption. Two-dimensional (2D) transition-metal (groups IV, V, VI) carbides (MXenes) with formulas M₃C₂ have been investigated as CO₂ conversion catalysts with well-resolved density functional theory calculations. While MXenes from the group IV to VI series have demonstrated an active behavior for the capture of CO₂, the Cr₃C₂ and Mo₃C₂ MXenes exhibit the most promising CO₂ to CH₄ selective conversion capabilities. Results predicted the formation of OCHO• and HOCO• radical species in the early hydrogenation steps through spontaneous reactions. This provides atomic level insights into the computer-aided screening for high-performance catalysts and the understanding of electrochemical mechanisms for CO₂ reduction to energy-rich hydrocarbon fuels, which is of fundamental significance to elucidate the elementary steps for CO₂ fixation.

2.2. Amine-modified nanomaterials for physical adsorption and chemisorption

Compared to physical adsorption, chemical adsorption using nanomaterials has a higher sorption capacity and stronger interaction with CO₂ molecules. Amine-modified nanomaterials have proven to be an effective solution for CO₂ chemical adsorption, due to their low energy consumption, chemical stability, and reversible nature. When in contact with CO₂ molecules, amine groups on the nanomaterials react to form carbamate or carbamic acid under dry conditions, or bicarbonate under moist conditions. Nanomaterials with porous structures, large surface areas, and abundant gas diffusion channels, such as nanosilica, carbon nanotubes, nano cellulose, MOFs, and porous alumina, are ideal support materials for the amine groups (Deng and Park, 2019).

For example, Xu et al. (2002) impregnated mesoporous silica with polyethylenimines containing amine groups, resulting in a nanoporous solid adsorbent which can serve as a “molecular basket” for CO₂ in the condensed form with twice the CO₂ adsorption capacity of pristine polyethylenimines. The novel “molecular basket” material can effectively adsorb CO₂ at very low CO₂ concentration, e.g., 0.5%, and it is stable in cyclical operations at relatively high temperatures.

Belmabkhout et al. (2010) chemically grafted amine-bearing mesoporous silica, which had a high CO₂ uptake, fast adsorption rate, and stability at low pressure. The increased CO₂ adsorption effectiveness is largely due to the increased accessibility of amine groups made possible by the porous and hierarchical structures of the supporting materials. In addition to unprecedentedly high CO₂ uptake at low pressure, high adsorption rate and stability, this material exhibited very high selectivity for CO₂ over N₂ and O₂, regardless of the presence of moisture. It is thus highly suitable for use in CO₂ removal from air, for example in air purification and in closed-circuit breathing systems (Belmabkhout et al., 2010b). Nanomaterials produced through physical loading are cost-effective and easy to prepare, while those produced through chemical binding have a higher CO₂ adsorption capacity and better structural stability. Primary amines react with CO₂ to form ammonium carbamate, which is strongly adsorbed on the amine sites and forms networks of hydrogen bonds. This can lead to diffusion barriers during CO₂ release.

On the other hand, secondary amines react with CO₂ to form weakly adsorbed carbamic acid species, which can be released by gas flow at 35°C (Zhai and Chuang, 2017). High CO₂ concentration is required to overcome the diffusion barriers of primary amines. Secondary amines are more expensive to produce, but they are more suitable for capturing low-concentration CO₂. On the other hand, primary amines are better suited for high-concentration CO₂ environments.

Hoshino et al. (2012) found that CO₂ can be adsorbed and desorbed through temperature-responsive phase transition of micro and nanogel particles containing amine groups. This differs from simply relying on the porous structure of nanomaterials for CO₂ adsorption. Amines in shrunken materials form ion pairs with absorbed bicarbonate ions at temperatures below the phase-transition temperature. Above the phase-transition temperature, the amines in shrunken materials release CO₂. This highlights the potential of temperature-responsive nanomaterials for efficient and low-energy CO₂ absorption. Metal-organic frameworks (MOFs) are a promising option for amine modification due to their well-defined adsorptive sites, adjustable pore sizes, and functionalities.

Z. Shi et al. (2020) created MOFs that were both thermally and chemically robust by appending amine groups to triazolate linkers. They developed a strategy based on appending amino groups to the triazolate linkers of MOFs to achieve exceptional chemical stability against aqueous, acidic, and basic conditions. These MOFs exhibit not only CO₂/N₂ thermodynamic adsorption selectivity as high as 120 but also CO₂/H₂O kinetic adsorption selectivity up to 70%, featuring distinct adsorptive sites at the channel center for CO₂ and at the corner for H₂O, respectively. This material had high adsorption selectivity, with distinct adsorptive sites at channel centers for CO₂ and corners for other gases.

