# A Review on Recent $CO_2$ Capturing Technology, a Nano-particle Adsorption Approach

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## Abstract

Innovative gas capture technologies with the objective to mitigate $CO_2$ emissions are discussed in this review. Emphasis is given on the use of Nanoparticles (NP) as Sorbents of $CO_2$, which is the most important global warming gas. The existing NP sorption processes must overcome certain challenges before their implementation to the industrial scale. These are: i) the utilization of the concentrated gas stream generated by the capture and gas purification technologies, ii) the reduction of the effects of impurities on the operating system, iii) the scale up of the relevant materials, and iv) the retrofitting of technologies in existing facilities.

Thus, an innovative design of adsorbents could possibly address those issues. Biogas purification and $CO_2$ storage would become a new motivation for the development of new sorbent materials, such as nanomaterials. This review discusses the current state of the art on the use of novel nanomaterials as adsorbents for $CO_2$. The review shows that materials based on porous supports that are modified with amine or metals are currently providing the most promising results. The $Fe_3O_4$-graphene and the MOF-117 based NPs show the greatest $CO_2$ sorption capacities, due to their high thermal stability and high porosity. Conclusively, one of the main challenges would be to decrease the cost of capture and to scale-up the technologies to minimize large-scale power plant $CO_2$ emissions.

# INTRODUCTION

## Global Warming and Low Carbon Economy

Generation of greenhouse gases resulting from human activities is becoming an important concern all over the world. Greenhouse gases trap some of the heat coming from the sun and make an important contribution to the greenhouse effect. Greenhouse effect is a natural process in which methane, carbon dioxide, water vapor, and other greenhouse gases absorb the beam reflecting from the surface and it causes an increase in Earth's temperature.[1]

The certain greenhouse gases contributing to global warming in the atmosphere are water vapor ($H_2O$), methane ($CH_4$) nitrous oxide ($N_2O$), fluorinated gases (F Gases), and carbon dioxide ($CO_2$)[2]. Water vapor is the most abundant greenhouse gas in the atmosphere. Increases in the amount of water vapor in the atmosphere causes the formation of clouds and it acts as a feedback mechanism to the climate change. $CH_4$ is the second prevalent greenhouse gases in the atmosphere and it is a hydrocarbon gas produced both petroleum systems and human activities [3]. $N_2O$ is one of the most powerful greenhouse gases generated by usage of synthetic fertilizer, burning of fuels, and as a byproduct of nitric acid [3]. Fluorinated gases have no natural sources. Only human-related activities causes the formation of fluorinated gases that includes hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride ($SF_6$), and nitrogen trifluoride ($NF_3$) [4]. $CO_2$ is the primary greenhouse gas resulting from human activities and natural processes.

At the global scale, the percentages of the emission of greenhouse gases into the atmosphere are given in Figure 1.1. The percentage of $CO_2$ emissions into the atmosphere is assumed that $CO_2$ has the greatest impact on greenhouse effect compared to other greenhouse gases.
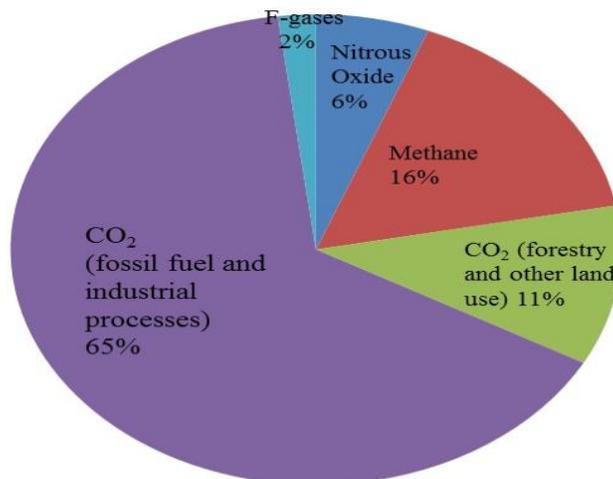


