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# **Progress in adsorption capacity of nanomaterials for carbon dioxide capture: A comparative study**

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## **Abstract**

With the gradual rise in atmospheric carbon dioxide brought about by human activities and industry effluents, research has now been geared toward carbon capture and storage. To achieve high carbon dioxide adsorption capacity, development of nanomaterials with optimized properties has been attracting growing interest for more than ten years already. Such multi-parameter investigations require a complex and rigorous analysis in order to compare the different developed adsorbents and improve their performances. In this review, we propose a state-of-the-art approach related to the four most studied nanostructured adsorbents for carbon dioxide capture: graphene, carbon nanotubes, zeolite, and metal organic frameworks. The capture processes and the nanomaterials of interest were described as well as the modifications applied to improve the efficiency of carbon dioxide capture. The present unprecedented analysis allows to correlate the nanomaterial properties, especially surface area and pore volume, to the CO<sub>2</sub> adsorption capacity. The results reveal that contrary the popular belief, the CO<sub>2</sub> capture improvement is not solely liable on the high surface area and the high pore volume

of the nanosorbents. This outcome may be useful in the course of improvement of nanostructured materials for CO<sub>2</sub> capture for future technologies.

**Keywords** CO<sub>2</sub> capture; adsorption; graphene; carbon nanotubes; MOF; zeolite

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## 1. Introduction

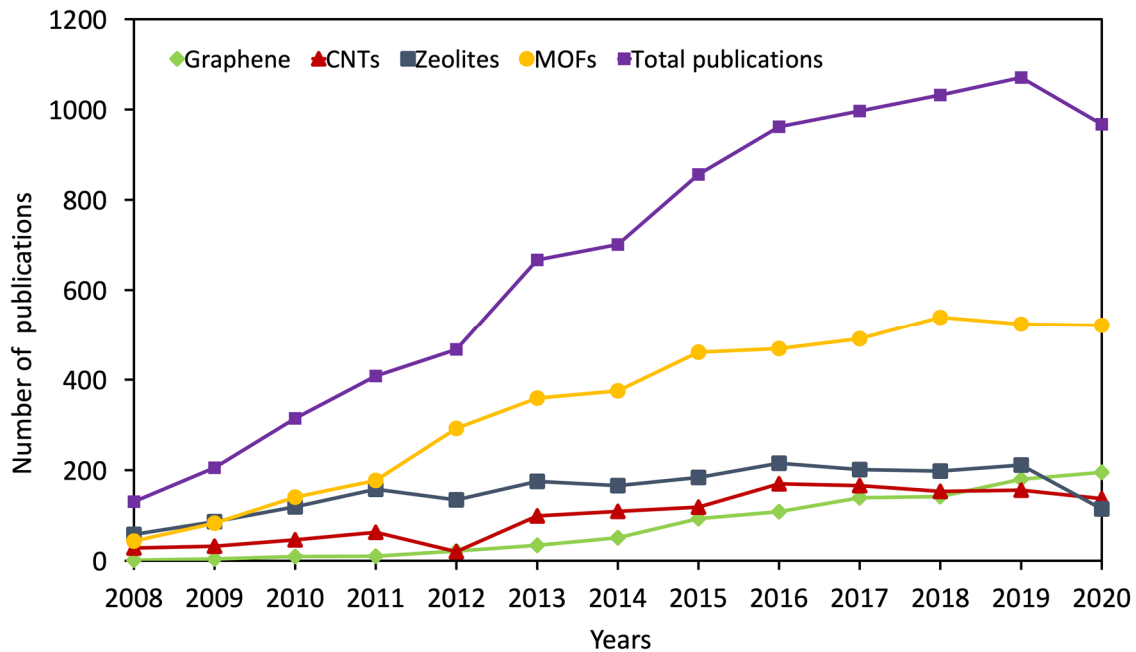
Carbon dioxide (CO<sub>2</sub>) has commonly been regarded as the primary contributor to greenhouse gases compared to other gases like methane, water vapor, nitrous oxide, and ozone,

accounting for nearly three-quarters of pollutions. The concentration of CO<sub>2</sub> in the atmosphere has been observed to keep on rising significantly as a result of high combustion of organic burning materials and fossil fuels, particularly coal, to meet the rising global demand for energy. According to the Carbon Dioxide Information Analysis Center, global emissions rose from 2 billion tons of CO<sub>2</sub> in 1900 to over 35 billion tons in 2015, while the data from Global Carbon Project showed an additional annual increase of 2.7% and 0.6%, respectively, in 2018 and 2019 (Le Quéré et al., 2015). In fact, increasing emission of CO<sub>2</sub> and other greenhouse gases has led to an increase in the average global temperature. Independent analyses by NASA and National Oceanic and Atmospheric Administration reported that the average global surface temperature of the earth has risen more than 2°C since 1880, and they believe emissions in this century will also further contribute to climate change in the short and long term (Smith et al., 2008). Additionally, according to NASA's Goddard Institute for Space Studies (GISS), rising atmospheric and ocean temperatures are driving to ongoing mass loss from Greenland and Antarctica, and also a spike in climate extremes such as heat waves, wildfires, and strong precipitation (GISTEMP Team, 2021; Lenssen et al., 2019). In order to combat global warming, Kyoto Protocol encourages 37 developed nations and the European Union to reduce their greenhouse gas emissions by an average of 5.2% below those of 1990 between 2008 and 2012 (Lau et al., 2009). Besides, the Paris Climate Agreement also intends to lessen the increasing rate of global temperature to 1.5°C or 2°C above pre-industrial level by 2100.

Concerns over the rapid increase of CO<sub>2</sub> levels in the atmosphere, as well as how it exacerbates climate change, have prompted a major research effort to capture and store CO<sub>2</sub> gas from point source pollution. In fact, it was reported that, improving carbon capture and storage (CCS) will minimize current CO<sub>2</sub> emissions from point sources by more than 50% at sustainable costs (Hasan et al., 2015). To design efficient strategies for CCS, it is necessary to understand each

capture process and the mechanism to choose a correct approach. Post-combustion is known as the most advanced and widely used technique for gas adsorption and storage applications using varieties of solid porous material bases, as it offers process simplicity, significantly less energy production, and implementation over a wide range of temperatures (Chao et al., 2020). Adsorption is identified as a major industrial process due to its high performance, convenience of design, simplicity of regeneration, and affordable price, and it does not contain harmful substances. It is a viable technology that relies on the development of novel adsorbents with high adsorption capability, selectivity, and fast kinetics in order to reversibly capture CO<sub>2</sub> from fuel gas stream. The scale-up production of nanomaterials for CO<sub>2</sub> capture application is still largely in the future, their life cycle assessment is a topic of a growing attention (Lee, 2021; Pathakoti et al., 2018; Sreenivasulu et al., 2015; Wang et al., 2014). The main studied and reported adsorbents are activated carbon (AC), AC fibers, ordered porous carbon and graphene, carbon nanotubes (CNTs) and non-carbonaceous adsorbents such as metal organic frameworks (MOFs), zeolites, porous polymers, alkali metal-based materials, silica materials and metal oxide carbonate materials. In general, according to published research, nanoparticles have a great potential for CO<sub>2</sub> capture-related technologies due to their large surface area and porosity structure. For the development of nanostructured porous materials, there are a limitless number of potentials; yet for significant progress, more studies are needed to clarify the mechanisms involved and improve the uptake capacity. Besides, to address the limitations of each nanomaterial, investigation in term of the novel structures, new functional groups, hybrid systems, and technologies are also needed. For such driving factors, there has been a tremendous effort over the last decade to address gas separation and adsorption using nanomaterials. Figure 1 depicts the number of publications on CO<sub>2</sub> capture using the four main

nanomaterials studied (graphene, CNTs, zeolites and MOFs) over the last 12 years, indicating the growing interest in nanomaterials as efficient solid sorbents.



**Figure 1** Number of publications on CO<sub>2</sub> capture using graphene, CNTs, zeolites and MOFs and CO<sub>2</sub> capture as topic (source Web of Science database).

Among the recently published reviews regarding CO<sub>2</sub> capture, some of them have focused on carbon-based adsorbents as they are identified as significant adsorbents for CO<sub>2</sub> because of its large availability, cost-effective, high surface area, simple pore structure alteration, and possible surface functionalization (Zhang et al., 2019). The two other solid adsorbents which are widely envisaged as efficient CO<sub>2</sub> adsorbents are zeolites and MOFs. With their high porosity and specific nature, they also offer relevant advantages for CO<sub>2</sub> capture. Some recent reviews discuss the characteristics and the advantages of each of these four mainly developed solid adsorbents (Abd et al., 2020; Patel et al., 2017; Yaumi et al., 2017; Younas, 2016).

One of the key challenges for adsorption-based gas separation to achieve market viability is the development of appropriate adsorbents that meet the efficiency requirements for coal- and gas-fired power plants. Thus, in order to develop new, highly effective adsorbents, certain material characteristics have to be optimized, such as the properties (*i.e.*, porous surface structure, high-specific surface area and high thermal, chemical and mechanical stability) (Dhillon and Kumar, 2019) as well as the surface chemistry of the nanomaterials. Each of these nanomaterials possesses its own specific characteristics and its own chemistry. For over 10 years of research on the subject, it remains unclear which parameter plays the major role in maximizing CO<sub>2</sub> adsorption capacity.

Recent reviews on CO<sub>2</sub> capture highlight the numerous parameters that could be considered in order to fully understand the adsorption mechanism on nanomaterials. In this review, based on the reported adsorption capacity of the mainly studied nanomaterials designed, we propose an unprecedented quantitative analysis which allows to compare the performances of the four main nanomaterials studied for CO<sub>2</sub> capture: graphene, CNTs, zeolites and MOFs. The CO<sub>2</sub> adsorption capacity of the most studied nanomaterials is tentatively related to their morphological (surface and pore volume) properties. The original and simple proposed analysis robustly reveals that the surface texture properties are not sufficient to predict the adsorption capacity and in agreement with other recent reviews, surface chemistry and pore size are especially believed to play an important role in CO<sub>2</sub> adsorption mechanisms (Belmabkhout et al., 2016; Singh et al., 2020; Wang et al., 2021).

This review is organized in six main sections. Carbonaceous adsorbents (graphene and CNTs) and non-carbonic adsorbents (zeolites and MOFs) are described after some generalities in the CO<sub>2</sub> capture process. The following section focuses on both the physical and chemical modifications applied to the nanostructured materials to enhance CO<sub>2</sub> capture. In particular, the

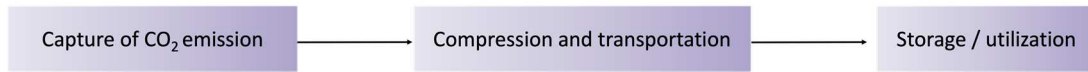
mechanisms, including physical and chemical adsorption, have been reviewed as a reference for the readers to obtain a clear perspective when designing and improving CO<sub>2</sub> adsorbents. Finally, the specifics of the chosen nanomaterials have been analyzed to better understand the relationship between the properties and the efficiency of the CO<sub>2</sub> capture.

## **2. Generalities about CO<sub>2</sub> capture**

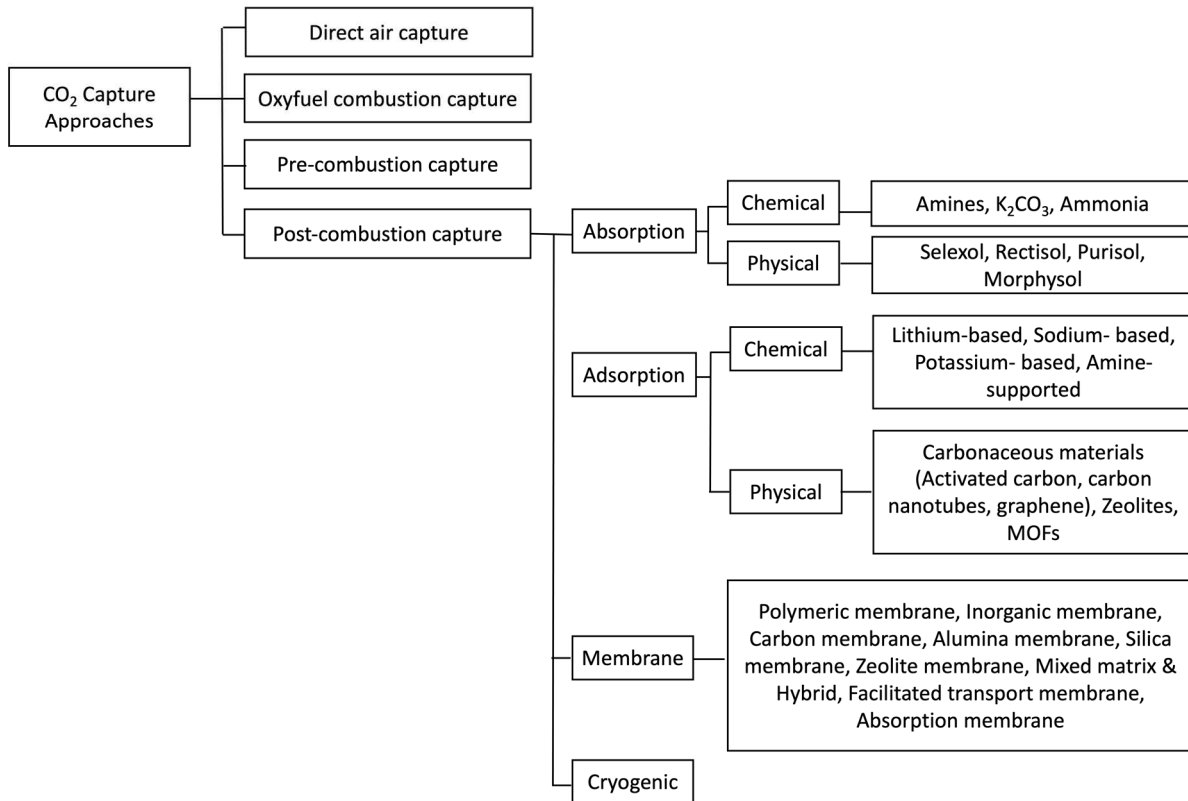
The main principle of the CCS is illustrated in Figure 2a. CO<sub>2</sub> emission is first captured; then, the compressed CO<sub>2</sub> is transported through pipelines for storage in geological formations including in ocean or mineral carbonates or used as feedstock for industrial processes.



