1   **Critical review of existing nanomaterial adsorbents to capture carbon dioxide**

2   **and methane**

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Abstract

Innovative gas capture technologies with the objective to mitigate CO_2 and CH_4 emissions are discussed in this review. Emphasis is given on the use of nanoparticles (NP) as sorbents of CO_2 and CH_4, which are the two most important global warming gases. 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 CH_4 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 and CH_4. 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.

Keywords: Adsorption, Nanomaterials, Methane, Carbon dioxide, Metal Organic Framework, Zeolite

1.   Introduction

1.1   Greenhouse gases – Problem statement

Global Warming (GW) is the result of the increased concentration of Green House Gases (GHGs), primarily carbon dioxide (CO_2) and methane (CH_4), but also of nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluorocarbon (F_6C). The GHGs that are most abundantly emitted today are CO_2 (56%) and CH_4 (18%) (Houghton et al., 2001; McCarthy, 2001). As CO_2 is the most important gas in terms of amounts emitted, it has been widely studied (Pacala and Socolow, 2004).

CO_2 is produced in many industrial processes (i.e. fossil fuel power plants) including new prospective areas, such as the purification of hydrogen from biomass. Fossil fuel power plants are the largest point sources of CO_2 emissions (40% of total CO_2 emissions) (D'Alessandro et al., 2010); thus, they are the main targets for imminent CO_2 reduction (Doman et al., 2010; Metz et al., 2005).

Atmospheric concentrations of CH_4 (~1,800 ppb) are currently much higher than those in preindustrial levels (~680–715 ppb) (Butler and Montzka, 2012). Anthropogenic CH_4 emissions account for 50–65% of the global CH_4 budget of ~395–427 $TgC \cdot y^{-1}$ (526–569 Tg CH_4) (Kirschke et al., 2013). It is estimated that the principal CH_4 anthropogenic sources are (i) livestock (enteric fermentation and manure management), (ii) natural gas production and distribution, (iii) landfills, and (iv) coal mining (EPA, 2016). Also, it is reported that a rise in natural wetland emissions and fossil fuel emissions probably accounts for the renewed increase in global methane levels after 2006, although the relative contribution of these two sources remains uncertain (Kirschke et al., 2013).

The most convenient path towards lower CO_2 concentrations in the atmosphere would be to strongly reduce CO_2 emissions through cleaner and more environmentally friendly industrial processes. However, it is not expected that this can be achieved in the imminent future (Ciferno et al., 2009). Several options exist to reduce CO_2 emissions, such as demand-side conservation, supply-side efficiency improvement, increasing

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dependence on nuclear and renewable energy, and implementation of Carbon Capture and Storage (CCS) systems (D'Alessandro et al., 2010; Ciferno et al., 2009; Spigarelli and Kawatra, 2013; Yang et al., 2008).

The CO_2 capture is preferred to be applied directly on-site, since the capture materials and technologies have demonstrated better performances at high CO_2 concentrations rather than at atmospheric levels (400 ppm in 2014, Mauna Loa Observatory) (Baltenaitre et al., 2016).

1.2 Capture of GHGs via sorption

The storage of CH_4 on adsorbents has been pursued actively as an alternative to high pressure compressed gas storage. Thus, the use of adsorbent materials, such as activated carbons and zeolites for the storage of natural gas at low pressures, has also been reported (Solar et al., 2010). However, it was concluded that none of those conventional adsorbents showed sufficient CH_4 storage capacity to meet that required for commercial viability (Saha et al., 2010). Advanced materials have been investigated as potential CH_4 adsorbents including modified activated carbons, metal-organic frameworks (MOFs) and other porous polymers (Kizzie et al., 2014).

The technologies based on adsorption processes, such as activated carbon, zeolites and mesoporous silica, present limitations on the CO_2 retention capabilities per adsorbent mass (Cinke et al., 2003; Lu et al., 2008; Smart et al., 2006). In this sense, there is a widespread interest in the development of advanced adsorbent materials with better characteristics than conventional materials and with a specialized functionality for each pollutant.