*Figure 1 : Global greenhouse gas emissions. Adapted from reference 5*

The carbon suppliers in the atmosphere, soils, oceans and rocks are related to a complex natural biochemical process called carbon cycle [6]. $CO_2$ is naturally present in the atmosphere as a part of carbon cycle. Natural sources, human activities, and burning of fossil fuels altering the carbon cycle by adding or consuming $CO_2$ [7]. Respiration and volcano eruption can be given as examples of natural sources of $CO_2$. Human activities such as deforestation are attributed to $CO_2$ emissions as well as natural sources. However; the major contribution to the amount of emitted $CO_2$ to the atmosphere comes from the combustion of fossil fuels like coal, coke, and natural gas [8]. Beside the burning of fossil fuels, the fermentation of carbohydrate materials and production of cement and lime also make the quantity of $CO_2$ in the atmosphere increase.[9]

## $Co_2$ capture technologies

As seen in the introduction one of the most important gases which cause some problems like global warming, greenhouse effect is $CO_2$.

In this chapter we concentrate on preventing it from entering the atmosphere and face such problems.
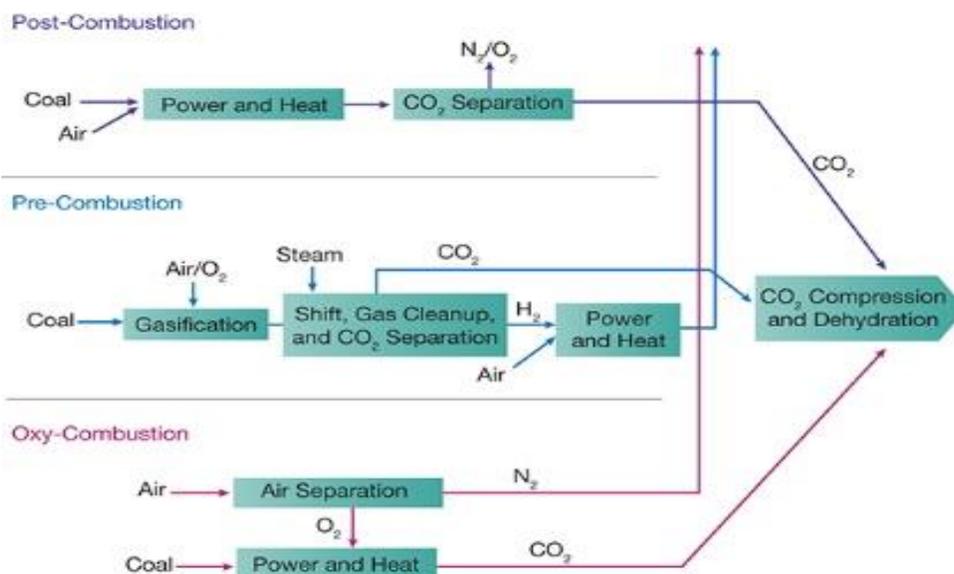
The biggest $CO_2$ generators are the power stations and now a day's oil and gas industry which burn fossil fuels for energy.

Now the most energy production is by using fossil fuels that produce $CO_2$ as a byproduct of energy.

$CO_2$

*Table 1*

| CO$_2$ capture technologies | | |
| --- | --- | --- |
| Pre-combustion | Post-combustion | Oxy-combustion |
| Integrated gasification combine cycle | Amine-based system | _ |
| Physical solvent process | Emerging technologies: | _ |
| Membrane | 1. Carbonate-based system<br>2. Aqueous ammonia<br>3. Membranes | _ |
| Pre-combustion sorbent | 4. $CO_2$ capture sorbent<br>5. Metal organic frameworks | |
| Chemical looping combustion and gasification | 6. Enzyme-based system<br>7. Ionic liquid | _ |
| Improved auxiliary process | | _ |

## Nanoparticles

Particles play in general a dominant role in many industrial processes and natural phenomena. 60% of the products made by major chemical companies such as Dupont, Dowor ICI are either made as particles or involve significant particle technology in their manufacture (PTL, 2004). Furthermore particle science and engineering is central to the environment (air pollution, climate change, greenhouse effect), energy utilization (fossil fuel combustion, turbine combustion, fly ash) and medicine (virus and bacteria transport,medicine delivery, allergies) (PTL, 2004).