(a) Conceptual CCS System



(b) CO<sub>2</sub> Capture Technologies



**Figure 2** (a) the main principle of the CCS (b) the types of CO<sub>2</sub> capture technologies

Capturing CO<sub>2</sub> is more likely to be implemented to large point sources like power plants as compared to small and mobile sources like transportation, as it is more cost-effective. Basically, there are four forms of carbon capture approaches depending on the source of fuel, CO<sub>2</sub> partial pressure, and gas flow pressure: (1) direct air capture (DAC), (2) oxyfuel combustion, (3) pre-combustion, and (4) post-combustion (Figure 2b). The summary of the CO<sub>2</sub> capture approaches is presented in Figure 1b. DAC is a process for adsorbing CO<sub>2</sub> directly from the atmosphere through chemicals (*e.g.*, sodium hydroxide). DAC is not being directly

linked to the existing energy infrastructure that generates CO<sub>2</sub>, and it deals with low CO<sub>2</sub> concentrations rather than concentrated streams. For oxyfuel combustion process, it is mainly based on separating O<sub>2</sub> from N<sub>2</sub>, which is more similar to the post-combustion system. Instead of separating CO<sub>2</sub> from N<sub>2</sub>, the fuel is combusted in oxygen; in this case, O<sub>2</sub> is separated first from N<sub>2</sub>. The flue gas which consists mainly of CO<sub>2</sub> and steam can be easily separated by condensation. Pre-combustion refers to the process of CO<sub>2</sub> capture before the combustion. In this process, the fossil fuels are converted into syngas, mainly composed of CO and H<sub>2</sub>. Then, the CO is further reacted with steam to generate CO<sub>2</sub> and more H<sub>2</sub>. The highly concentrated H<sub>2</sub> gas could be supplied as an energy source, while the eliminated CO<sub>2</sub> from the system is stored. Separating CO<sub>2</sub> by pre-combustion seems to require less energy, and it is much economical compared with post-combustion (Chen et al., 2020). In addition, the conversion from carbon fuel to non-carbon fuel could bring extra goods and profits to the factory. Post-combustion implies the absorption of CO<sub>2</sub> after the burning of fossil fuel with air, ensuring that CO<sub>2</sub> is sequestered from the NO<sub>x</sub> and SO<sub>2</sub> flue gas. There are few methods used in this approach including absorption (Fang et al., 2020), adsorption (Manyà et al., 2020; Zhang et al., 2016), cryogenic distillation (Fu et al., 2016), and membrane and gas hydrates [17]. Table 1 summarizes the benefits and drawbacks of these carbon capture approaches.

**Table 1** Advantages and drawbacks of carbon capture approaches.

	Advantages	Drawbacks
Pre- combustion capture	· more economic and low emission	· Required comprehensive support system · Additional cooling costs

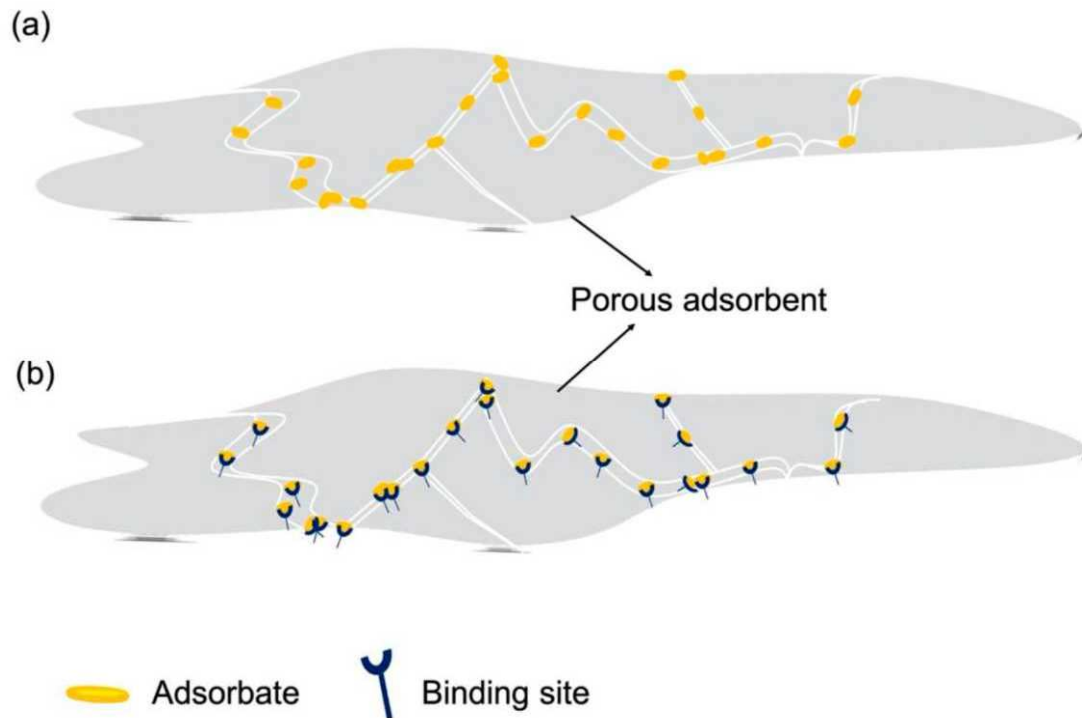
	<ul style="list-style-type: none"> <li>· High CO<sub>2</sub> concentration and output pressure to improve the efficiency of sorption</li> </ul>	<ul style="list-style-type: none"> <li>· Lack of performance in water-gas shift section</li> </ul>
Post- combustion capture	<ul style="list-style-type: none"> <li>· High kinetics performance</li> <li>· More economical approach for the extraction of energy from fuel</li> <li>· Redevelop systems easily in existing plants</li> <li>· applicability over a relatively wide range of temperature and pressure conditions</li> </ul>	<ul style="list-style-type: none"> <li>· Corrosion due to basic solvent</li> <li>· Solvent regeneration necessitates a significant amount of energy.</li> <li>· Degradation of the solvent</li> <li>· Owing to foaming properties and viscosity, the solvent concentration is limited.</li> <li>· High capital costs and operating expenses for existing systems of sorption</li> </ul>
Oxyfuel combustion	<ul style="list-style-type: none"> <li>· The volume of gas to be treated reduced and smaller size of boiler required</li> </ul>	<ul style="list-style-type: none"> <li>· Increased SO<sub>2</sub> concentrations can accelerate machinery corrosion.</li> <li>· Combustion of pure oxygen would be challenging.</li> </ul>

- 
- |   |   |
|---|---|
| <ul style="list-style-type: none"> <li>· Potential to lower energy consumption with membranes</li> <li>· CO<sub>2</sub> separation is not required</li> </ul> | <ul style="list-style-type: none"> <li>· High production cost due to large production of cryogenic</li> <li>· Decreased process efficiency</li> </ul> |
|---|---|
- 

### 3. Mechanism of adsorption process

Theoretically, adsorption is described as an equilibrium-diffusion-reaction of a molecule from a liquid or gas into solid surface (Julbe et al., 2019), which passes through the gas and liquid channels simultaneously or counterfactually through a packed column. In practical terms, adsorption capacity is intensively driven by the mass transfer between the adsorbate and adsorbent surfaces as well as the adsorption reaction rate. Adsorption can also trigger in surface energy as the surface molecules experience bond deficiency, thus making them energetically favorable to adsorption of molecules. Contrariwise, the inability of the particles to leave the surface can be called as desorption. In general, the principle of adsorption involves four stages: (1) the isolated sites on the sample surface begin to adsorb gas molecules at low pressure; (2) once gas pressure rises, the area of adsorbed molecules expands to form a monolayer; (3) additionally increasing gas pressure can cause multilayer coverage to begin, and smaller pores in the sample will first fill in; and lastly (4), a further rise in gas pressure would cause the sample to be entirely covered and all pores filled (White, 2013). Besides this principle, the adsorption mechanism is also a critical thing to emphasize. The mechanism of adsorption can be classified into two, which is either by physical or chemical adsorption. The difference between these two mechanisms arises in terms of specificity, bonding, characterization, surface area, molecular layer, and consequence of various factors in the whole process. Figure 3 shows

the mechanisms of both physical and chemical adsorptions, and they are described in more details below.



**Figure 3** Mechanisms of (a) physisorption and (b) chemisorption process.

### ***3.1 Chemical adsorption***

Chemisorption is a chemical adsorption process where a molecule adsorbs onto a solid surface by spontaneous formation of a chemical bond-like hydrogen bonding, covalent and ionic bond. The process commonly works at very low concentrations, and the chemisorbed particles are often irreversible. In chemical adsorption, the electrons are obviously transferred between adsorbents and adsorbates (J. Liu et al., 2017). This process takes place when the gas molecules are adsorbed by valence bonds on the adsorbent surface, then forming a monolayer. In addition, it may also require high regeneration energy. The energy of chemisorption between gas

molecules and adsorbents can differ considerably depending on the strength of the adsorbent and adsorbate specie bonding. In terms of adsorption kinetics, chemisorption process is an exothermic reaction, and the enthalpy values are normally high due to the formation of chemical bonds. Xu *et al.* investigated the chemical process of carbon-based/Fe oxyhydroxide composites, with synthesis through one-step pyrolysis process in CO<sub>2</sub> capture. The main advantage of this material is it has the potential to be a low-cost and efficient adsorbent. Also, these carbon-based/Fe oxyhydroxide composites also could adsorb CO<sub>2</sub> by physical and chemical adsorbent. In this work, physical adsorption happens first, and as the content of Fe increases, the mechanism changes from physical to chemical adsorption due to favorable interactions between Fe oxyhydroxides and CO<sub>2</sub> molecules. As a result, the ability to adsorb CO<sub>2</sub> increases and adsorption kinetics decreases (Xu et al., 2020). Besides, according to Gomez-Pozuelo *et al.*, there are three routes to prepare amine-functionalized porous adsorbents. First one is by grafting organosilanes with aminopropyl (AP) and diethylenetriamine (DT); second is by impregnation with polyethyleneimine (PEI); and, finally, it is the double functionalization by impregnating earlier grafted samples. Among these routes, they found that the second method showed the highest CO<sub>2</sub> capture. Theoretically, the CO<sub>2</sub> molecules are adsorbed on the adsorbent non-polar surface, which is dominated by oxygenated functional groups. The reaction is here supported by the interaction between adsorbent and adsorbate at a moderate temperature resulting in an exothermic reaction in nature. Consequently, the adsorbent surface is regenerated by reversing the adsorption state to reuse it for the next adsorption process. Additionally, the incorporation of amine groups into solid adsorbent materials is expected to promote polarization and improve CO<sub>2</sub> since it was directly linked with primary and secondary amines. Therefore, owing to the chemical reaction between CO<sub>2</sub> and amines, the major contribution of chemisorption on amino groups to complete CO<sub>2</sub> adsorption

is achieved (Gómez-Pozuelo et al., 2019). Furthermore, the performance of capture systems would also rely on the regeneration potential of amine or nitrogen-functional solid adsorbents. In a study by Baltar *et al.*, two different amine-based solvents, that is, dimethylethanolamine (DMEA) and diethylethanolamine (DEEA), were utilized to analyze the adsorbent surface behavior in CO<sub>2</sub> capture. Besides, they mainly focus on the solvent regeneration process (stripping operation), which considers the aspects related to cost and efficiency. As per their findings, they have determined that the regeneration methods increase the interest for the solvents due to the good behavior in the absorption step. A significant decrease in driving force due to an incomplete regeneration could be clarified by comparing the results achieved for aqueous solutions of DMEA, thanks to regeneration cycles using stripping (Baltar et al., 2020).

### ***3.2 Physical adsorption***

Physical adsorption or physisorption is defined as a form of adsorption that attaches the target adsorbate to the adsorbent via hydrogen bonding, van der Waals, electrostatic forces, and hydrophobic interactions, which are interactions typically reversible depending on pressure and temperature. Tan *et al.* used different types of carbon nanoporous structure to examine the surface morphology, porous structure, and oxygen physisorption capability of pulverized coals. The porous substances are typically ideal adsorbents, because the porous nature is correlated with the rising surface area. Their results showed that the amount of adsorbed oxygen corresponds to the topological dimension of the carbon pores and the volume of coal nanopores, but inversely to the number of pores filled within the material. Besides, they have also found that the physical adsorption rate increases with an increased number of folds and surface area, and they noticed low desorption temperatures of physisorbates due to weak interactions (Tan et al., 2020). Physisorption is usually described as an exothermic reaction with low enthalpy

values due to weak attraction forces from van der Waals (Shahabi and Raissi, 2016) and it can also be related to an adsorption energy. For these cases, the particle adsorption is always a spontaneous process with no limits, whereas desorption of adsorbed molecules should prevent the binding energy from a surface; thus, the value of adsorption energy is often positive (Xia and Tang, 2012). Research on the CO<sub>2</sub> binding mechanisms was carried out using various materials including pure silica support and modified amine-grafted mesoporous silica. The result showed that the enthalpy value of unmodified pure silica support was lower compared with the reacted species on the surface, confirming that the main binding mechanism is physisorption. The low activation energy for physisorption on pressure swings also allows for maximum reversibility. In addition, the pore size distribution observed corresponds well with the fact that the sites are focused on low enthalpies. These signals would lead to the CO<sub>2</sub> emissions physisorbed (Sánchez-Zambrano et al., 2020). The exothermic reaction occurs more readily at lower temperatures. According to Wang *et al.*, at 0°C and 25°C and low pressure, the CO<sub>2</sub> adsorption isotherm curve was noted to have a steep rise until it slowly reached a maximum at 1 bar. In the case of physical adsorption of gas over solids, the rate of adsorption increases with an increase in pressure as the density of the gas reduces throughout the adsorption process (Wang, 2019). This can also be explained by the Le-Chatelier's principle. When a complex balance is disrupted by the changing conditions of concentration, pressure, or temperature, the position of the equilibrium shifts to combat the change (Treptow, 1980). Table 2 summarizes the classification of the main differences between physical and chemical adsorption.