Since CH_4 often co-exists with CO_2 in gaseous mixtures, such as natural gas, biogas and landfill gas, selective removal of CO_2 is an important process to upgrade the energy content of those mixtures (Li et al., 2013).

Nanotechnology can be defined as the engineering of functional systems "designed to measure" molecular scale. One of the benefits of these nanomaterials is the high surface to volume ratio and the ability to be synthesized with specific physicochemical properties. Nanotechnology has been applied in various areas of environmental sciences, such as catalysis, sensors and water treatment (Birgisson et al., 2012).

122 Several articles on water purification processes using NPs have been published

123 focusing on the removal of metals (Contreras et al., 2015; Recillas et al., 2010; Sánchez

124 et al., 2011; Xu and Zhao, 2007) or nutrients (Abo Markeb et al., 2016a; Abo Markeb et

125 al., 2016b; Choe et al., 2000; Sá et al., 2009). This shows the potential of

126 nanotechnology to remove contaminants. Only recently, certain nanomaterials, namely

127 the metal-organic frameworks (MOFs), have achieved satisfactory CO_2 removal

128 capacities at low concentrations (Bhatt et al., 2016; Shekhah et al., 2014).

129

130 1.3 Gaps in knowledge and objectives

131 Recently, there have been studies on the use of nanomaterials (i.e. carbon nanotubes

132 (CNTs) and amine functionalized nanotubes) to remove CO_2. The comparison of those

133 materials with traditional commercial adsorbents, such as active carbon and zeolite,

134 suggests that these nanomaterials are good candidates to capture CO_2 (Li et al., 2011;

135 Lu et al., 2009). In addition, there is limited work on the use of inorganic NPs to remove

136 and recycle CO_2. There are even scarcer reports on the removal of other GHGs such as

137 N_2O, CH_4 or fluorinated compounds. For these reasons, it is necessary to systematize

138 the studies on different types of NPs and nanomaterials under the same operating

139 conditions, and to investigate their ability to adsorb at different reaction conditions and

140 their potential for reuse to reduce processing costs.

141 The use of nanoparticles as sorbent materials for GHG capture has only recently

142 attracted the interest of researchers. Therefore, this review aims to discuss the current

143 research status on the use of such nanomaterials for the sorption of CO_2 and CH_4 and to

144 make a comparison with conventional sorption materials.

145

146 2.Conventional and novel adsorbents for CO_2 and CH_4 capture

147

148 2.1 Conventional adsorbents

149 Adsorption of a gas onto a solid surface (adsorbent) can be defined as the gain of one or

150 more constituents of the gas (adsorbate) in the gas-solid interface (Solar et al., 2010).

151 CO_2 capture using solid adsorbents is considered one of the most promising

152 technologies for CCS (Figueroa et al., 2008). Adsorption can reduce energy and cost of

153 the capture or separation of CO_2 in post-combustion capture technologies (Solar et al.,

154 2010). However, the success of this approach depends on the development of easily

155 recoverable and durable adsorbents with high CO_2 selectivity and adsorption capacities

156 (Songolzadeh et al., 2012).

157   The most common conventional CO_2 adsorbents are natural zeolites, activated

158 carbon and alkali-based metal materials. Table 1 shows the main characteristics, key

159 strengths and main drawbacks of the aforementioned three groups.

160

161   (Table 1 here)

162

163 **2.2 Novel adsorbents**

164 There is a huge interest in the development of advanced adsorbent materials that present

165 better features than the conventional materials and have specialized functionalities for

166 each pollutant (Li et al., 2013). These novel sorbents are i) ionic liquids, and ii)

167 modified porous supports.