Nano-sized materials are naturally present from forest fires and volcanoes, but are also generated unintentionally from anthropogenic sources as a by-product of combustion and deliberately as manufactured nanomaterials. Nanoparticles have been used for centuries. Thecoloured glass that we see in many old cathedrals from the middle ages was made of gold nano sized clusters that created different colours depending on the size of the nanoparticles. The most prominent example of engineered nanoparticulate material is carbon black which has been around us for decades in applications like printing inks, toners, coatings, plastics, paper, tires and building products. However, carbon black would for many be excluded from the nanoparticle category, as nanotechnology is about deliberately and knowingly exploiting the nanoscale nature of materials (Holister, Weener, Vas, & Harper, 2003).Two of the major factors why nanoparticles have different properties (optical, electrical,magnetic, chemical and mechanical) than bulk material are because in this size-range quantum effects start to predominate and the surface area to volume ratio is increased(Holister et al, 2003). The increase in the surface-area-to-volume ratio is a gradual

progression as the particles get smaller which leads to that atoms on the outside of the particle will increasingly begin to dominate the ones inside the particle. This changes the individual properties of the particle and how it interacts with other materials in the surroundings. The increase of relative surface area makes them very interesting for the industry, as high surface area is a critical factor in for instance efficient catalysis and in structures like electrodes. This can improve the performance of products like batteries, but also reduce resource usage in catalytic processes and hence decrease the amount of waste.The large surface area also increases the mixing with other materials in the surrounding and is especially beneficial in intermixed materials like composites.

Once particles become small enough they start to exhibit quantum mechanical behaviour.Classical mechanics can explain the relation between theory and observation for large objects. However, only quantum mechanics can explain the behaviour of objects as small as electrons. Quantum mechanics describes the matter and radiation taking quantization3 into account.Nanoparticle are currently made out of a very wide variety of materials, the most common ceramics, which can be split into metal oxide ceramics, such as titanium, zinc, aluminium and iron oxides, and silicate nanoparticles (silicates, or silicon oxides are also ceramics), generally in the form of nanoscale flakes of clay (Holister et al, 2003). Silicate nanoparticles, as any nanoparticles, can be mixed into polymers. Pure metal nanoparticles can mix together into a solid composite at lower temperatures than for larger particles, which can improve coatings and make the coatings easier to create, harder and more durable. The formation of coatings and bulk materials at lower temperature reduces the manufacturing costs compared to their non-nano counterparts. Metal oxide ceramic, metal and silicate nanoparticles are the majority of nanoparticles that have existing applications.