**Table 2** Comparison between the two adsorption processes: physical and chemical (De et al., 2013; Králik, 2014; Panic et al., 2013; Wei and Seo, 2010)

Physisorption	Chemisorption
---------------	---------------



- 
- |   |   |
|---|---|
| <ul style="list-style-type: none"> <li>• No electron transfer<br/>(maybe polarization might occur)</li> </ul> | <ul style="list-style-type: none"> <li>• Electron transfer leading to formation of the bond</li> </ul>                      |
| <ul style="list-style-type: none"> <li>• Van der Waals forces between molecules</li> </ul>                    | <ul style="list-style-type: none"> <li>• Strong chemical bond; (e.g.: hydrogen bonding, covalent and ionic bond)</li> </ul> |
| <ul style="list-style-type: none"> <li>• Reversible process</li> </ul>  | <ul style="list-style-type: none"> <li>• Irreversible process</li> </ul>  |
| <ul style="list-style-type: none"> <li>• Monolayer or multilayer adsorption</li> </ul>                        | <ul style="list-style-type: none"> <li>• Monolayer adsorption</li> </ul>  |
| <ul style="list-style-type: none"> <li>• Low adsorption heat<br/>(10-40 J/mol)</li> </ul>                     | <ul style="list-style-type: none"> <li>• High adsorption heat<br/>(20-400 kJ/mol)</li> </ul>                                |
| <ul style="list-style-type: none"> <li>• Low activation energy</li> </ul>                                     | <ul style="list-style-type: none"> <li>• High activation energy</li> </ul>  |
| <ul style="list-style-type: none"> <li>• Adsorption increase when pressure increase</li> </ul>                | <ul style="list-style-type: none"> <li>• No effect on the adsorption when change of pressure</li> </ul>                     |
| <ul style="list-style-type: none"> <li>• High binding energy (10-100 meV)</li> </ul>                          | <ul style="list-style-type: none"> <li>• Low binding energy (1-10 meV)</li> </ul>   |
- 

## 4. Nanomaterials for CO<sub>2</sub> capture

### 4.1 Carbon-based nanomaterials

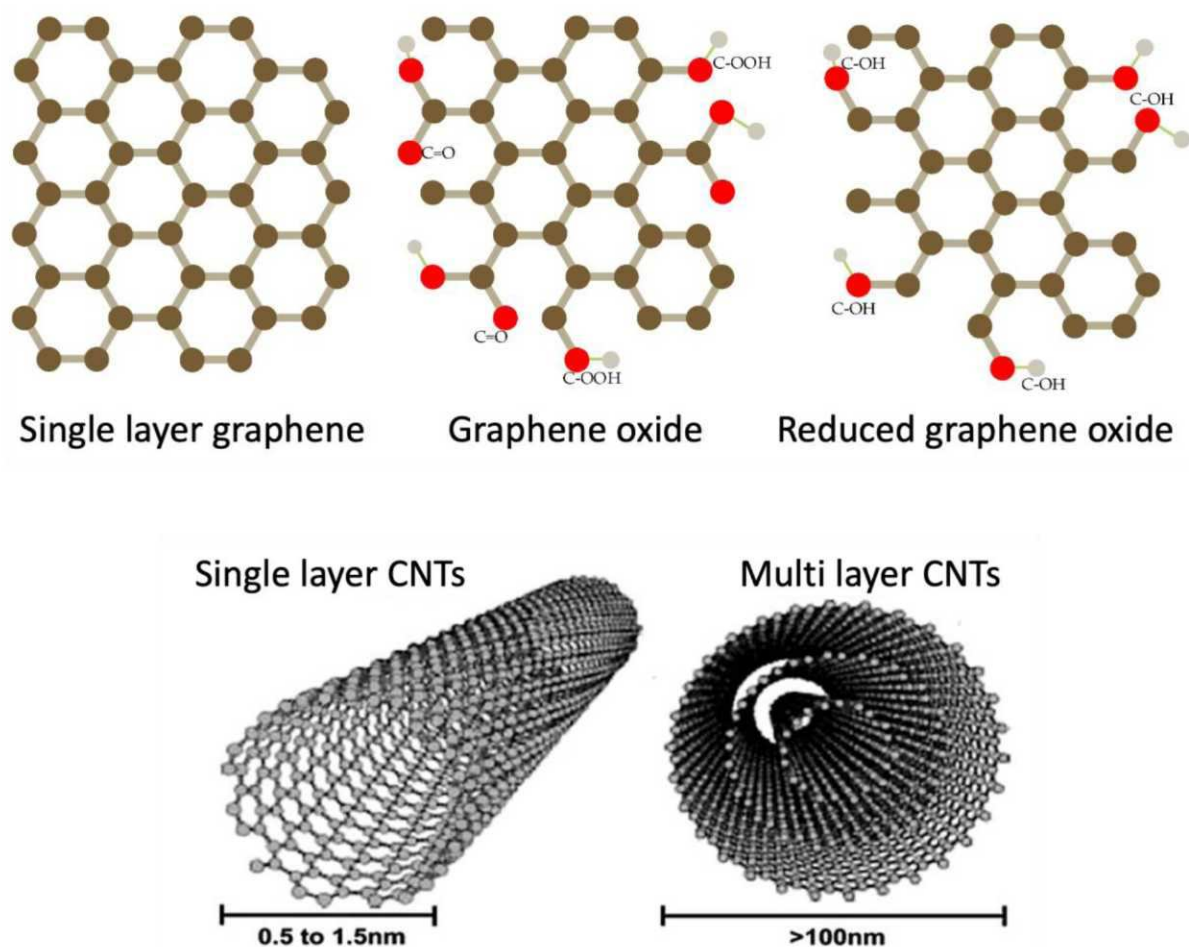
AC was historically among the first carbon-based adsorbents used for CO<sub>2</sub> capture due to its abundant feedstock, low-cost materials, high available surface, and high adsorptive characteristics (Singh, 2019; Singh et al., 2019a, 2019b, 2018). More recently, nanostructured carbon-based adsorbents, especially graphene and CNTs, are identified as significant

adsorbents of CO<sub>2</sub> due to their large availability, cost-effective, high surface area, adjustable pore structure, possible surface functionalization and ease of regeneration. Figure 3 shows the structure of graphene and carbon nanotubes. Generally, graphene is a single-atom thick layer of a hexagonal structure made of sp<sup>2</sup>-bonded carbon atoms. Various types of graphene exist including single-layer graphene, few-layer graphene, multilayer-layer graphene, graphene oxide (GO), graphene nanoplatelets (GNPs) and reduced graphene oxide (rGO), among the main graphene derivatives. Graphene derivatives can be self-assembled to form porous 3D materials. The architecture, morphology, and properties of these graphene-based materials (GBMs), such as the type, chemical properties of the surface, structural strength, and even the physical properties depend on the synthesis process (Mohd Firdaus et al., 2020). For example, Chowdhury and Balasubramanian fabricated a highly ordered GBMs with large specific surface area and interconnected hierarchical pore networks (Chowdhury, 2016). More significantly, through various stacking techniques, the gas flow channel and pores can be controlled, resulting in excellent CO<sub>2</sub>/N<sub>2</sub> stability and fast adsorption kinetics as well as stable CO<sub>2</sub> adsorption/desorption cycling process. Besides, the addition of functional compounds such as oxygen-containing groups has also been shown to be useful for the design of a good porous material for CO<sub>2</sub> absorption (Liu et al., 2018). Sui *et al.* synthesized 3D hydrothermal rGO (HRGO) with high pore capacity and large surface area (Sui and Han, 2015). Their graphene-based adsorbent displayed an enhanced CO<sub>2</sub> capture efficiency due to textural properties and various molecular interactions, *e.g.*, acid-base interactions, polar interactions, and hydrogen bonding between CO<sub>2</sub> and HRGO. Similarly, the incorporation of functional groups of doping heteroatoms, such as nitrogen, sulfur, oxygen, and phosphorus, has also been shown to be promising dopants for CNTs and graphene-based adsorbents to improve their capacity to absorb CO<sub>2</sub> (Bandosz et al., 2016; Li et al., 2016). A nitrogen-doped graphene aerogel (NGA)

adsorbent was synthesized by a simple hydrothermal method using ammonia as a dopant (Sui et al., 2015). The NGA possessed a hierarchical structure with high porosity significantly conducive to the mass diffusion process and the exposure of adsorption sites for adsorbates. Besides, high charge density at nitrogen sites of NGA could maximize the contact with polarizable carbon dioxide molecules through interactions between dipole and quadrupole which can greatly impact the efficiency of CO<sub>2</sub> capture.

CNTs are often made of graphite, which has a tubular shape with an extremely porous and large surface area that could facilitate gas adsorption and storage applications (Figure 4). The nanotubes contain a single layer and multilayer ranging from around 3 to 100 nm for the outer diameter. They also possess a high thermal and electrical conductivity. Besides, the surface modification of CNTs through covalent or non-covalent functionalization is vital for the development of high-performance adsorbents. These properties make them very promising materials for efficiently and selectively adsorbing and desorbing of CO<sub>2</sub>. Presently, the surface of grafted adsorbents with polymerizing materials with either a short- or long-chain polymer amine groups in each monomer has been examined to maximize the performance of CO<sub>2</sub> adsorption (Ngoy, 2014). In addition, a grafted long-chain polymer with diamine has also provided a large CO<sub>2</sub> anchoring site for carbamate formation, covering multi-walled carbon nanotubes (MWCNTs) to improve surface area and pore volume. Recently, CNTs were used to form microtubular sorbents through the immobilization of PEI (Keller et al., 2018). Along with that, they have functionalized small-sized CNTs with a wet impregnation method to ensure fast heat and mass transfer, which is essential for efficient swing sorption processes. Similarly, Irani *et al.* have prepared CO<sub>2</sub> sorbent by immobilizing tetraethylenepentamine (TEPA) onto functionalized CNTs, and they believed that MWCNTs/TEPA sorbent had potential for application to CO<sub>2</sub> capture (Irani, 2017). The optimal TEPA loading on the

functionalized MWCNTs offered high CO<sub>2</sub> adsorption capacity. However, after a further increase in weight% of TEPA, CO<sub>2</sub> adsorption became low and unstable due to agglomeration. Khalili *et al.* proposed a two-step process to prepare functionalized CNTs using mixture of acid and amine compounds (Khalili et al., 2013). In a refluxed system, the CNTs were combined with nitric and sulfuric acids to generate carboxylated CNTs, and a subsequently amine functionalization using 1,3-phenylenediamine was applied. Even though, after modification, the pore volume and surface area were noted to decrease, aminated CNTs have shown higher adsorption capacity compared to the pristine due to the existence of great affinity between CO<sub>2</sub> molecules as a Lewis acid and basic amine sites on the modified CNT surface. Apart from grafting and impregnating with amine functional groups, Oliveira *et al.* modified CNTs with CaO pellets as it is considered a cheap material which can absorb large amounts of CO<sub>2</sub> (Oliveira et al., 2020).

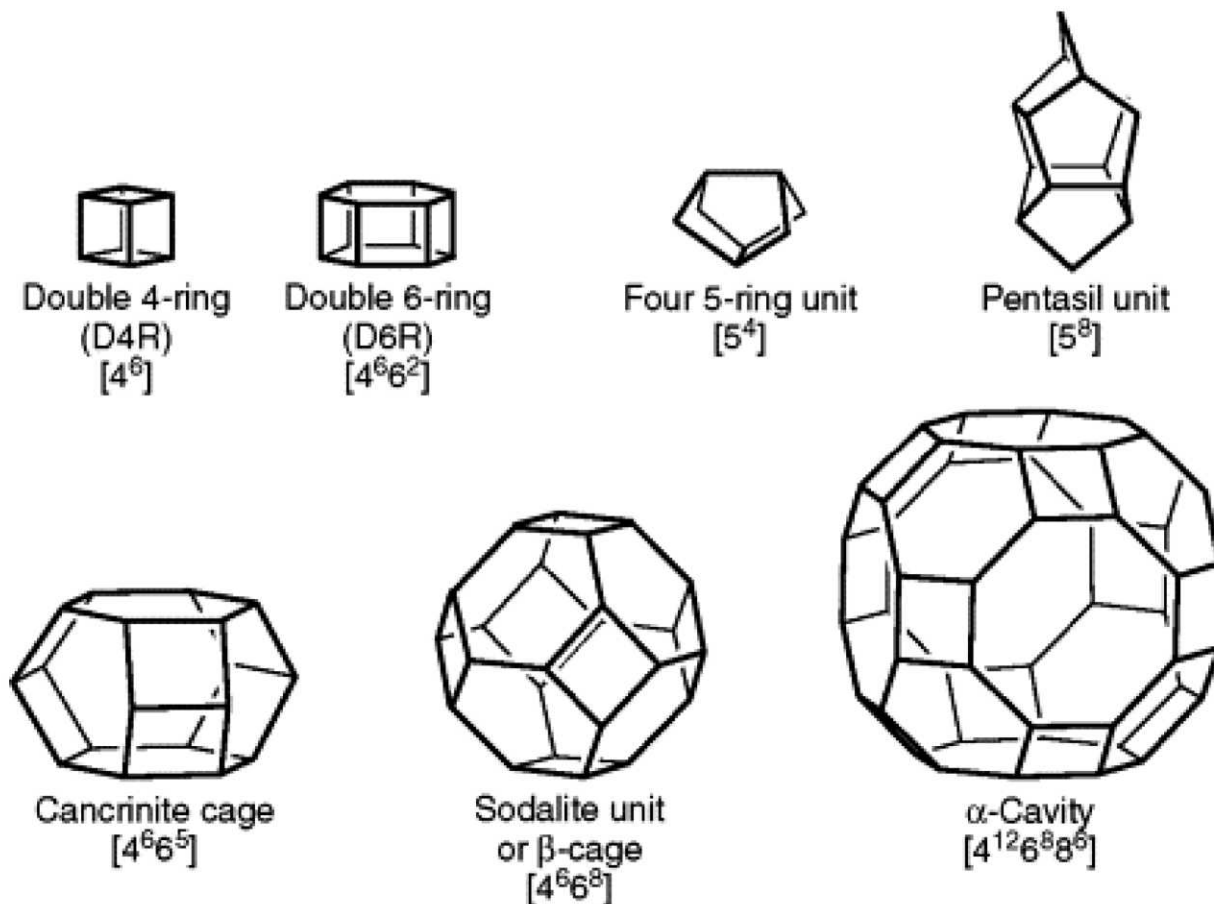


**Figure 4** Different types of graphene and carbon nanotubes. Reproduced with permission from refs. (Li et al., 2019; Ribeiro et al., 2017)

#### 4.2 Zeolites

Zeolites including zeolite Y (Murge et al., 2019; Su et al., 2010), 4A (Panda et al., 2019), 5A (Kusumastuti et al., 2018) and 13X (Su and Lu, 2012) are also commonly examined adsorbents for CO<sub>2</sub> capture. Zeolite materials are beneficial due to their porosity, pore size, acidity, basicity, and surface area and can be easily modified according to specifications and applications. Moreover, owing to their molecular sieving effect and good electrostatic interactions between CO<sub>2</sub> molecules and alkali-metal cations in the zeolite framework, zeolites

have been extensively researched for CO<sub>2</sub> capture. The cations in zeolites, such as Li, Na, and Al, could impact the adsorption heat of CO<sub>2</sub> as increase in negative charges, the heat of adsorption increase (Lee and Park, 2015). In addition, zeolites can also be characterized by having uniform pore size of 0.5 nm to 1.2 nm, which facilitates ion exchange, gas adsorption, separation, and purification. Adsorption of zeolites is primarily dependent on the matrix structure and composition, as seen in Figure 5, which can be split into three families: (1) small pore structures consisting of six, eight, or nine tetrahedral; (2) medium pore frameworks with 10 tetrahedral; and (3) large pore zeolites with one membered rings and ultra large structure (Feng et al., 2015).