168

169 *2.2.1 Ionic liquids for CO_2 removal*

170 Ionic liquids (IL) are solvent sorbents that are based on a stable liquid composed by a

171 combination of inorganic or organic anions and large organic bulky asymmetric cations

172 (Han et al., 2012). Due to their thermal stability, negligible vapour pressure, tunable

173 physico-chemical characteristics and high CO_2 solubility, IL are utilized in CO_2

174 removal applications (Park et al., 2015). Furthermore, modification of IL with

175 functional groups (Bates et al., 2002) to better adsorb and solubilize CO_2 has been

176 developed. For instance, Galán Sánchez et al. (2007) functionalized ILs with an amine

177 group or a hydroxyl functional group and successfully enhanced their performance for

178 CO_2 capture at room temperature and pressures up to 1 MPa compared to the non-

179 functionalized ionic liquids (Lee et al., 2012).

180   The high CO_2 solubility in ionic liquids, when compared to CH_4, gives them the

181 potential to be utilized in the separation of CO_2 from natural gas (Ramdin et al., 2015).

182 Some other studies have demonstrated the potential of different ionic liquids to remove

183 CO_2 from natural gas based on the CO_2 / CH_4 solubility and selectivity. However, those

184 studies had been based on Monte Carlo simulations (Ramdin et al., 2015).

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6

186   *2.2.2. Modified porous supports*

187   Zeolite-templated N-doped carbons exhibit a high CO_2 uptake capacity in comparison to

188   carbonaceous or inorganic and organic porous materials. Their sorption capacity can

189   reach up to 304.5 mg/g at 273 K and ambient pressure, or up to 192.7 mg/g at 298 K

190   and ambient pressure. Considering their excellent recyclability and regeneration

191   stability, as well as their high selectivity for CO_2, the N-doped zeolite-templated

192   carbons are among the most promising solid-state adsorbents for CO_2 capture and

193   storage (Xia et al., 2011). Figure 1 shows the effect of the N-doping samples on the CO_2

194   uptake capacity at 273 K, and 298 K and at 0.1 MPa (adapted from Xia et al., 2011).

195

196   (Figure 1 here)

197

198   HZSM-5 zeolites modified with Zn^{2+} ions (1.9 wt%), (i.e. ZnZSM-5), were tested

199   for methane adsorption at room temperature at different equilibrium pressures

200   (Kazansky et al., 2004). Methane adsorption by ZnZSM-5 did occur at the distantly

201   separated zinc ions.

202   On the other hand, the use of waste for the synthesis of materials as adsorbents is a

203   recent research area. For instance, the CO_2 capture process by zeolites synthesized from

204   paper sludge and scrap glass has been recently reported (Espejel-Ayala et al., 2014).

205   Zeolite analcime showed higher CO_2 sorption capacity (74.71 mg/g) at 320 K than the

206   commercial zeolite ZSM-5 at the same conditions (Espejel-Ayala et al., 2014).

207   There have been many attempts to add amine-based functional groups on different

208   original supports to improve CO_2 capture capacities. It is reported that CO_2 capture

209   capacities of the modified sorbent have been successfully increased. For instance,

210   Przepiorski et al. (Przepiórski et al., 2004) used NH_3-treated CWZ-35 activated carbon

211   to adsorb CO_2 and obtained a sorption capacity of 76 mg/g. Kim et al. measured a CH_4

212   adsorption capacity of 85 mg/g on a multi-walled carbon nanotube (MW-CNT)

213   preloaded with water at 10 MPa and at 275 K (Kim et al., 2008). Son et al. impregnated

214   KIT-6 silica adsorbent with polyethylamine (PEI) and measured a CO_2 capacity of 135

215   mg/g (Son et al., 2008).

216   Regarding CH_4, Lee et al. tested phenol-based activated carbon for its adsorption

217   and measured a sorption capacity of 128.9 mg/g at 3.5 MPa and at 193.15 K (Lee et al.,

218 2007). Zhou et al. obtained a CH_4 adsorption capacity of 85mg/g on an MW-CNT
219 preloaded with water at 10 MPa and 275 K (Zhou et al., 2005).