## Classification of nanoscale materials based on their dimensions

The mainstay of nanotechnology is the use of materials. Each material in space has three dimensions: length, width and height. If in a material at least one of these three dimensions are in the nanometer range, it is called a material, a nanostructure. A common division in nanomaterials (nanostructures) is their division based on the number of dimensions in the nanometer range. If all three dimensions of a material are in the nanometer range, then they refer to the dimension zero nanostructure. Similarly, if two dimensions of the material are in the range of the nanoscale, then it is a one-dimensional nanostructures, and if one dimension is within a nanometer range, then it is called a two-dimensional nanostructure. In this naming, because the nanometer dimension is smaller than the other dimensions, the dimension next to the nanoscale is considered dimensionless (no length). To illustrate this, a number of nanostructures are shown in Figure schematic and image of the electron microscope.
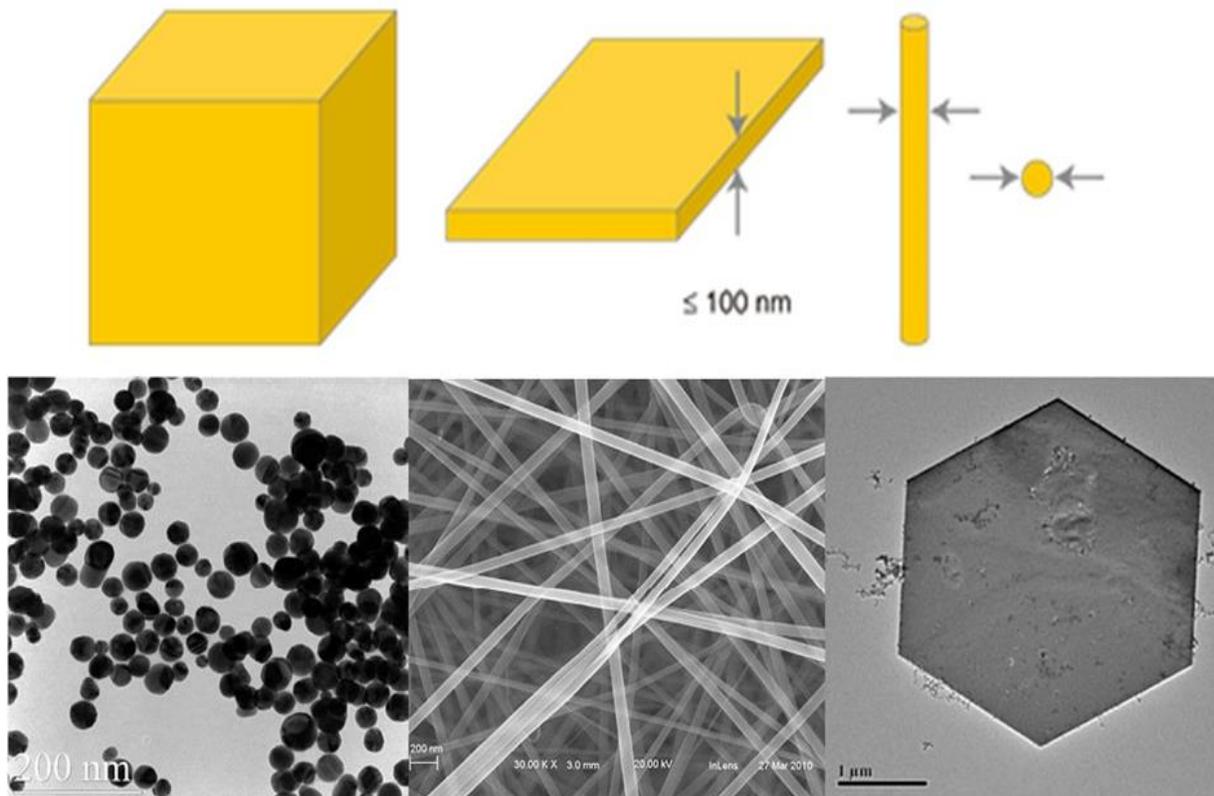
Above is a schematic representation of the types of nanostructures, at the bottom, respectively, from left to right, electron microscopy images of the dimensional zero, one dimensional and two-dimensional nanostructures

## Conventional adsorbents

Adsorption of a gas onto a solid surface (adsorbent) can be defined as the gain of one or more constituents of the gas (adsorbate) in the gas-solid interface (Solar et al, 2010). $CO_2$ capture using solid adsorbents is considered one of the most promising technologies for CCS (Figueroa et al, 2008). Adsorption can reduce energy and cost of the capture or separation of $CO_2$ in post-combustion capture technologies (Solar et al, 2010). However, the success of this approach depends on the development of easily recoverable and durable adsorbents with high $CO_2$ selectivity and adsorption capacities (Songul Zadeh et al, 2012). The most common conventional $CO_2$ adsorbents are natural zeolites, activated carbon and alkali-based metal materials. Table 2 shows the main characteristics, key strengths and main drawbacks of the aforementioned three groups.*Table 2*