Ionic liquids (ILs) have garnered attention for CO₂ adsorption due to their structure tunability, CO₂ affinity, and low volatility. Nanomaterials with high levels of amine-modified ionic liquids have potential for CO₂ chemisorption. For example, Yu et al. (2014) created a “ship-in-a-bottle” system of amine-functionalized ionic liquids in zeolite materials for CO₂ chemical adsorption. The genuine host-guest systems were thoroughly characterized and tested in CO₂ capture from simulated flue gas. It was evidenced the encapsulated ILs are

more stable than the bulk ILs. This host-guest system showed high sorption capacity and rapid reversibility, even after multiple cycles under harsh conditions. The chemisorbed CO₂ can be desorbed rapidly by flushing with N₂ gas at 50 °C. The excellent physicochemical properties and the CO₂ capture performance of the host-guest systems offer them great promise for the future practice in the industrial CO₂ capture.

García-Gutiérrez et al. (2019) developed cellulose-supported solid ionic liquids (SolILs) for CO₂ adsorption with increased sustainability. They have been demonstrated recently to be effective and low-cost sorbents for CO₂ capture. The results of this study can be used to target the hotspots and improve the environmental performance of cellulose-supported SolILs through sustainable design. Hierarchical amine-modified solid ionic liquid-based nanomaterials could be a promising research direction for CO₂ chemical adsorption in the future.

2.3. Moisture-swing nanomaterials for chemisorption

A novel moisture-swing technique has been put forward to further reduce energy consumption in CO₂ adsorption, with the ability to capture CO₂ under dry conditions and release CO₂ under moisture conditions. The adsorption and desorption processes are directly controlled by humidity variations in the ambient environment and are not dependent on outside high energy consumption (X. Shi et al., 2020). Moisture-swing offers cost-effective CO₂ capture using water without high energy consumption and simplifies the design of CO₂ adsorption systems by eliminating the need for heating and cooling units. This flexible technique can also be combined with other applications and can continuously provide suitable CO₂ concentrations for plants in greenhouse facilities. However, the water used in moisture-swing should be clean to avoid substrate contamination, and the technique may be affected by weather. The released CO₂ concentration is comparatively low and needs to be enriched for further applications. The mechanism of the moisture-swing technique is based on the reversible conversion of carbonate and bicarbonate ions under dry and wet conditions (Shi et al., 2016).

For instance, T. Wang et al. (2011) presented a resin that utilizes moisture-swing technology for capturing CO₂ from air in regular conditions. An amine-based anion exchange resin was prepared in an alkaline form and dispersed on a flat sheet of polypropylene to capture CO₂ from air. The resin, featuring quaternary ammonium cations attached to the polymer and hydroxide or carbonate groups as mobile counterions, absorbs CO₂ when dry and releases it when wet. In the presence of ambient air, the moist resin naturally dries and then absorbs CO₂.

Improving the CO₂ adsorption ability of moisture-swing materials by enhancing their porosity and surface area is a promising approach. For example, Song et al. (2019) introduced a simple grinding/sieving method to improve the porosity and surface area of an ion-exchange resin for the moisture-swing technique. The resulting hierarchical porous structures greatly improved the accessible surface area and facilitated the diffusion of CO₂ and H₂O molecules. The CO₂ sorption capacity of the porous resin was much higher than that of the dense and smooth counterpart. Song et al. (2018) presented quaternized chitosan/polyvinyl alcohol aerogels with hierarchical nanostructures and large surface area for moisture-swing CO₂ adsorption. The porous structures in the aerogels provided ordered nano-channels for highly efficient diffusion of CO₂ and H₂O molecules, and the moisture-swing aerogels delivered 38% higher CO₂ capacity than commercially available polymer resins. The modified pseudo-first-order kinetic model they proposed fit the experimental results well and provides a theoretical method for designing moisture-swing materials. In conclusion, the moisture-swing technique is still in its early stages and has many challenges and opportunities that need to be addressed in future work. The construction of nanoscale ordered channels in moisture-swing materials is crucial for improving material exchange efficiency during CO₂ adsorption/desorption processes. Advanced in-situ characterization techniques can be used to gain a deeper understanding of moisture-swing processes, which is crucial for designing high-performance CO₂ sorbents.

3. Conclusion

The escalating issue of global climate change caused by excessive carbon dioxide emissions is one of the most pressing challenges facing modern society. This review outlines recent advancements in the use of nanomaterials for the adsorption of CO₂. Various technologies and nanomaterials for CO₂ adsorption are discussed, including physical sorbents, chemical sorbents, and moisture-swing sorbents. Physical sorbents are cost-effective and chemically stable but have low adsorption capacity and poor selectivity with other gases. Chemical sorbents based on amine-modified nanomaterials have higher CO₂ sorption capacity and better selectivity, but their chemical stability depends on the adhesion strength of the amino groups to the substrate. Moisture-swing sorbents allow for CO₂ adsorption and desorption through ambient moisture control, however, the materials currently available are limited to a few polymer resins and more functional nanomaterials need to be developed in the future.

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