220 Table 2 shows the main characteristics, key strengths and main drawbacks of the
221 aforementioned novel materials for CO_2 and CH_4 sorption.

222
223 (Table 2 here)
224

225 In summary, although new materials and techniques are being developed, several
226 challenges are still to be overcome, in particular with regard to methane sorption.
227 Therefore, CO_2 and CH_4 storage becomes a new motivation to develop novel materials.
228 In fact, advances in nanoscale science and engineering are providing unprecedented
229 opportunities to develop more cost effective and environmentally acceptable gas
230 purification systems, since it is preferable to have a low-cost, widely available raw
231 material and a simple synthesis process to develop a gas removal system (Songolzadeh
232 et al., 2012).

233

234 **3. Nanomaterial based CO_2 and CH_4 capture systems.**
235 Many of the sorbent materials presented here have a natural origin and their uses and
236 properties are known for centuries. It has been during the last 50 years, however, that
237 researchers focused their efforts on the development of novel materials with engineered
238 features in the nano-range (Fox-Rabinovich and Totten, 2006). Due to their small size
239 and high surface area per unit volume or mass, nanomaterials show unique electric,
240 magnetic, optical, structural, mechanical, and chemical characteristics that are already
241 exploited in a large number of industrial and consumer products (Royal Society and
242 Royal Academy of Engineering, 2004). In this context, the high adsorption capacity of
243 nanomaterials has been demonstrated in several cases.

244 Nanomaterials have a number of physicochemical properties that make them
245 particularly attractive as separation supports for gas purification and gas capture. One is
246 the ability to be functionalized with different compounds (such as surfactants) so that to
247 enhance their affinity towards target molecules (Buzea et al., 2007). In addition, their
248 size makes their surface especially reactive and their nature provides them with an extra
249 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-Garcia and Rodríguez, 2007).

Novel nanomaterials, like advanced nanoporous materials, MOFs and 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 CH_4 and CO_2 adsorption and have gained increased interest recently. In fact, several research papers have reported improved CO_2 sorption and, more interestingly, improved CH_4 adsorption capacity compared to conventional sorbents. In particular, MOFs were the ones that exhibited the highest adsorption (Saha et al., 2010). Figure 2 shows different MOFs used to capture CO_2 and CH_4.

(Figure 2 here)

In Figure 3, Mason et al. studied different MOFs and compared the effects of the volumetric and gravimetric adsorption on CH_4 uptake (Mason et al., 2014).

(Figure 3 here)

A bibliography search (Web of Knowledge) using the keywords "nanomaterials" and "CO_2 capture" detected 20 publications from 2007 to 2016; 8 of them were related to this study and are discussed later on. A similar search for "CH_4 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.

Amongst 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 nanoadsorbents.

3.1 Nanosized zeolites versus conventional zeolites

Zeolites are 3-dimensional highly ordered porous crystalline aluminosilicates that contain alkali and alkaline earth elements (usually, Na^+, K^+ and Ca^{2+}). Zeolites have been used in the petroleum refining industries for many decades as ion exchangers, adsorbents and selective catalysts (Yang and Xu, 1997). The key characteristics of zeolites that are of interest for adsorption processes, such as the separation of CO_2 from air, include molecular pore size distribution, polarity, reversibility, selectivity and adsorption capacity. Their high adsorption capacity at ambient temperatures and pressures, and their uniform molecular-sized pores (3–8 Å) (Flanigen, 1991) give zeolites their high molecular sieving property. Zeolites have a high affinity towards polar molecules such as H_2O and CO_2 (Flanigen, 1991). Zeolites favour CO_2 adsorption, but they show significant decreases in sorption capacity at elevated temperatures and humid conditions. Adsorption capacities at mild operating conditions range from 4 to 300 mgCO_2/g zeolite. Although zeolites adsorb gases physically, it has been found that part of the CO_2 does irreversibly chemisorb on the zeolite surface in the form of carbonates and carboxylates, which complicates desorption. Despite that, complete regeneration of zeolites can be accomplished using a temperature swing system at temperatures around 620 K (D'Alessandro et al., 2010; Lee et al., 2008).