Summary of characteristics of conventional adsorbents for $CO_2$

| Sorbent | $CO_2$ adsorption capacity (mg $CO_2$/g sorbent) | Experimental conditions | Process scale | Key strengths | Main drawbacks |
|---|---|---|---|---|---|
| NaXzeolite | 263 | 0.1 MPa, 303 K | Lab scale | • Good adsorption kinetics | • Impurities |
| Zeolite 5A | 222.7 | 1.4 MPa for $CO_2$, | Lab scale | • Good performance at mild conditions | • Elevated temperatures for regeneration |
| Zeolite 13X | 324.37 | 3.2 MPa for $CO_2$, | Lab scale | | |
| Activated carbon (MAXSORB) | 1408 | 3.2 MPa for $CO_2$, | Lab scale | • High thermal stability. <br> • Good adsorption kinetics. <br> • Cheap raw material <br> • Large adsorption capacity at elevated pressures. <br> • Easy regeneration | • Low capacity at mild conditions <br> • Low selectivity <br> • Impacted by NOx, SOx. |
| $K_2CO_3/TiO_2$ | 119 | 0.1 MPa, 333 K | Lab scale | •Enhancement of regeneration capacity compared to other oxide based sorbents | • Lower capture capacity than other oxide based sorbents |
| Alkali based $Li_2ZrO_3$ | 220 | Patm, 873 K | Lab scale & simulation | • Unique thermal stability <br> • 20 absorption/regeneration cycles <br> • Small volume change during cycles | • Slow absorption kinetics |

Patm: atmospheric pressure.

## Nanomaterial based $CO_2$ capture systems

Many of the sorbent materials presented here have a natural origin and their uses and properties are known for centuries. It has been during the last 50 years, however, that researchers focused their efforts on the development of novel materials with engineered features in theNano-range (Fox-Rabinovich and Totten, 2006). Due to their small size and high surface area per unit volume or mass, nanomaterials show unique electric, magnetic, optical, structural, mechanical, and chemical characteristics that are already exploited in a large number of industrial and consumer products (Royal Society and Royal Academy ofEngineering, 2004). In this context, the high adsorption capacity of nanomaterials has been demonstrated in several cases. Nanomaterials have a number of physicochemical properties that make them particularly attractive as separation supports for gas purification and gas capture. One is the ability to be functionalized with different compounds (such as surfactants) so that to enhance their affinity towards target molecules (Buzea et al, 2007). In addition,their size makes their surface especially reactive and their nature provides them with an extra stability and robustness intended for many uses and an easiness of use (Buzea et al, 2007). Gas treatment with nanoparticles (NPs) can be considered an attractive field. Hence, the occurrence of this phenomenon in gas-solid interactions is a major focus of nanotechnology research today (Fernández-García et al., 2006).Novel nanomaterials, like advanced Nano porous materials, MOFsand porous organic polymers, have received considerable attention in adsorption storage applications due to their exceptionally high surface areas and their chemically-tunable structures (Gadipelli and Guo,2015). Some of these materials have been tested for $CO_2$ adsorption and have gained increased interest recently. In fact, several research papers have reported improved $CO_2$ sorption and, more interestingly. In particular, MOFs were the ones that exhibited the highest adsorption (Saha et al, 2010). Fig. 2 shows different MOFsused to capture $CO_2$
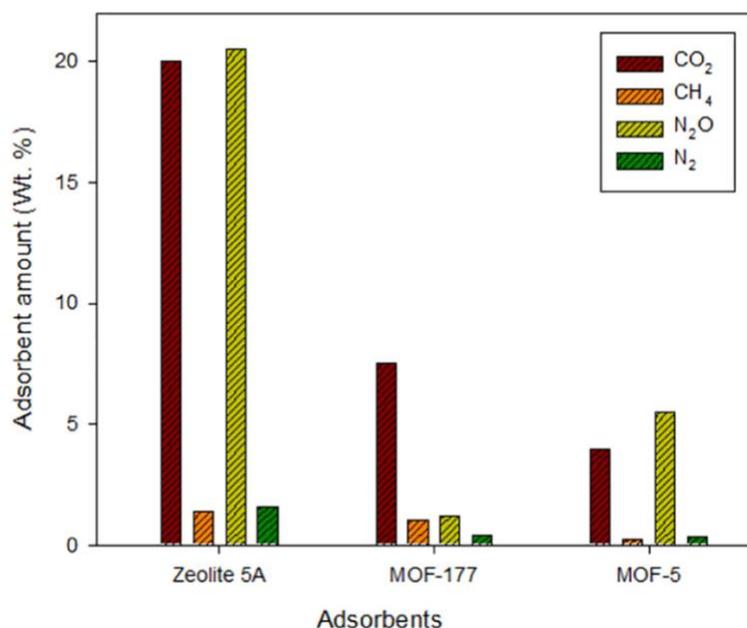
*Figure 2*