**Figure 5** Relative sizes of n-rings frequently found in zeolites. Reproduced with permission from ref. (McCusker and Baerlocher, 2007)

The presence of pores in the modified zeolite could promote rapid gas diffusion within the pores and thus achieve better CO<sub>2</sub> adsorption efficiency for good CO<sub>2</sub> regeneration (Ci et al., 2017). From the study by Megias-Sayago *et al.*, the zeolite composite materials achieved high CO<sub>2</sub> capture

(Minelli et al., 2018). Their work took advantage of the composites combining a functional microporous zeolite with a mesoporous geopolymer matrix. Such approach enables the zeolite phase to be effectively blended, which could relevantly comply at the industrial scale. Another study investigates the capture of CO<sub>2</sub> adsorption efficiency using PEI-modified 13X zeolite by showing an improvement in CO<sub>2</sub> uptake capacity by a factor of 2.3 over unmodified 13X zeolite (Karka et al., 2019). The strength of the work arises from the fact that the branching of the impregnated molecular amine zeolite composite could trigger greater adsorption potential at optimum reaction parameter. This was explained by the kinetic modeling study. The developed zeolite-based adsorbent was believed to be a cost-effective technique for applying to control circumstances of flue gas for a wider scope of application of the CO<sub>2</sub> capture. Moreover, the effect of type (linear or branched) and the molecular weight of PEI on the efficiency of CO<sub>2</sub> capture have been also studied by Li *et al.* (Li, 2014); as per the latter's findings, it was determined that as the molecular weight of PEI increases, the adsorption capacity of CO<sub>2</sub> decreased. In fact, branched PEIs had a higher adsorption capacity due to higher mobility compared to linear PEIs.

#### ***4.3 Metal organic frameworks***

MOFs are the current class of solid sorbents which consist of metal cations and organic ligands (as shown in Figure 6a). To date, more than 20,000 different MOFs, including computational

and experimental perspectives, have been reported and explored from an engineering point of view (Furukawa, 2013). On the basis of different metal ions and organic linkers (*e.g.*, transition metals, actinides, alkaline earth metals, mixed metals, carboxylates, sulfates, phosphonates, azoles, heterocyclic compounds, etc.), the multi-component arrangement of the MOFs enables the morphology and microstructures to be tuned, offering them a greater advantage in numerous fields, especially CO<sub>2</sub> (Li et al., 2018; Lin et al., 2017; Seoane et al., 2015; Yu et al., 2017). According to Liu *et al.*, there are three main mechanisms involved in CO<sub>2</sub> capture by MOFs which are (1) MOFs with open metal sites; (2) MOFs with ultra-microporous structures, and (3) amine-functionalized MOFs (Liu et al., 2018). The open metal sites within MOFs, also known as coordinated unsaturated sites, are described as unsaturated metal centers generated during the activation process (Figure 6b) (Sladekova et al., 2020). Among the MOF family, the most extensively explored frameworks with open metal sites are HKUST-1, M-MIL-100, M-MIL-101, and M-MOF-74, where M represents the metal site. Three members of the MIL-100(M) including isostructural series (M = Cr, V, Sc) were synthesized by Cabelo and coworkers to investigate the interaction between unsaturated metal sites in MIL-100 framework and the CO<sub>2</sub> (Cabello et al., 2014). In this study, the thermodynamics of the CO<sub>2</sub> adsorption process was evaluated by FTIR spectroscopy, and they found that incorporation of highly charged metal centers in the framework increases CO<sub>2</sub> affinity. Sumboon *et al.* synthesized and characterized a 3-D pillared-layer M-DABCO MOF (M = Co, Ni, Cu, Zn) series, and further studied the influence of metal identity on surface area, pore volume, and CO<sub>2</sub> uptake. It was concluded that the metal atom influences the stability and adsorptive characteristics, with Ni-DABCO MOF achieving the highest CO<sub>2</sub> adsorption (at 1 bar and 298 K) and CO<sub>2</sub>/CH<sub>4</sub> selectivity (Chaemchuen et al., 2015). The metal ions with strong basic properties such as Ca, Mg, Zn, Li, Mn, and Cu are promising to construct an ideal MOF structure. It is thus important

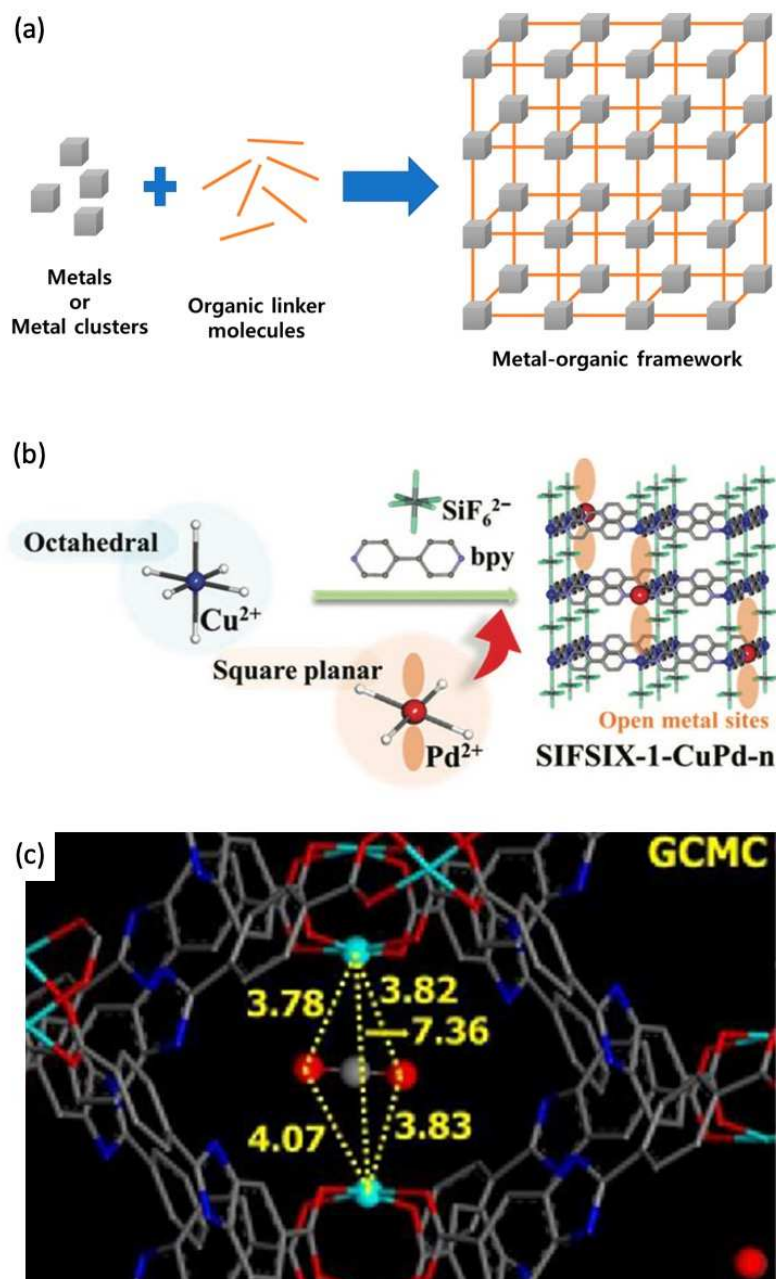


to sort metal particles together via a managed system to increase CO<sub>2</sub> adsorption using these open metal sites. In addition, the introduction of classical Cu metal ions and urea groups, by presenting high-density open metal sites and Lewis basic sites, also promotes CO<sub>2</sub> adsorption from both (B. Liu et al., 2017). The pore size of some ultra-microporous MOFs can be precisely controlled by exchanging organic ligands and metal ions within the framework. As shown in Figure 6c, a MOF-based material on Cu<sub>2</sub> paddle wheels was constructed with ultra-microporous structure that showed high CO<sub>2</sub> adsorption capacity, also thanks to a uniform distribution of adsorptive sites and reasonably strong CO<sub>2</sub>-framework interface (Nandi et al., 2018). Amine-functionalized MOFs are also promising for CO<sub>2</sub> capture due to their tunability thanks to the presence of these functional groups (Darunte et al., 2016). Indeed, nitrogen atoms belonging to the amine group are classified as one type of electronegative atom. It can form strong bonds along with its propensity to create a triple bond with itself and other components that are typically used to provide active sites for CO<sub>2</sub> capture. For MOFs, there are two known strategies often used to graft an amine functional group. First, amine is attached to open metal sites through a strong bonding interaction between the positive N atom and the unoccupied orbital of the open metal cation. Second, the amine group is linked to organic ligands. In the case of amine grafting by ethylenediamine (EDA), for instance, it has been shown that the ability of CO<sub>2</sub> adsorption and kinetics have been significantly improved (Cabello et al., 2015).

The MOF hybrid method is another aspect of modification that can be addressed. The objective of hybrid systems is to increase the density of higher affinity sites in order to promote good CO<sub>2</sub> interactions. Recently, a new class of hybrid systems has been investigated by Alfe *et al.* using MOF-based with graphene layers (MOF/GL). Three benzene-1,3,5-tricarboxylic acid (BTC)-based MOFs (Cu-HKUST-1, Al-MIL96, and Fe-MIL100), as well as their hybrids incorporating graphene like (GL) layers (5 wt.%), were synthesized and structurally

characterized in this study. They observed that adding GL to MOFs at a concentration of 5 wt.% did not significantly impact their textural properties. However, in CO<sub>2</sub> adsorption isotherms, it revealed the appearance of significant interactions corresponding to chemisorption in Cu- and Al-based MOFs, whereas physisorption takes place in Fe-MIL100 and its hybrids. Despite the MOF hybrid composite promising textural characteristics, intercalation with GL layers causes changes in the physicochemical/chemistry of the pores, which restricts the adsorption properties (Alfe et al., 2021). Similarly, Pourebrahimi *et al.* used MIL-53(Al) and graphene-based materials to create a hybrid MOF composite. In this work, they used two steps to activate the hybrid composite adsorbents and they found that the incorporation of GNP on MIL-53(Al) caused an improvement in term of the microporosity of the framework. Furthermore, MIL-53(Al)/GNP exhibited a 35% of increment in CO<sub>2</sub> adsorption capacity (Pourebrahimi et al., 2015).

All the above nanomaterials are promising adsorbents for CO<sub>2</sub> capture as they can minimize the energy requirements for the regeneration process. Many post-synthesis modifications like chemical functionalization or activation of their textural properties have been proposed to enhance their adsorptive performance. The commonly used methods can be classified in two main families: the physical and the chemical modifications.



**Figure 6** (a) Basic schematic diagram of the MOF structure; the mechanism involved in  $\text{CO}_2$  capture (b) MOFs with open metal sites; and (c) Interactions and distances between  $\text{CO}_2$  molecules and the ultra-microporous structures of the MOFs using simulations. Reproduced with permission from (Heo et al., 2020; Harada et al., 2019; Nandi et al., 2018), respectively.

## **5. Modification technology for enhancing the porous adsorbents**

Selectively removing CO<sub>2</sub> from different components of the flue gas mix requires specific interaction forces between the gaseous molecules and the solid surface. Thus, researchers have developed different strategies involving physical and chemical routes in order to maximize the interactions of the material surface with CO<sub>2</sub> and also to improve the adsorption processes. Further controlled material alteration could also facilitate the opening of pores and increase surface area, making them more ideal materials for CO<sub>2</sub> capture.

### ***5.1 Physical modification***

Physical activation is defined as a method of carbonizing porous materials usually treated at high temperatures with activation agents, either by steam or CO<sub>2</sub>. Basically, the mechanism begins with a thermal decomposition of the carbon source material, which is followed by the addition of an activating agent (Mohamad Nor et al., 2013). This is a slow oxidation process in which oxygen interacts with carbon atoms, resulting in the formation of pores. The oxygen in the system is also slightly chemisorbed to the surface, creating oxygen-based complexes. Besides, the physical activation surface is a less expensive and environmentally friendly approach as the chemicals are readily accessible, and the system is relatively easy and effective.