Further development needs to be done on the modification of zeolites in the nanoscale range to improve CO_2 adsorption. Unfortunately, few studies of nanocrystalline zeolites for CH_4 adsorption exist. The T-type zeolite is an intergrowth-type zeolite with an effective pore size of 0.36 nm × 0.51 nm. This is smaller than the molecular size of N_2 (0.364 nm) and CH_4 (0.38 nm) and larger than the molecular size of CO_2 (0.33 nm) (Jiang et al., 2013). T-type zeolite NPs were synthesized and resulted in an 176 mg CO_2/g adsorption capacity, which was 30% higher than that of the micro-level T-type zeolite at 288 K and 0.1 MPa (Jiang et al., 2013).

Zeolite NaA nanocrystals with a size of 100 nm presented a high CO_2 uptake capacity (220 mg/g at 293 K at 0.1MPa) (Shakarova et al., 2014).

All-silica zeolite deca-dodecasil 3R (DD3R) is a silica based-membrane composed by dodecasil 3R (clathrasil with zeolite properties) (Gies et al., 1982) and a pore size of 0.36 x 0.44 nm (Auerbach et al., 2003). The reported adsorption isotherms

313 of all-silica DD3R for CO_2 and CH_4 were 27 mgCH4/g and 123 mgCO2/g at 298 K,

314 respectively (Himeno et al., 2007).

315

316 **3.2 Mesoporous silica nanoparticles**

317 Mesoporous silica nanoparticles (MSNs) is a recent development in material science.

318 They were synthesized in 1990 by researchers in Japan and were later produced at

319 Mobil Corporation laboratories (Kresge et al., 1992). Later on, Kruk et al. developed

320 silica NPs with a hexagonal array of pores up to 30 nm, named SBA-15 (Kruk et al.,

321 2000). An ordered mesoporous carbon, synthesized with the SBA-15 as a template,

322 showed a high adsorption capacity of 412 mgCH4/gC at 275 K and at pressures less than

323 7 MPa at the presence of water. This sorption capacity is 31% higher than the largest

324 sorption capacity measured in activated carbon at the presence of water (Liu et al.,

325 2006).

326   A novel high efficiency solid nanocomposite sorbent for CO_2 capture has been

327 developed based on oligomeric amine (PEI) functionalized mesoporous silica capsules,

328 which exhibit high capture capacities of up to 347 mgCO2/g under simulated flue gas

329 conditions (Qi et al., 2011). This material is inexpensive, easy to recover and useful in

330 high concentration streams (Meth et al., 2012).

331   Atriamine-grafted pore-expanded mesoporous silica (MCM-41; TRI-PE-MCM-41)

332 was recently investigated. It exhibited a CO_2 capacity twice higher than that of Zeolite

333 13X (i.e. 112.6 mg/g at 298 K). However, the methane adsorption capacity for this

334 material was low (Belmabkhout et al., 2009).

335   These findings indicate that acidic gases (CO_2) can be succesfully separated from

336 CH_4-containing mixtures (i.e. natural gas and biogas).

337

338 **3.3 Metal organic frameworks (MOFs) with embedded nanoparticles**

339 MOFs are an emerging class of nanoporous crystalline structures composed of central

340 cation molecules linked together by organic linkers to form a 3D structure. MOFs are

341 getting attention due to their application in separation, catalysis, nonlinear optics, and

342 gas storage (Hafizovic et al., 2007). They have a broad flexibility and variety in shapes,

343 geometries and functionalities, and present a high selectivity and capacity in the

344 adsorption of gases, due to the tunable size of their particle pores (Huang et al., 2003).