Mason et al. studied different MOFs and compared the effects of the volumetric and gravimetric adsorption on $CH_4$ uptake(Mason et al., 2014).A bibliography search (Web of Knowledge) using the keywords"nanomaterials" and "$CO_2$ capture" detected 20 publications from2007 to 2016; 8 of them were related to this study and are discussed later on. A similar search for "CH4 capture" detected 8 publications.The majority of those studies were based on simulations, rather than

on experimental work, demonstrating a promising research opportunity using experimental work.Among all the nanomaterials used for $CO_2$ or $CH_4$ capture, this review focuses on the most significant ones, namely: 1) Nanosized Zeolites; 2) Mesoporous Silica NPs; 3) MOFs and derived MOFs with embedded NPs; 4) Metal and Metal Oxide NPs (MNPs and MONPs),and 5) Carbonaceous Nano adsorbents.

In summary, the $Fe_3O_4$-graphene and the MOF-117 based NPs have the greatest $CO_2$ sorption capacities among all materials tackled in this review. Among all adsorbents for $CH_4$ capture, IRMOF-6, ordered mesoporous carbon, MOF-177 and MOF-5 have shown the highest adsorption capacities compared to the graphene-based NPs. This was due to their high thermal stability and the presence of high porosity in thosematerials.Table 3