#### ***5.1.1 CO<sub>2</sub> activation***

Activation of CO<sub>2</sub> is a method of extracting any carbon from solid and then converting it to CO at a temperature higher than 800°C. This is one of the approaches to develop highly porous materials with an expected maximized adsorption due to the large surface area produced. In particular, electron transfer can activate the CO<sub>2</sub> molecules to promote a shift of its electron character, making it nucleophilic and much reactive with C-C (or C-H) bonds. For example, Li *et al.* work reported a facile CO<sub>2</sub> activation approach without any template to produce porous carbon spheres (PCS) (Li, 2016). The CO<sub>2</sub> flow was introduced to activate the sample at a

temperature of 1000°C for 150 min, and the porous carbons prepared by CO<sub>2</sub> activation were found to have high pore capacity and large surface area of 1.75 cm<sup>3</sup> g<sup>-1</sup> and 3350 m<sup>2</sup> g<sup>-1</sup> respectively. As a result, an exceptional CO<sub>2</sub> and CH<sub>4</sub> uptake at 20 bar and 298 K, respectively, was successfully achieved, and these findings have shown that the CO<sub>2</sub>-activation PCS has a good capacity to store energy source-related gases at high pressure. The development of such materials could be due to the production of new pores by opening closed pores or enlarging existing pores caused by devolatilization and carbon- CO<sub>2</sub> reaction. Graphene-based nanostructures have been investigated as precursor by various groups. Xia *et al.* synthesized hierarchically macroporous graphene-based carbons (HPGCs) through CO<sub>2</sub> activation. Interestingly, they observed that the optimal temperature for CO<sub>2</sub> activation is 750°C. Such relatively low temperature helped in preserving graphic sp<sup>2</sup> structure, while activation at higher temperature has been shown to form defects. Besides, HPGCs displayed high-specific surface areas with a wide pore volume of up to 532 m<sup>2</sup> g<sup>-1</sup> and 1.67 cm<sup>3</sup> g<sup>-1</sup>, respectively, with maximum adsorption capacities of 1.76 mmol g<sup>-1</sup> for CO<sub>2</sub> at 273 K and 1 bar (Xia et al., 2014). Similarly, through a simple CO<sub>2</sub> activation approach, Chowdhury *et al.* have constructed 3D folded graphene-based porous adsorbents with highly entangled networks with rGO a precursor at various temperature ranging from 750 to 950°C. Furthermore, according to the N<sub>2</sub> adsorption/desorption profile, as the activation temperature rose, the observed gradual sharpening of the isotherm curve indicated a decrease in the micropore size distribution and the creation of smaller micropores (Chowdhury and Balasubramanian, 2016a). Jin *et al.* have reported a hierarchical macroporous-microporous structure of modified CNTs with carbon composite monoliths (CCM). In their study, they have found that CNT-CCM is much more reactive with CO<sub>2</sub> during activation, exhibiting a significant burn-off phenomenon and a very short activation duration (15 min instead of 60 min). Apart from that, the adsorbent retains a

hierarchical macroporous-microporous structure with superior CO<sub>2</sub> adsorption capacity and kinetics, shown as CO<sub>2</sub> over N<sub>2</sub> (Jin et al., 2013).

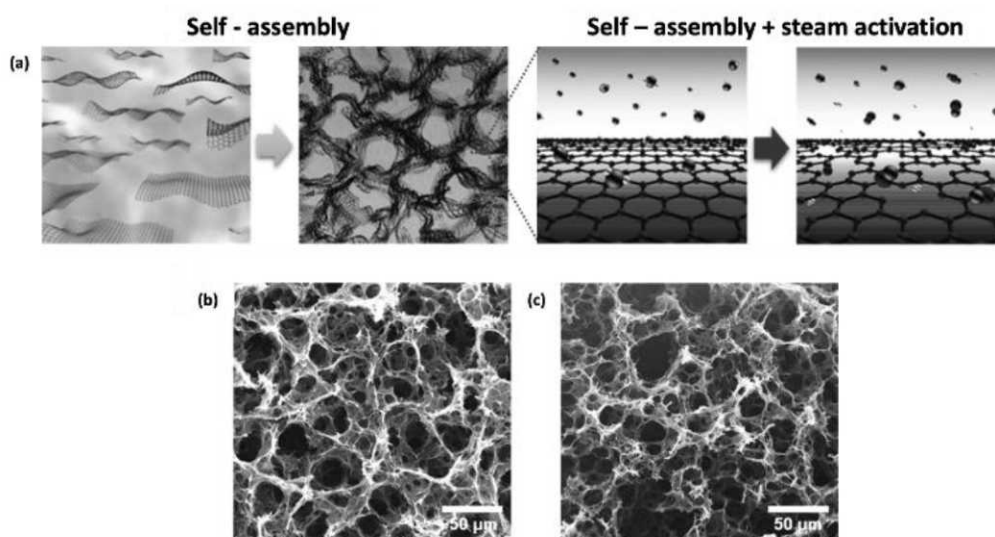
### **5.1.2 Steam activation**

Steam activation is often described as a process of opening and developing a carbon material porosity caused by mild oxidation through the passing of hot steam. Water normally reacts with carbon at 800–1100°C and generates CO and dihydrogen (H<sub>2</sub>). Steam activation was commonly performed under inert conditions and high temperatures to prevent oxidation of porous carbon (Heo and Park, 2015). This kind of activation appears to be likely effective because of the fast kinetics between carbon and steam reaction (Hetemi et al., 2020). Since the general reaction is essentially carbon conversion into carbon dioxide, the process is therefore exothermic, and it is feasible to use this energy to provide a self-sustaining cycle. Furthermore, steam activation could also render the pore structure and surface area more accessible. The reaction between carbon and steam has led to remove carbon atoms from the pore walls, thereby enlarging the pores. Heo and Park have prepared ultra-microporous carbonaceous adsorbents by a two-step-approach which are carbonization and activation process for enhancing CO<sub>2</sub> capture. The carbonization process was performed for 30 min, followed by CO<sub>2</sub> activation for 60 min at a temperature range of 700–850°C. According to the Brunauer-Emmett-Teller (BET) evaluation, the specific surface area was 1018 m<sup>2</sup> g<sup>-1</sup> with a total pore volume of 0.429 cm<sup>3</sup> g<sup>-1</sup>; further, they have found an excellent CO<sub>2</sub> uptake of 3.776 mmol g<sup>-1</sup> at 298 K (1 bar). In this study, they concluded that steam activation was effective without chemical activation in developing optimized CO<sub>2</sub> capture micropores (Heo and Park, 2015).

Sui *et al.* synthesized graphene aerogel (GA)-based adsorbents by steam activation to achieve high adsorption capabilities for toluene and methanol at saturated vapor pressure and room temperature. The GA was activated under a flowing nitrogen and steam atmosphere at various

temperatures from 750°C to 900°C. The BET analysis showed that the specific surface area of the GA with steam activation (SAGA) possessed a higher surface area of 830–1230 m<sup>2</sup> g<sup>-1</sup> with a pore volume of 2.2–3.6 cm<sup>3</sup> g<sup>-1</sup> compared to GA with a surface area of 600 m<sup>2</sup> g<sup>-1</sup> and a pore volume of up to 1.60 cm<sup>3</sup> g<sup>-1</sup>. In particular, SAGA could also be a potential porous material for CO<sub>2</sub> capture as they have observed that there was an enhancement in the adsorption capacities (Sui et al., 2014). Similarly, through a self-assembly and steam activation process, Yun *et al.* reported that the 3D rGO monoliths revealed large specific surface area approaching 1600 m<sup>2</sup> g<sup>-1</sup> and an exceptionally high porosity of >98% after steam activation. During activation, thermal stress was imposed on the surface of the sample and made it more crumpled by the defects and thermal stress, as demonstrated in Figure 7. The steam activation at high temperature offers better access to pore surface adsorption sites due to the provoked wrinkled and crumpled morphology (Yun et al., 2016). Moreover, Iruretagoyena *et al.* reported that the number of micropores has increased, and the capacity has been controlled by physical interaction, mainly involving n-complexation. Steam seems particularly successful despite its small molecular size promoting diffusion, resulting in the formation of a microporous structure (Iruretagoyena et al., 2020). These physical modification strategies, however, have both strengths and weaknesses. On one hand, physical modification is capable of synthesizing high surface and high-quality structure, while on the other hand, it requires high energy consumption. Although the adsorbents prepared through physical modification possess many excellent properties, there are still some points to be addressed. For example, in terms of pore sizes, as synthesized adsorbents often have pore size ranging from hundreds of nanometers to hundreds of micro-meters. In fact, the required pore size of the adsorbents for CO<sub>2</sub> capture must be less than 2 nm (microporous structures), as the pore size of the CO<sub>2</sub> molecule is 0.33 nm. Improvements of the strategy approach can thus be made by selecting an appropriate method

that can simplify the overall process as well as contribute to a greater control over the adsorbent structural properties.



**Figure 7** (a) Schematic illustration of self-assembly and steam activation procedures applied to rGO-based 3D structures; SEM images (b) before and (c) after steam activation. Reproduced with permission from (Yun et al., 2016).

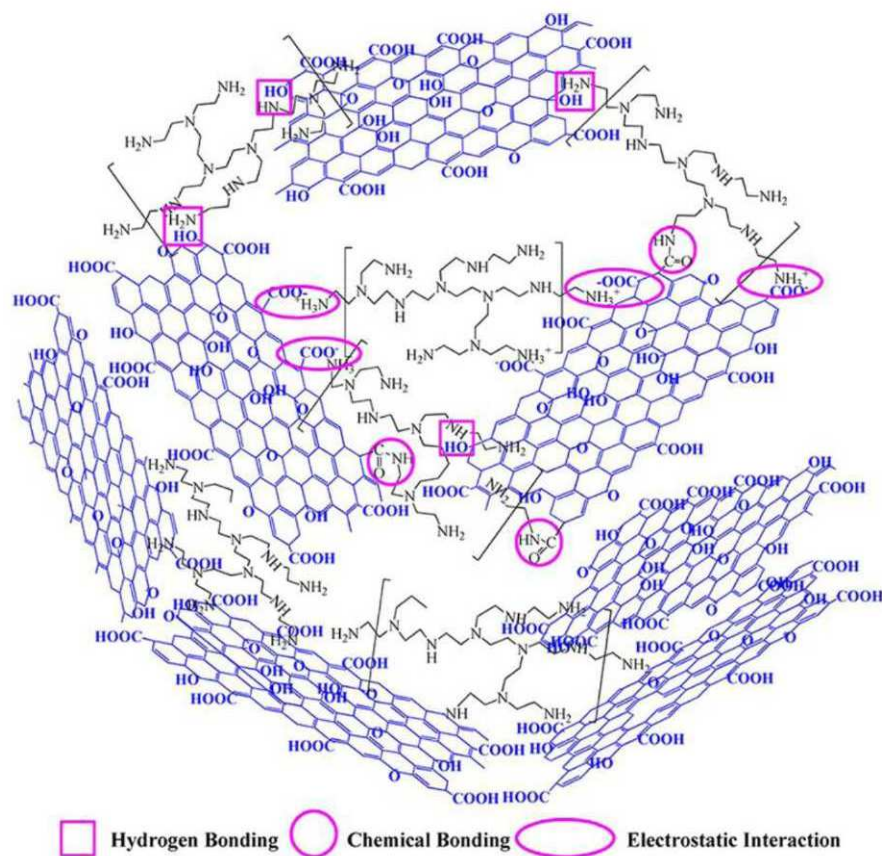
## 5.2 Chemical modification

Essentially, the surface chemistry of nanomaterials is driven by the presence of functional groups, doping of heteroatoms (Morales-Torres et al., 2020), metal or metal oxide, and coating of organic polymer on the surface. The addition of nitrogen function could also modify nanomaterial surface chemistry. The presence of nitrogen-containing groups within the carbon matrix promotes an increase in the functional basicity that increases the capacity for adsorption (Rozas and Leonor, 2011). Moreover, the basicity of the adsorbent nanomaterials is also reinforced by the delocalized  $\pi$  electrons of aromatic rings and unsaturated valence (Gadipelli and Guo, 2015; Navalon et al., 2017). The amination principle is crucial for the development of nitrogen functionalities in such conditions and it occurs when N-containing species such as



ammonia, urea, melamine, and etc. are present. To date, 3D-GBM architectures have been considered as promising materials thanks to their properties including porous network, ultralight weight, high surface area, electrical conductivity, or mechanical strength. Sui *et al.* synthesized 3D amine-graphene porous materials with two different methods: (1) by hydrothermal reduction of graphene (HTG) using Teflon-lined stainless-steel autoclave at 180°C for 12 h and (2) by cross-linking approach under mild conditions (Sui *et al.*, 2013). The CO<sub>2</sub> adsorption capacities of GO-PEI showed a maximum value of ~2.5 mmol g<sup>-1</sup>, which is larger than that of HTG (~1.8 mmol g<sup>-1</sup>) or GO (~1.7 mmol g<sup>-1</sup>). They have also found that the efficiency of the CO<sub>2</sub> adsorption increases by 32% after the introduction of basic sites from PEI polymers on the GO surface. FTIR and XPS spectra confirmed the presence of PEI polymers as some PEI chains were covalently linked to the GO surface by amide bonds (as shown in Figure 8). Similarly, Pruna *et al.* investigated the adsorption behavior of EDA-functionalized graphene aerogels by a single-step hydrothermal process and successfully obtained a high range of adsorption capacity of 0.68 to 1.12 mmol g<sup>-1</sup> at 1 bar and 298 K (Pruna *et al.*, 2019). The increase in CO<sub>2</sub> adsorption capacity with an increase of temperature from 273 to 298 K could be attributed to various factors, including chemical absorption, increased mobility of CO<sub>2</sub> molecules, activity sites, and improved pore filling (Lozano-Castelló *et al.*, 2004). Other than insertion of functional groups on the surface or edges of nanomaterials, the doping of sole heteroatoms such as nitrogen, boron, oxygen, and sulfur or the mixture of heteroatoms is also one of the methods used for tuning the favorable properties of nanomaterials and optimizing the capture of CO<sub>2</sub>. For instance, Babu *et al.* reported that nitrogen in the form of pyridinic and pyrrolic/pyridonic functionality was introduced by N<sub>2</sub> plasma treatment on the vertically oriented CNTs surface, and heteroatoms were confirmed to be homogeneously distributed in the carbon framework using energy-filtered TEM. The presence of nitrogen functionality tends

to affect the properties of CO<sub>2</sub> adsorption as the novel vertically oriented N-doping CNTs exhibiting a good adsorption capacity of almost 8 mmol g<sup>-1</sup> at 298 K and 36 bar (Babu et al., 2017).



**Figure 8** Mechanisms of chemical interactions between GO and PEI in GO-PEI hydrogel. Reproduced with permission from (Sui et al., 2013).

In parallel, the introduction of metals (*e.g.*, Ni, Ce, Zn, Co, Ag, and Cu) or metal oxides (*e.g.*, Li<sub>2</sub>O, Na<sub>2</sub>O, MgO, CaO, and Al<sub>2</sub>O<sub>3</sub>) has attracted considerable attention as it could increase the tendency for CO<sub>2</sub> to influence the adsorption capacity. This is due to the fact that CO<sub>2</sub>, as an acidic gas, is known to adsorb more strongly on the basic sites of some metal oxides, especially those with a lower charge which are more ionic and have more strongly basic sites. The effect of transition metals (*e.g.*, Co (II), Ni (II), Zn(II), Fe(III), Cu(II), Ag(I), La(III), and Ce(III)) on

CO<sub>2</sub> adsorption was investigated by Sun *et al.* In their work, a thermal treatment was used to prepare transition metal ion-exchanged SSZ-13 (Sun et al., 2019).