However, they have poor adsorption capacities at low CO_2 partial pressures (Bloch et al., 2013).

Several modifications have been performed on MOFs to enhance their adsorption capacity. Some strategies are based on functionalizing the pore-surface with amines, creating accessible metal sites (Xiang et al., 2011), exposing Lewis base sites and exchanging counter ions included in the charged framework (Hong and Suh, 2012). All these tunable properties open a promising field of research in the study of MOFs to store gases. For instance, Millward and Yaghi measured CO_2 adsorption on various Zn-based MOFs and found that MOF-177, a framework consisting of a Zn_4O_6 cluster and 1,3,5- benzenetribenzoate (BTB) ligands, can adsorb 1452 mg/g of CO_2 at 4.5 MPa and at room temperature. This is higher than that of MOF-5 ($Zn_4O(BDC)_3$, 1,4-benzenedicarboxylate, BDC), which was 479.8mg/g and of those of other porous materials (Millward and Yaghi, 2005). The same trend was reported with regard to the adsorption of CH_4 by the two MOFs; the CH_4 adsorption capacity of MOF-5 was 171.5 mg/g and 220.3 mg/g for MOF-177 (Saha et al., 2010).

Other examples are the isostructural M_2(dhtp) MOFs [M: open metal; dhtp: $C_8H_2O_6$)], which have high densities of open metal sites in their crystal structures providing an exceptionally high adsorption capacity. Among the various MOFs, the recorded CH_4 adsorption capacities are 283.4 mg/g for Ni_2(dhtp) and 363 mg/g for Mg_2(dhtp) (Wu et al., 2009a).

On the other hand, zeolite imidazolate frameworks (ZIFs), a subclass of MOFs, have emerged as a novel type of crystalline porous materials, which combines highly desirable properties from both zeolites and MOFs, such as microporosity, high surface areas, and exceptional thermal and chemical stability. In particular, ZIF-8 (1,6,7 zeoliticimidazolate framework-8) has been investigated as a potential gas storage medium (CO_2, H_2, and acetylene). At 0.1 MPa and room temperature, the ZIF-8 crystals adsorbed 14 times more CO_2 than CH_4 (Venna and Carreon, 2010). In addition, amino-functionalized Zr-MOF (amino-Zr-MOF) showed good CO_2 and CH_4 absorption behavior. The CO_2 adsorption capacity on amino-Zr-MOF was 396 mg/g at 0.988 MPa and at 273 K, while CH_4 adsorption capacity was 59.2 mg/g at 0.900 MPa and 273 K (Abid et al., 2013).

In the specific case of the CH_4 adsorption, Eddaoudi et al. reported that a new material, namely IRMOF-6, which is based on isoreticular metal-organic frameworks, presented the advantage of higher crystallinity over activated carbon. IRMOF-6 exhibited a high CH_4 uptake equal to 409mg/g at 3.5 MPa, based on physical adsorption (Düren et al., 2004), as measured experimentally.

It is worth mentioning that some researchers determined the CH_4 locations and orientations in MOFs. Upon methane loading, the MOFs first attracted the gas adsorbents onto the strongest and primary binding sites (i.e. the organic linkers or metal clusters in, for instance ZIF-8 and MOF-5, respectively) and this molecular interaction fully defined the methane molecular orientation. Hence, these sites are essential for an ideal MOF to store methane (Wu et al., 2009b).

Other strategies have been investigated to construct the targeted MOFs, such as the employment of highly aromatic pillars that can enhance the stability of the material and increase CH_4 uptake through favorable $\pi \cdots CH_4$ electronic interactions. These interactions could be further enhanced by functionalizing the aromatic rings with methyl groups in the presence of Co^{2+}, Cu^{2+}, and Zn^{2+}. The inducement of the CH_4-framework interaction enhancement can lead to the increase of the total CH_4 storage capacity. The Cu-tbo-MOF-5 showed excellent structural stability and methane sorption capabilities compared to HKUST-1. CH_4 adsorption measurements revealed that Cu-tbo-MOF-5 exhibits high volumetric storage capacities (Spanopoulos et al., 2016).