Summary of characteristics of nanomaterial based sorbents for $CO_2$

| Sorbent | Maximum $CO_2$ capacity (mg $CO_2$/g sorbent) | Experimental conditions (P,T) | Process scale | Key strengths | Main drawbacks |
|---|---|---|---|---|---|
| DD3R nano zeolite | 123 | 3 MPa, 273–348 K | Lab scale | • High selectivity for $CO_2$.<br>• Used for biogas separation. | • At pressures higher than 2000 kPa, high-pressure data points deviate from the MSL model-fit lines. |
| T-type Zeolite NPs | 176.4 | 0.1 MPa, 288 K | Lab scale | • Potential application in the natural gas purification process.<br>• Recyclability<br>• Applicability for post-combustion $CO_2$ separation. | • >100 h to synthesize the T-type zeolite.<br>• Decrease of the adsorption capacities with increasing temperature from 288 to 313 K. |
| Zeolite NaA nanocrystals | 215.6 | 0.1 MPa, 293 K | Lab scale | • Use of a cost-effective method for the synthesis of highly active nanosized zeolites.<br>• High adsorption capacity for $CO_2$. | • No expected dependence of the diffusion time constant on the square of the radius of the crystals for the $CO_2$ uptake. |
| Ordered mesoporous carbon, SBA-15 template | – | <7 MPa, 275 K | Lab scale | • Wet material has adsorption capacity 31% higher than AC | • Long time to reach the equilibrium if the water content is higher than the critical value |
| PEI-mesoporous silica | 347.6 | $P_{atm}$, 348 K | Lab scale | • Inexpensive material<br>• Can be regenerated<br>• Easy to operate<br>• Fast $CO_2$ adsorption kinetics | • Lack of the selectivity factor for both $CO_2$ and $H_2S$ |
| TRI-PE-MCM-41 | 112.6 | 0.1 MPa, 298 K | Lab scale | • Potential application in purification of biogas<br>• Separation of biogas | • Low $CH_4$ adsorption |
| MOF-177 | a) 1452<br>b) 396.9 | a) 4.5 MPa, RT<br>b) 1.4 MPa, 298 K<br>c) 10 MPa, 298 K | Lab scale | • High thermal stability<br>• Extra high porosity<br>• High adsorption capacity at elevated pressures | • Negatively impacted by NOx, SOx, and $H_2O$.<br>• Low selectivity in $CO_2/N_2$ gas streams. |
| MOF-5 | 480 | 1.4 MPa for $CO_2$, | Lab scale | • Easily tunable pore and chemical characteristics. | • Lack of experimental data on performance after multiple cycles. |
| $Ni_2$(dhtp) MOF | – | 3.5 MPa, 298 K | Lab scale | | • Desorption approaches have not been adequately researched. |
| $Mg_2$(dhtp) MOF | – | 3.5 MPa, 298 K | Lab scale | | • Chemical instability upon time. |
| IRMOF-6 | – | 3.500 MPa, 298 K | Lab scale & simulation | | • High pressures |
| MgO/SBA-15 | 80 | Patm, 298 K | Lab scale | • Thermally stable NPs.<br>• Can be regenerated.<br>• High selectivity to $CO_2$<br>• Can be used in different technologies applications for $CO_2$ separation. | • Slight decrease of surface area and pore volume. |
| CaO nanopods | 770 | Patm, 873 K | Lab scale | • Can be regenerated during 50 cycles<br>• Better than commercial CaO | • High temperatures |
| $Fe_2O_3$ on AC | 103.7 | Patm, 298 K | Lab scale | • Enhancement the surface area of $Fe_2O_3$/AC | • Decrease the adsorption capacity of $CO_2$ comparing to AC |
| MW-CNTs@JUC32 | 67.8 | Patm, 273 K | Lab scale | • 70% and 90% higher than non-modified MW-CNTs<br>• Increase the $CO_2$ adsorption enthalpy | |
| APTS-CNTs | 96.3 | Patm, 298 K | Lab scale | • 40% higher than non-modified CNTs | • Lack of information on the reusability, maximum adsorption capacity, and kinetics |
| $Fe_3O_4$-Graphene | 2640 | 1.1 MPa, 298 K | Lab scale | • Easy synthesis<br>• Can be reused | • High pressures |
| Graphene | 950.4 | 1.1 MPa, 298 K | Lab scale | • High adsorption capacity compared to other carbon nanostructures.<br>• Possible use for industrial applications | • High pressures |

Patm: atmospheric pressure.

*Table 3 shows a summary of the most representative nanomaterials for $CO_2$ sorption.*

## Conclusions

The conclusions drawn from this review are:

• The introduction of nanomaterials for the capture of $CO_2$ is expected to be efficient due to their exceptional and unmatchable properties. Adsorbents based on porous supports, modified with amine or metals, are currently providing the most promising results in terms of sorption capacity for the aforementioned GHGs.

• The $Fe_3O_4$-graphene and the MOF-117 based NPs showed the greatest $CO_2$ sorption capacities, due to their high thermal stability and the presence of high porosity.

• One of the main challenges is to decrease the cost of capture and to scale-up the technologies to the size required in order to address large-scale power generation emission issues and to render them $CO_2$ emission free.

• Further research is needed to prove the long-term efficacy of nanomaterials as sorbents in real scale applications. In addition, the precise mechanisms of adsorption of the GHG onto the nanoparticles need to be further elucidated and researched in future studies.

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