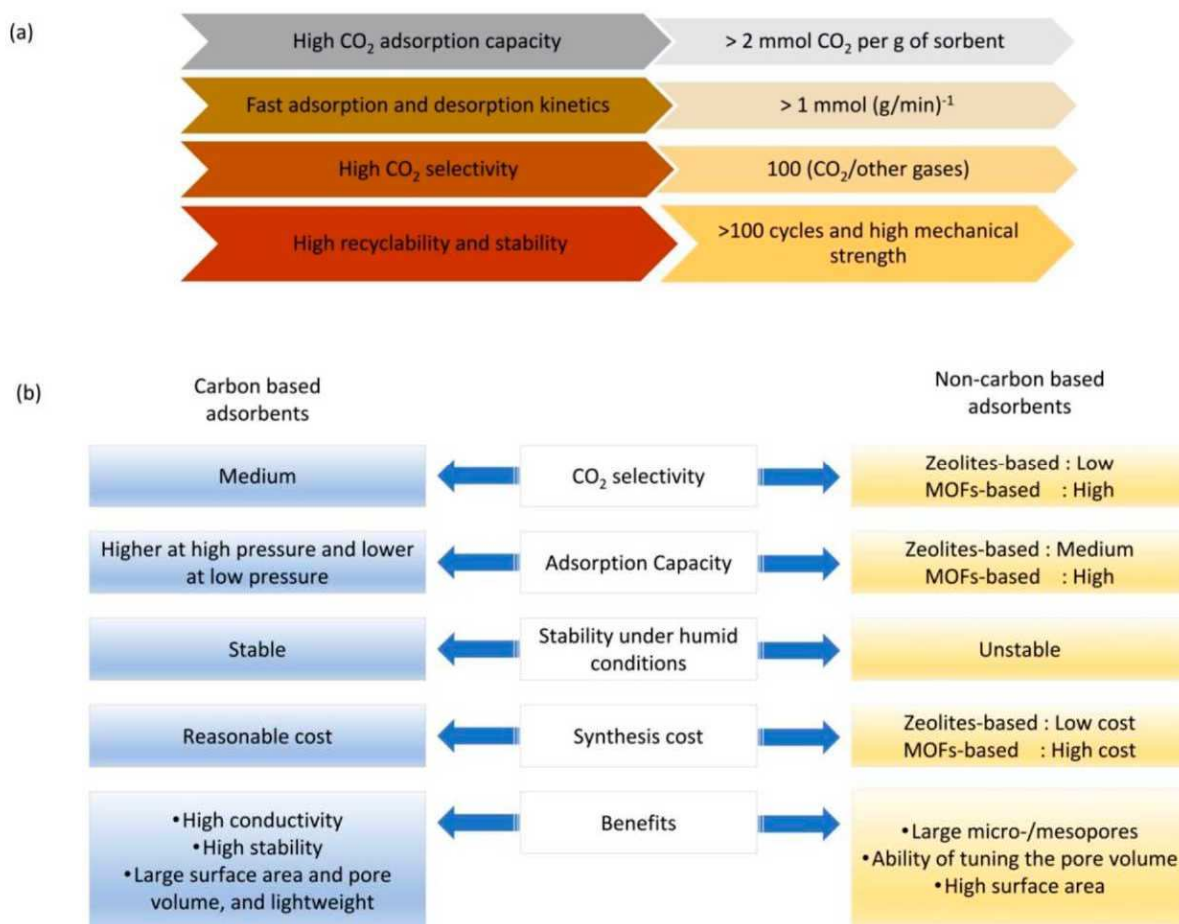
From the BET analysis, the surface area and the total pore volume of the adsorbents were found in the range of 600 m<sup>2</sup> g<sup>-1</sup>–950 m<sup>2</sup> g<sup>-1</sup> and 0.3–0.6 cm<sup>3</sup> g<sup>-1</sup>, respectively. Among the investigated transition metals, Co (II)/SSZ-13 and Ni(II)/SSZ-13 showed the highest CO<sub>2</sub> uptake (4.49 and 4.45 mmol g<sup>-1</sup>, respectively) and a superior selectivity of CO<sub>2</sub>/N<sub>2</sub> at 273 K and 1 atm. This may also be due to an improvement in the reaction strength between CO<sub>2</sub> and the used transition metal. In addition, the combination of polymers has also shown beneficial effects in improving the CO<sub>2</sub> adsorption properties of nanostructured adsorbents. Politakos *et al.* performed the reduction-induced self-assembly process at mild conditions to produce 3D rGO/poly(methyl methacrylate (PMMA)) (rGO-Pol) (Politakos et al., 2020). The reduction reaction was performed using ascorbic acid as reducing agent; after that, it was placed in an oven at three different temperatures (45, 60, and 90°C). The BET analysis was carried out in order to characterize the porous texture of the monoliths, and at temperature 90°C, the BET surface area was the highest (171–244 m<sup>2</sup> g<sup>-1</sup>) as the reduction reaction took place very fast at higher temperatures compared to temperature 40 and 60°C. The amount of PMMA can also influence the self-assembly phase of rGO as it can create highly durable structures. At the synthesized condition of GO (ascorbic acid ratio of 1:1 and 10% polymer weight percent), the highest adsorption capacity of 3.85 mmol g<sup>-1</sup> at 25°C and 1 atm was achieved. In this work, the preparation conditions of the graphene-based adsorbent, *i.e.*, the reducing agent amount and the reduction temperature, were crucial for the efficiency of CO<sub>2</sub>. Thus, in this case, the surface area was not the only primary consideration for high performance.

### ***5.3 Optimization of solid nanomaterials adsorbents for CO<sub>2</sub> capture***

The sorbent-based approach has been proven to be among the future research methodologies for capturing CO<sub>2</sub>. The main process can be described by molecular interactions between CO<sub>2</sub> and the sorbent surface. Most research works show regeneration energy and operating simplicity; the specific surface area and porosity are vital characteristics for effective diffusion through the developed material. Thus, in this section, the few relevant criteria reported to be of great importance to achieve a high CO<sub>2</sub> capture efficiency are discussed. Figures 9 shows the key parameters to optimize performances of ideal nanomaterials (Figure 9a) and a comparison of performance features of different solid nanomaterials for CO<sub>2</sub> adsorption (Figure 9b). Porous adsorbents are expected to meet several criteria for successful commercial deployment. They are based on technical requirements of the capture process, and a perfect balance must be achieved among most of them. First, suitable CO<sub>2</sub> adsorbents require good interactions with CO<sub>2</sub> molecules resulting in a sufficiently high CO<sub>2</sub> adsorption capacity. Generally speaking, an adsorption capacity is considered effective above 2 mmol of CO<sub>2</sub> per gram of sorbent (Ben-Mansour et al., 2016; Chen et al., 2019; Deng and Park, 2019; Politakos et al., 2020). Commonly, both temperature and pressure can have an influence on CO<sub>2</sub> capture efficiency for carbonaceous materials like graphene, CNTs, and AC. The adsorption potential of CO<sub>2</sub> increases significantly as temperature and pressure decreases and increases, respectively. Contrariwise, CO<sub>2</sub> adsorption is enhanced at a moderately high temperature for non-carbonaceous materials such as zeolite and MOFs as they exhibit high kinetic energy and a higher pore size and pore volume than those of carbon-based materials (Younas, 2016). In fact, the modification of solid adsorbents by certain methods, including acid treatment, amine grafting, alkaline metal-based modification, organic and inorganic linking, carbonate-based impregnation, and attachment of polymer, could increase the performance of CO<sub>2</sub> adsorption.

Second, the adsorbents need to have fast adsorption/desorption kinetics for carbon dioxide. Basically, the adsorption or desorption kinetics is often used to predict the coefficient at which the adsorbent adsorbs and desorbs (Wang et al., 2016). This coefficient offers a baseline for optimizing the adsorbent design to enhance the CO<sub>2</sub> adsorption capacity from different target streams. There are different common kinetic models that have been widely used, such as Pseudo 1<sup>st</sup>, Pseudo 2<sup>nd</sup>, and Avrami kinetic models. Fast adsorption/desorption kinetics are critical for effective CO<sub>2</sub> adsorption under operating conditions for both carbonaceous and non-carbonaceous materials, since the faster an adsorbent will adsorb/desorb CO<sub>2</sub>, the less adsorbent would be required to capture a given volume of CO<sub>2</sub> (Varghese and Karanikolos, 2020). In addition, others have also stated that the overall kinetics of CO<sub>2</sub> adsorption may also be affected by the presence of functional groups (Chiang et al., 2019), and even the pore size and distribution of the support (Fletcher et al., 2007).

Third, gas selectivity is defined as the ratio of permeability coefficients of two gases. An ideal adsorbent should selectively adsorb CO<sub>2</sub> over other flue gas components. The degree of selectivity achieved has a direct impact on the purity of the CO<sub>2</sub> and thus subsequent pumping and storage processes. The adsorption of CO<sub>2</sub>, which is more than 3 mmol g<sup>-1</sup>, shows a significant improvement toward selectivity. Ideally, one needs 100 times or more selectivity to make a significant impact.



**Figure 9** (a) The four key optimal performance features of the ideal nanomaterials (b) Comparison of several characteristic of solid nanomaterials for adsorption of CO<sub>2</sub>

Lastly, regeneration and recycling of adsorbents have been identified to be vital, as they must be used for several cyclical operations without significant loss of accuracy and, at the same time, maintain its adsorption performance (Gibson et al., 2016). There are primarily two methods of regeneration in basic form: temperature swing adsorption (TSA) and pressure swing adsorption (PSA). Adsorption-based processes using microporous materials comprise a cost-effective technique that is very interesting to examine. In a pressure swing adsorption (PSA) process, the adsorbent is regenerated by lowering the pressure (Siqueira et al., 2017), whereas in a temperature swing adsorption (TSA) operation, the regeneration is carried out by

increasing the temperature (Raganati et al., 2020). In contrast with these two approaches, PSA is typically considered to be the most feasible and convenient process because of its simple operation, low operating and capital investment costs, and higher energy efficiency.

## **6. Nanomaterials and the Economic Perspective**

Generally, according to the market study by Research and Market, the nanotechnology industry is expected to grow by US\$69.5 billion by 2025, with an average annual growth rate (AGR) of 13.8 %. The nanotechnology market in the United States is expected to be worth US\$13.2 billion in 2021, while China is expected to reach a market size of US\$5.1 billion by 2026, representing 1.2 % AGR over the forecast period. Aside from the United States and China, Japan and Canada are two other dominant global markets for nanotechnology, with economic projections of 8.1 % and 9.4 % over the expected timeline, respectively, whereas Germany is expected to achieve an annualized rate of 8.2 % within the Europe. Interestingly, experts estimate that nanomaterials will make a decent profit with this percentage, contributing to global growth with a market value of approximately US\$98.9 billion by 2025. In this context, the market studies available on internet show a significant expected growth of the global market, with an expected average range. The data show that the forecast for economic growth considering applications of nanomaterials is significant in the next 5 years. Furthermore, since the global nanomaterial market has grown tremendously, they have a strong potential to reach a wide range of stakeholders, as everyone engaged in nanotechnology challenges is investing heavily in the research field. Table 3 shows the price of the four types of nanomaterials studied in this study, including graphene, CNTs, zeolites and MOFs. According to our findings, pristine nanoparticles are less expensive than modified nanomaterials. This is to be expected, as modified nanomaterials are frequently manufactured using complex techniques that involve additional chemical and energy consumption. As a result, in order to generate high-quality products, reasonable and reliable modification technology is required. For instance, graphite powder is a low-cost starting material for making other graphene derivatives, and thanks to a simple graphite modification technology discovered years back, GO and other graphene derivatives have become more widely available in the market and have been extensively used in some applications, including efficient electronics (Szkopek and Martel, 2021), flexible displays (Wang et al., 2020), efficient solar panels (Wei et al., 2021), faster DNA sequencing (de Souza et al., 2020), drug delivery (Lu et al., 2020), and as adsorbent in adsorption studies

(Varghese et al., 2020). According to the most recent market assessments, the energy and storage industry has the largest economic and technological potential for nanomaterial applications, because these materials cover an amazing range of electrical (Glad et al., 2020), chemical (Mahmoudi, 2021), optical (Huang et al., 2020) and mechanical properties (Wu et al., 2020) perhaps the most impressive discovery is that they can be combined freely to create altogether new materials, so-called van der Waals heterostructures (Myers, 2020). Additionally, experts predict that in the coming years, the bulk production costs of nanomaterials, particularly graphene-based materials, will fall below the price of silicon, which is commonly used in semiconductor applications such as computing, chip manufacturing, sensors, solar cells, and etc., allowing graphene to enter all markets currently dominated by silicon. This is also because of silicon cannot be integrated into future flexible smartphones, as it is brittle and breaks when bent. Besides, silica gels are the low water exchange and that is because a very high relative pressure is required for adsorption and the limited quantity storage capacity. In this sense, nanomaterials offer a competitive solution.

Table 3 Comparison price of four different types of nanomaterials: graphene, CNTs, zeolites and MOFs.

Type of Nanomaterials	Price (€/g)
<b>Pristine Graphite</b>	
Graphite	42
<b>Modified Graphene</b>	
GNPs	684
GO	136
rGO	952
Sulfonated rGO	588
<b>Pristine CNTs</b>	
Single-walled	1480
Double-walled	1468



Multi-walled	145
<b>Modified CNTs</b>	
single-walled, octadecylamine functionalized	5290
single-walled, polyaminobenzene sulfonic acid functionalized	6330
multi-walled, carboxylic acid functionalized	138
<b>Zeolite</b>	
Zeolite	934
Zeolite 13X	3200
Zeolite Y	1420
<b>MOFs</b>	
HKUST-1	15
MIL-53(Al)	37

## 7. Nanomaterials properties-performance relationships

Nanomaterials are considered more efficient than bulk materials in adsorbing CO<sub>2</sub> due to their exceptional properties. However, the CO<sub>2</sub> capture processes, and the role of each nanomaterial characteristics remain to be unclear. Thus, in this present section, the proposed analysis is based on the CO<sub>2</sub> adsorption capacity and the main relative properties of the used nano adsorbents. Due to the different adsorption conditions used and the various nature of the commonly studied adsorbents, it is always difficult to compare their efficiency. In Table 4, we have gathered the surface area and pore volume of the four families of nanomaterials discussed in this work. These two properties are indeed those searched by scholars for the purpose of improving their adsorption capacity. For each work, the reported CO<sub>2</sub> adsorption capacities in mmol/g for all designed adsorbent along with the used conditions for the measurements are provided in Table

4. The commonly used conditions to conduct CO<sub>2</sub> adsorption study are a pressure of 1 atm, and most of the time, the adsorption experiments are performed at 273 and/or 298 K. These operating temperatures are preferred for most of the studies. Temperature is one of the key variables for adsorption kinetics in CO<sub>2</sub> capture; usually, the CO<sub>2</sub> adsorption mechanism is exothermic in nature; this is the reason why low-temperature adsorption processes are preferred. As temperature is increased, surface energy of the system and molecular diffusion are boosted, and adsorbed CO<sub>2</sub> becomes more unstable on the surface of the adsorbents, resulting in desorbing of the gas molecules. The conditions out of these commonly used conditions (273 and 298 K and 1 atm), less investigated, are not included in Figures 10 and 11. These latter allow us to propose a rational analysis based on relevant aspects in the field we have chosen to enlighten.