Overall, it seems that MOF-177 has been the material with the highest adsorption capacity for CO_2 and CH_4. That is, MOF-177 can be the adsorbent of choice for removing CH_4 from air with an adsorption capacity at 220mg/g at 298 K and at 10 MPa (Llewellyn et al., 2008; Saha et al., 2010). Also, the comparison of the volumetric capacity of MOF-177 with that of the current benchmark materials, namely zeolite 13X and MAXSORB (Table 1), showed that MOFs represent a new direction for removing CO_2 and CH_4 in exhaust gases (Millward and Yaghi, 2005). However, it is not easy to compare all those nanomaterials for their effiency to capture both CO_2 and CH_4 given that the pressure and temperature experimental conditions were different in all cases.

Furthermore, one of the problems of the application of MOFs in packed bed columns is that their crystals are difficult to compress into larger pellets which is usually required to limit the pressure drop over the adsorption column or the catalytic

408 reactor (Finsy et al., 2009). Although most MOF materials show relatively good CO_2

409 and CH_4 uptakes, their CO_2 and CH_4 adsorption capacities can be enhanced by using

410 nanomaterial-modified MOFs; for instance, through the incorporation of carbon

411 nanotubes (CNTs) (Khdary and Ghanem, 2012; Xiang et al., 2011).

412

3.4 Metal and Metal Oxide Nanoparticles (MNPs and MONPs) versus alkali-metal

413

414 **based absorbents**

415 Alkali-metal based adsorbents are alkali metal carbonates immobilized onto inorganic

416 supports, such as solid silica, zirconia, ceramics and alumina (Duan et al., 2011).

417 Chemically, CO_2 adsorption is achieved by reaction with moisture (carbonation), and

418 desorption is performed through decarbonation (Lu et al., 2006). Two alkaline-earth

419 metal oxides (CaO and MgO) have attracted special attention because of their

420 accessibility and favorable thermodynamics. This is particularly true for CaO because it

421 has a high CO_2 adsorption capacity (Feng et al., 2006) and a high raw material

422 availability (e.g. limestone) at a rather low cost. However, in general, the long-term

423 stability and performance of alkali metal-based sorbents under actual flue gas conditions

424 remains to be established (Songolzadeh et al., 2012). Recently, Li-, Na- and K- based

425 silicates or zirconates also gained interest due to their high CO_2 absorption capacities

426 (Kumar and Saxena, 2014). Two examples of the materials used in this technique with a

427 high CO_2 capture potential are the Li-based zirconate (Li_2ZrO_3) and the Li-based silicate

428 (Li_4SiO_4). Li_2ZrO_3 showed an excellent CO_2 sorption capacity (220 mg/g, Table 1)

429 (Ochoa-Fernández et al., 2005). On the contrary, they present problems with long term

430 stabilities (Pfeiffer, 2010). No literature has been found so far on the use of this

431 technology on methane adsorption.

432 Another important issue is the study of post-combustion treatment from the point of

433 view of Life Cycle Assessment (LCA). To our knowledge, there is limited work on this

434 topic. Several studies have proved that CO_2 sorption in liquid materials presents up to a

435 10-fold increase in the toxic impact to freshwater ecosystems and a minor increase in

436 the toxic impact to terrestrial ecosystems when compared to solid based adsorption

437 technologies (Veltman et al., 2010). In a more generic work, Nie et al. presented a

438 comparative life cycle assessment of alternative CO_2 capture technologies after a

439 combustion process. In most cases, the capture of CO_2 resulted in a reduction of the