**Table 4** Comparison between different nanomaterials type in terms of the properties and CO<sub>2</sub> adsorption capacity

Type of nanostructure	Synthesis approach	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Adsorption capacity (mmol g <sup>-1</sup> )	Pressure (bar)	Temperature (K)	Publication year	Reference
<b>Graphene- -based adsorbents</b>								
3D porous graphene/PEI	Hydrothermal reduction	476	~1.3	2.20	1	273	2013	(Sui et al., 2013)
CuBTC/GO composites	Mixed solvent method	1772	0.718	8.02	1	298	2020	(Shang, 2020)
Monolith aerogels of chitosan/GO	Wet impregnation	412	1.23	4.15	1	298	2013	(Alhwaige et al., 2013)
ZnO/N-doped reduced graphene	Thermal and coprecipitation method	1122	0.60	3.55	1	298	2016	(Li et al., 2016)
Porous graphene frameworks	Chemical reduction and	484	0.68	2.89	1	273	2016	(Chowdhury, 2016)

	thermal treatment							
NGA	Hydrothermal reduction	830	1.6	2.57	1	273	2015	(Sui et al., 2015)
3D rGO	CO <sub>2</sub> activation	1316	1.07	2.45	1	298	2016	(Chowdhury and Balasubramanian, 2016a)
Carboxylated GO Cryogels	Carboxylic acid/amine coupling	21.37	-	2.00	1	298	2020	(Pruna et al., 2020)
rGO	Hydrothermal process	530	0.66	2.38	1	273	2015	(Sui and Han, 2015)
TiO <sub>2</sub> /GO nanocomposites	Immobilization of TiO <sub>2</sub> particles	99.536	0.382	1.88	1	298	2015	(Chowdhury et al., 2015)
Holey graphene frameworks	Wet chemical impregnation method	524	1.27	1.87	1	273	2016	(Chowdhury and Balasubramanian, 2016b)
Functionalize GO	Acid treatment	45.3	-	1.83	1	298	2020	(Varghese et al., 2020)

3D porous graphene/EDA	Hydrothermal reduction	167.66	0.023	1.18	1	298	2019	(Pruna et al., 2019)
PEI-GO	Wet impregnation	16	0.051	0.75	1	298	2016	(Shin et al., 2016)
Clay/rGO hybrid	Hydrothermal reduction	50.7709	0.078786	0.49	1.1	298	2019	(Stanly et al., 2019)
Chitosan/GO aerogel	Wet impregnation and amine coupling	33	0.0005 – 0.002	1.18	1	298	2019	(Hsan et al., 2019)
NGA	Hydrothermal reduction	830	1.6	2.57	1	273	2015	(Sui et al., 2015)
Nanoporous spongy graphene	Wet chemical reduction	348.2	0.04	0.86	1	37.84	2015	(Kostoglou et al., 2015)
				0.48		21.12		
<b>CNT -based adsorbents</b>								
3D CNTs hierarchical porous composite	Chemical and thermal activation	2164	< 2	5.70	1	273	2020	(Hao et al., 2020)
				3.70		298		

Hierarchical N-doped CNTs	Wet chemical impregnation method; Carbonization ; SiO <sub>2</sub> etching; Chemical activation	1195	0.45	4.50	1	273	2019	(Wang et al., 2019)
N-doped hollow porous carbon/CNTs	Pyrolysis	561	-	4.43	1	273	2019	(X. He et al., 2019)
Amine-modified CNTs	Wet impregnation	8.94	0.0565	2.97	1	298	2012	(Ye et al., 2012)
MWCNTs/TEPA	Chemical activation and wet impregnation	2.2	0.03	2.50	-	298	2017	(Irani, 2017)
Amine-modified CNTs	Wet impregnation	9.02	0.004	2.45	1	298	2011	(Su et al., 2011)

MWCNTs/PAA	Heating in an oil bath at temperature 190°C- 250°C	60.4	0.4	1.59	1.1	298	2014	(Ngoy, 2014)
MWCNTs-ZnO-SiO <sub>2</sub>	Hydrothermal and sol-gel method	27.3	0.168	1.32	1	273	2019	(Jena, 2019)
CNTs/APTS	Reflux method	198	0.63	1.32	1	298	2008	(Lu et al., 2008)
Amine-modified CNTs	Wet impregnation	67.1	0.186	0.64	1	298	2018	(Zhou et al., 2018)
Functionalize MWCNTs	Acid treatment	126.48	0.18	0.33	1	298	2020	(Mukhtar et al., 2020)
<b>3D zeolite-based adsorbents</b>								
Na-chabazite	Chemical impregnation and hydrothermal process	580	0.24	5.70	1	298	2017	(Min et al., 2017)

3D Printed SAPO-34 / graphite zeolite	3D Fiber Deposition (3DFD)	534	0.19 5	4.90	1	273	2018	(Couck, 2018)
(3D)-Printed 5A zeolite monoliths	3D printing technique	571	0.26	~4.4	1	298	2016	(Thakkar et al., 2016)
(3D)-Printed 13X Zeolite Monoliths		543	0.25	~4.30				
Chitosan/zeolite-Y	Wet impregnation	795	< 1	1.64	1	298	2020	(Kumar et al., 2020)
Chitosan/ZSM-5		444		2.39				
LTA zeolites	Chemical impregnation	140	0.35	3.18	1	273	2014	(Chen and Ahn, 2014)
<b>3D MOF -based adsorbents</b>								
GO/HKUST-1 composite	Solvothermal synthesis	1554	0.711	9.2	1	273	2016	(Xu et al., 2016)
PANI/MIL-101(Cr) composite	Wet impregnation	2564	1.33	5.9	1	273	2018	(Yoo et al., 2018)
MOF/GO nanocomposites	Wet impregnation	635	0.304	6.8	1	273	2018	(Asgharnejad et al., 2018)



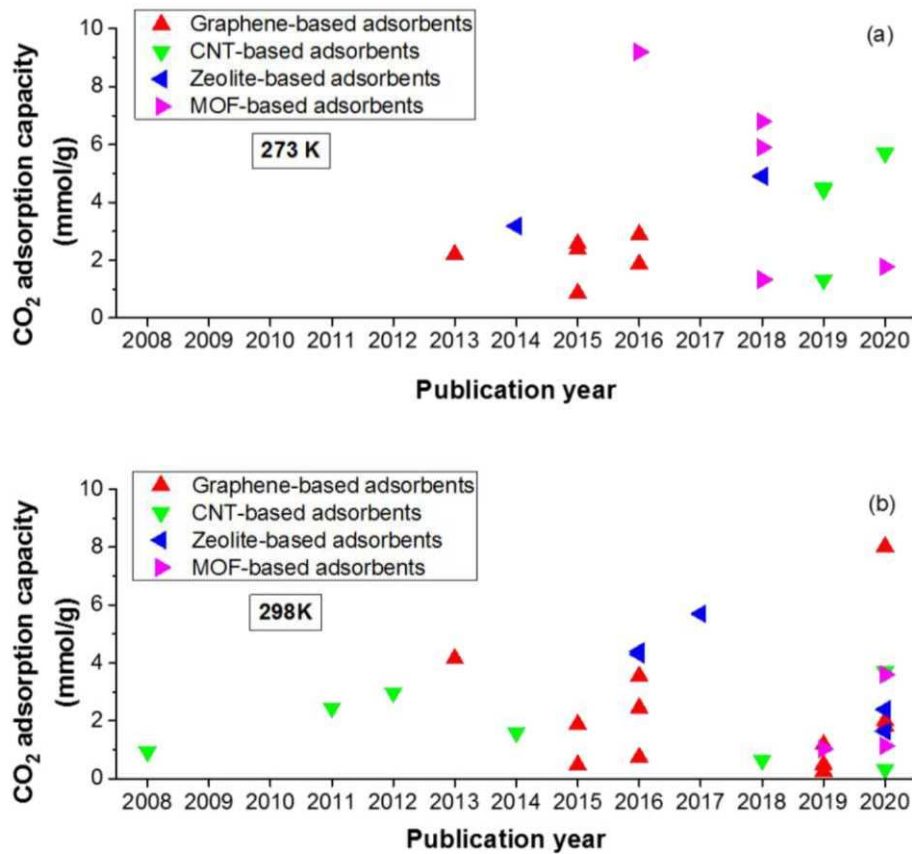
MOF-177	Solution-based techniques	1721.09	0.87	1.03	1	298	2019	(Ullah et al., 2019)
MOF -101/ polymethacrylamide	Hydrothermal process	2410	1.22	3.60	1	298	2020	(Yoo et al., 2020)
3D-printed MOF-74(Ni) monoliths	3D printing technique	737	0.32	1.35	1	273	2018	(Thakkar et al., 2016)
3D-printed MOF-UTSA-16(Co) monoliths		568	0.23	1.31				
3D Porous d-p heterometallic MOF	Self-assembly by solvothermal reaction	221	-	1.77	1	273	2020	(Liu et al., 2020)
				1.14		298		

PAA: Polyaspartamide; ZnO: Zinc oxide; SiO<sub>2</sub> : Silicon dioxide; TiO<sub>2</sub> : Titanium dioxide; SAPO : Silicoaluminophosphate; ZSM-5 : Zeolite Socony Mobil-5; HKUST-1 : Metal organic framework -199; MOF-UTSA- 16(Co) : A novel MOF with chemical formula K<sub>2</sub>Co<sub>3</sub>(cit)<sub>2</sub>

### ***7.1 Achieved progress of CO<sub>2</sub> adsorption capacity in research***

CO<sub>2</sub> capture using solid sorbents has been recognized as a useful strategy that has drawn considerable discussion from both academia and industry over the last decade. Moreover, in the last 5 years, there has been a significant rise in research activities globally. The sorbent systems have been enlarged regarding the nature of the material used as substrate and its functionalization and combination with other compound such as metal oxide nanoparticles (Goharibajestani et al., 2019; Philemon and Korir, 2020; Rodríguez-García et al., 2019); polymers (Flaig et al., 2017; G. He et al., 2019; Minelli et al., 2018; Politakos et al., 2020) and catalytic metal nanoparticles (such as Rh, Pd, Pt or Au) (Cui et al., 2018).

In Figure 10, the CO<sub>2</sub> adsorption capacity found in literature at 273 (Figure 10a) and at 298 K (Figure 10b) for the examined types of nanomaterials was reported as a function of the publication year.



**Figure 10** CO<sub>2</sub> adsorption capacity of graphene-, CNT-, zeolite- and MOF-based adsorbents used in the reported works as a function of the publication year of the corresponding paper for adsorption measurements performed at (a) 273 K and (b) 298 K.

For both temperatures, the CO<sub>2</sub> adsorption capacity is distributed on a scale with a maximum adsorption capacity around 10 mmol of CO<sub>2</sub> adsorbed for 1 g of adsorbent. Even if some prepared adsorbents remain in the lowest part of this scale, a significant improvement in CO<sub>2</sub> capture is evidenced in the figures for both examined temperatures. This present overview shows indeed that positive progress was achieved in this research domain in the past years. Such observation can also explain the growing interest for the topic, and it consolidates and might emphasize this tendency in the research community.

Back in 2008, work from Lu *et al.* developed an adsorbent using (3-aminopropyl)triethoxysilane (APTS)-modified CNTs with a CO<sub>2</sub> adsorption capacity of 1.32 mmol/g at 298 K (cf. Table 4 and Figure 10b). They have used a two-step approach: first a reflux monoethanolamine (MEA)/NH<sub>3</sub>/APTS/toluene is performed for 24 h, and, second, a thermal treatment under N<sub>2</sub> gas for 1 h was conducted (Lu et al., 2008). The developed approach is one of the proven techniques to overcome the agglomeration issue related to the sidewall hydrophobicity of CNTs and the strong  $\pi$ - $\pi$  interactions between individual tubes. However, low yield of CNTs was observed due to the extreme conditions of oxidation leading to degradation and loss of MWCNTs as well as apparent structural damage (Jun et al., 2018). In 2020, the synthesis method of CNT-based adsorbents has been improved a lot. For instance, Hao *et al.* have developed a 3D hierarchical porous structure of composite with CNTs containing numerous heteroatom groups in 2020 (Hao et al., 2020). The specific surface area of this developed CNT-based adsorbent was then increased by a factor of 11, and it exhibited a maximum adsorption capacity of 5.7 and 3.7 mmol g<sup>-1</sup> at temperature 273 and 298 K, respectively (Table 4 and Figures 10a and 10b). These CO<sub>2</sub> adsorption capacities are among the best values reported to date. Although the precursor used is still CNTs, the method of synthesis has progressed a lot over the research years, especially in terms of control of the structure and configuration of the adsorbent. For example, development of 3D structure can boost the CO<sub>2</sub> adsorption not only because of enhancement of surface area, but also 3D structure offers a new CO<sub>2</sub> capture mechanism, since it could speed up the diffusion of gas and maximize the use of micropores. MOFs and GBMs exhibit the highest CO<sub>2</sub> capture at 273 and 289 K, respectively (Figures 10a and 10b). Xu *et al.* developed GO/HKUST-1 composites, which has recorded the highest reported CO<sub>2</sub> adsorption capacity up to 9.2 mmol g<sup>-1</sup> (Table 4) (Xu et al., 2016). In this work, HKUST-1 was synthesized by solvothermal method; after, it was modified with GO by using

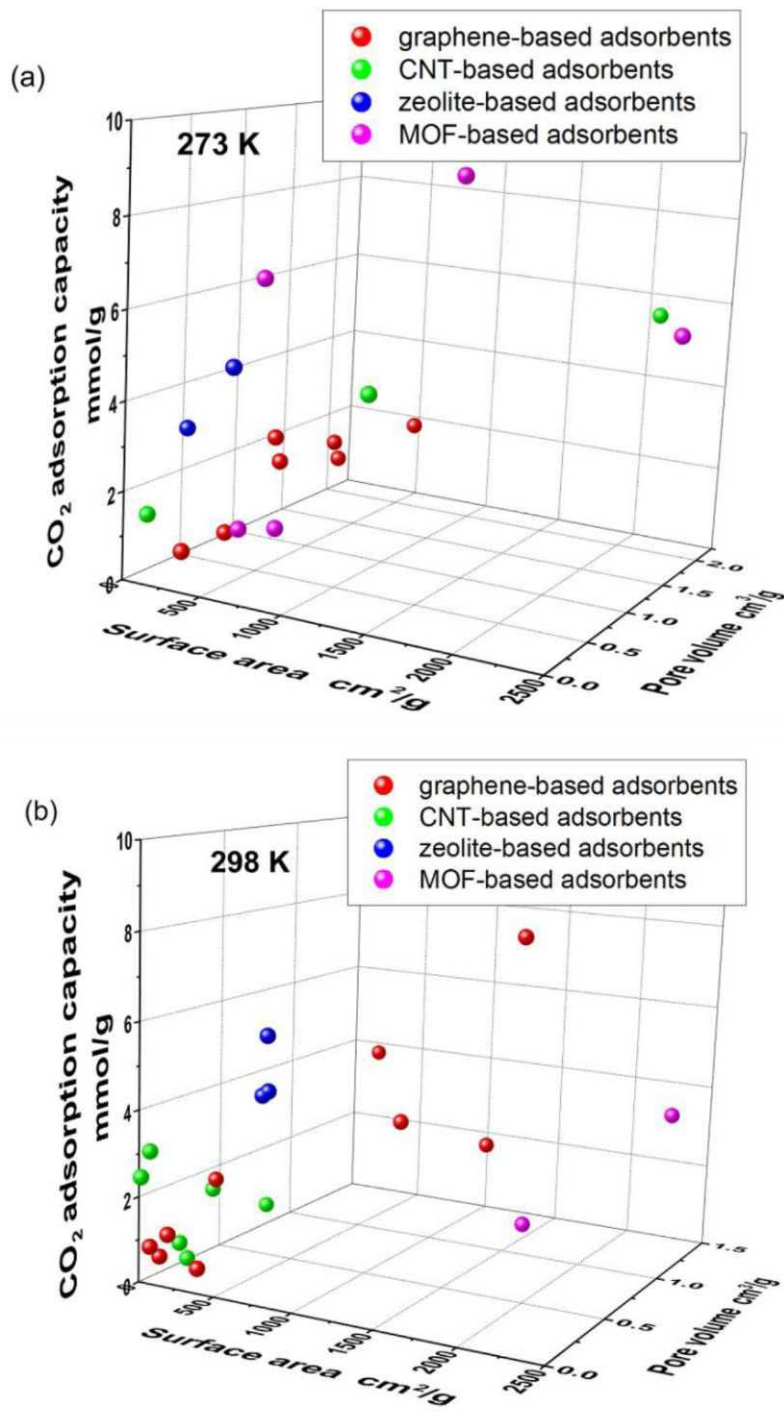
(Zn, Cu) hydroxyl double salt intermediate via ultrafast room temperature synthesis method to prepare the composite adsorbents of GO/HKUST-1. From the BET results, that composite materials reveal a high-specific surface area ( $1554 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume ( $0.711 \text{ cm}^3 \text{ g}^{-1}$ ), which could maximize the performance of  $\text{CO}_2$ . The performance found for this study was significantly higher compared with other works (Figure 11a). Moreover, the synthesis process of these MOF-based composites appears to be relevant to envisage an industrial scale. Within these 5 years, GBMs became one of the most studied nanomaterials that showed the best  $\text{CO}_2$  capture (Figure 10b). For example, Shang *et al.* have developed a simple strategy to synthesize high surface copper benzene-1,3,5-tricarboxylate (CuBTC)/GO composites to enhance  $\text{CO}_2$  adsorption (Shang, 2020). The experiment was conducted using solvothermal techniques wherein different types of solvents were mixed and kept in a Teflon autoclave at temperature 353–413 K, and from the BET study, the authors showed that the CuBTC/GO composite surface area increases compared to the pristine. And the  $\text{CO}_2$  adsorption was significantly improved from  $8.02 \text{ mmol g}^{-1}$  to  $8.9 \text{ mmol g}^{-1}$  as the high surface area creates more binding sites and increases the affinity of the surface. In the next section, a focus is made on the two key parameters when optimizing adsorbents for  $\text{CO}_2$  capture.

## ***7.2 Pore volume and surface area***

In the design of ideal nanomaterial adsorbents, particularly for the absorption of  $\text{CO}_2$ , it is beneficial to develop or to understand the existing correlations between the material structure and the adsorption properties. Beyond that, structuring the porous hierarchy of materials will lead to a variety of features and functionalities that may be as well suitable for a wide range of applications. BET is a method commonly used for determining the textural properties of the porous materials. The BET principle relates to multilayer adsorption process where penetrating

gases do not react chemically with the substrate surface (Thommes et al., 2015). Typically, nanomaterials with a modified surface and porosities have shown enhanced adsorption capacities. In the case of the nanostructured adsorbents examined here, this conducted analysis aims at investigating in which extent the surface area and/or the pore volume play(s) the major role in maximizing CO<sub>2</sub> capture. This is the reason why, in Figure 11, the reported CO<sub>2</sub> adsorption capacity (same works of that in Figure 10) is represented as a function of pore volume and surface area for each prepared adsorbent (cf. also Table 4).

From Figure 11, it can be noticed that the best performances for CO<sub>2</sub> capture do not simply correspond to the nanomaterials with the highest surface areas and/or for a specific range of pore volume.



**Figure 11** CO<sub>2</sub> adsorption capacity recorded at temperature (a) 273 K and (b) 298 K as a function of surface area and pore volume of different sorbents.

For example, both works by Xu *et al.* (Xu *et al.*, 2016) and Yoo *et al.* (Yoo *et al.*, 2018) have studied MOF-based materials. They achieved good CO<sub>2</sub> capture at 273 K (Table 4 and Figure

11a) with 9.2 and 5.9 mmol g<sup>-1</sup>, respectively. The first one, GO/HKUST-1 composite, revealed a surface area of 1154 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.71 cm<sup>3</sup> g<sup>-1</sup>. Meanwhile the second one, polyaniline (PANI)/chromium terephthalate metal (MIL-101(Cr)) composite, has a surface area of 2564 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 1.33 cm<sup>3</sup> g<sup>-1</sup>. Even if the surface is higher by a factor of more than 2.2 for PANI/MIL-101(Cr), its CO<sub>2</sub> adsorption capacity is almost twofold less than GO/HKUST-1 composite. In fact, the two groups have used two distinct methods to prepare their MOF-based porous nanomaterials. In Yoo *et al.*'s work, they introduced PANI on highly porous MOFs to improve the CO<sub>2</sub> capture efficiency, and they increased the amount of PANI from 2 to 10 mM. The specific surface area and the total pore volume were reported to decrease slightly after the chemical modification. Apart from that, the pore volume formed was sufficiently large, about 1.33 cm<sup>3</sup> g<sup>-1</sup>, to exhibit high CO<sub>2</sub> capture (from 4.6 to 5.9 mmol g<sup>-1</sup> at 1.0 bar and 273 K) even after PANI loading, making the adsorbents suitable for adsorption of CO<sub>2</sub> and N<sub>2</sub> (Yoo *et al.*, 2018). In addition, the works by Chowdhury and Balasubramanian (Chowdhury and Balasubramanian, 2016a) and Shang *et al.* (Shang, 2020) both investigated the performance of CO<sub>2</sub> capture using 3D GBMs. In their study, Chowdhury and Balasubramanian have used physical modification to form 3D rGO-based structure, while Shang *et al.* proposed a chemical modification for the development of CuBTC/GO composites. They obtained good surface area and pore volume as for 3D rGO-based material; the surface area was 1316 m<sup>2</sup> g<sup>-1</sup> and pore volume of 1.07 cm<sup>3</sup> g<sup>-1</sup>. For CuBTC/GO composites, the surface area and pore volumes were 1772 m<sup>2</sup> g<sup>-1</sup> and 0.718 cm<sup>3</sup> g<sup>-1</sup>, respectively. The surface area of both GBMs is in a high range, and the measured pore volumes are not strongly different. In terms of performance, both 3D rGO-based adsorbent and CuBTC/GO composites achieved interesting CO<sub>2</sub> capture at temperature 289 K (Table 4 and Figure 11b) of 2.45 and 8.02 mmol g<sup>-1</sup>, respectively. Although the surface area and the pore volume value of the two adsorbents tend



to be in the same range, the CO<sub>2</sub> adsorption capacity value showed a vast difference where for CuBTC/GO composites, the value increases by factor of almost 4. This improvement was attributed to partial positive charges on metal sites in Cu-BTC, which could lead to good CuBTC- CO<sub>2</sub> gas interactions and provide potential for the enhancement of CO<sub>2</sub> capture.

Asgharnejada *et al.* developed nanocomposites using the wet impregnation method Ni-based MOF and found that the introduction of GOs into Ni-A could reduce the surface area (635 m<sup>2</sup> g<sup>-1</sup>) and the pore volume (0.304 cm<sup>3</sup> g<sup>-1</sup>) of the adsorbent (Asgharnejad *et al.*, 2018). Although the surface area of MOF/GO nanocomposite appears to be almost four times lower compared to PANI/MIL-101(Cr) (Yoo *et al.*, 2018) (Table 4 and Figure 11a), yet it still showed a remarkable CO<sub>2</sub> capture efficiency. There are some reasons that can cause this situation to happen, such as the presence of differing polar functional groups (epoxy, hydroxyl, carboxylic) on the GO or the addition of metal to the MOF, which increases the dispersive forces and increases the adsorption of gas. Additionally, graphene and zeolite have been revealed to be among the most predominant materials with higher adsorption capacity and surface area at operating temperatures 298 K. Ullah *et al.* (Ullah *et al.*, 2019) and Li *et al.* (Li *et al.*, 2016), for example, studied MOF-based (MOF-177) and GBMs (ZnO-based N-doped rGO), respectively (Table 4 and Figure 11b). According to the BET study, MOF-177 tended to have a surface area of 1721.09 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 1.03 cm<sup>3</sup> g<sup>-1</sup>. For ZnO-based N-doped rGO, the surface area and pore volume obtained were 1122 m<sup>2</sup> g<sup>-1</sup> and 0.6 cm<sup>3</sup> g<sup>-1</sup>, respectively. Besides, the reported values seem to be slightly identical to those determined for MOF-177, yet in terms of performance, CO<sub>2</sub> adsorption capacity of ZnO-based N-doped rGO (3.55 mmol/g) is almost three times higher than that of MOF-177 (1.03 mmol/g). The above implies that this is another example illustrating the adsorption capacity is not directly influenced by the surface area and the porosity. Among those two factors, pore size might indeed play a role in improving CO<sub>2</sub>

adsorption. Another strategy for improving CO<sub>2</sub> adsorption capacity is to design microporous nanomaterials with abundant and narrow micropores with pore sizes less than 1 nm. According to a purely molecular sieving mechanism driven primarily by gas diffusion, further reduction in pore size close to 0.33 nm may lead to further enhancement of CO<sub>2</sub> selectivity. Typically, non-carbon-based materials, such as MOFs and zeolites contain an internal ordered channel, pores, or a combination of the two, which may contribute to an increase in pore size and resulting in a decrease in CO<sub>2</sub> capture at low pressure. But, when considering the heterogeneous slit-shaped holes of graphene and CNTs which are generally not possess homogenous pore network, the CO<sub>2</sub> absorption is more difficult to predict (Belmabkhout et al., 2016). In all of these cases, it is reasonable to conclude that nanomaterials with high specific surface area, large pore volume, and relatively small pore size would be ideal textural properties for CO<sub>2</sub> absorbent.

## **7. Concluding remarks**

In this review, some aspects regarding the mechanisms involved in CO<sub>2</sub> capture and the preparation of CO<sub>2</sub> adsorbents have been reviewed. Four nanostructured adsorbents (graphene, CNT, MOF, zeolite-based nanosorbents) which are among the most studied have been chosen for adsorption capacity analysis. Their comparison is carried out by means of a robust analysis. The present analysis approach, which has never been reported yet, allows to relate the performances of the developed nanomaterials to their surface area and their pore volume which are among the two most relevant properties examined for development of adsorbents for CO<sub>2</sub> capture. This present in-depth analysis of the adsorption capacities in relation to the surface area and/or the pore volume shows that there is no obvious tendency regarding an

interdependence between them. The surface chemistry seems also to play a significant role in the CO<sub>2</sub> adsorption phenomenon. In fact, various modifications have been commonly reported, including physical and chemical modifications, which could alter the surface properties of adsorbents. Supplementary investigations focused on understanding the particular mechanisms involved in the adsorption of CO<sub>2</sub> on the modified surface have been poorly conducted so far, and both theoretically and experimentally, approaches would be of high interest for that purpose. Further studies in this domain are highly desired since the properties of materials at a molecular level offer the potential for their further improvement. Interactions between CO<sub>2</sub> and the adsorbent surface and especially the functionalities it bears are rarely studied as a real parameter impacting CO<sub>2</sub> adsorption. Computational simulations would furnish a complementary approach to experimental studies. For the experimental approach, modifying the nature and/or the density of the surface functional groups in a controlled way, even if it remains challenging, would be of great interest to better understand the involved molecular mechanisms. Besides, we can claim from this work that researchers who successfully control the synthesis methods have made a lot of progress in modifying the specific morphology and surface chemistry of the engineered adsorbents. Especially, adsorbents such as 3D assemblies of nanomaterials or composite structures have shown excellent performance of CO<sub>2</sub> capture. The cost of preparation of these nanomaterials has been continuously decreasing, which, in turn, provides an opportunity to them in practical applications in the future.

### **Declaration of competing interest**

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

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