14

440 Global Warming Potential by 78.8% and 80.0%, respectively, compared to conventional

441 plants without CO_2 capture (Nie et al., 2011). Other environmental impacts, such as

442 Ecotoxicity, Human toxicity and Acidification, varied significantly with the different

443 CO_2 capture routes employed.

444   In the case of methane, several technologies were analyzed through LCA. However,

445 the works published were at a lab scale and have mostly used costly adsorbents and to a

446 limited extent natural low-cost materials. For instance, Azevedo et al. presented the

447 environmental benefits of using microporous activated carbon samples prepared from

448 coconut shells, although no Life Cycle Assessment was specifically performed

449 (Azevedo et al., 2007). Other studies on adsorption of CH_4 in biogas have been

450 presented, but in this case the simultaneous adsorption of CO_2 and CH_4 hampered the

451 interpretations of the Life Cycle Assessment results (Starr et al., 2012).

452   Both metal and metal oxides have been also produced in nanoporous form.

453 Bhagiyalakshmi et al. produced mesoporous MgO using mesoporous carbon obtained

454 from SBA-15 as a template, and obtained a CO_2 adsorption capacity of 80 mg/g at 298

455 K (Bhagiyalakshmi et al., 2010). However, in general, the adsorption capacities

456 of MgO-based systems are usually small (<15 wt.%), and, therefore, strategies to

457 improve those capacities are desirable (Wang et al., 2011).

458   CaO is another material that was developed in nano-hollow structured. Absorption

459 capacity of CaO nanopods (770 $mgCO_2$/g) was apparently higher than commercial CaO

460 (532 $mgCO_2$/g) (Lee et al., 2012; Yang et al., 2009).

461   Other nanomaterials reported, i.e. hydroxylated Fe_2O_3, y-$Al_2O_3$and TiO_2NPs, have

462 been tested for CO_2 adsorption at 296 K. In addition, the different species of CO_2

463 formed on the oxide surface of the different nanomaterials were analyzed. Bicarbonate

464 was the most abundant species adsorbed on Fe_2O_3 and γ-Al_2O_3 NPs, whilst bidentate

465 carbonate was adsorbed on TiO_2 NPs (Baltrusaitis et al., 2011; Lee et al., 2012).

466 Moreover, activated carbon was used to enhance the surface area of metal oxides, which

467 are mainly responsible for physical adsorption. Fe_2O_3 supported on activated carbon

468 was used for CO_2 adsorption at 298 K and exhibited an adsorption capacity of 115.2

469 mg/g. The CO_2 adsorption mechanism is based on the initial adsorption of CO_2

470 molecules by the empty pores of activated carbon followed by the adsorption using the

471 activated carbon pores filled with Fe_2O_3. Thus, the mechanism is based on

472 physisorption in addition to the chemical interaction on the Fe_2O_3 surface as carbonate
473 complexes (Hakim et al., 2015).

474 γ-Al_2O_3 does not show any affinity for CO_2 below 673 K, whereas K_2CO_3-
475 promoted γ-Al_2O_3 has a CO_2 adsorption capacity of 12 mg/g at 22 wt% K_2CO_3 loadings
476 (Walspurger et al., 2008).

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478 **3.5 Carbonaceous nano-sorbents versus conventional carbonaceous sorbents**
479 Carbonaceous adsorbents have been widely used for CO_2 capture or storage due to their
480 wide availability, low cost, electrical and heat conductivity, high thermal and chemical
481 stability and low sensitivity to moisture (Cheng-Hsiu et al., 2012). However, the weak
482 CO_2 adsorption of carbonaceous materials in a range of 323–393 K leads to high
483 sensitivity in temperature and relatively low selectivity in operation. Carbonaceous
484 materials have a limited application in high pressure gases as well (Sevilla et al., 2011).

485 Activated carbon adsorption capacity depends on the textural properties and surface
486 groups of the carbon-based adsorbents. Generally, adsorption capacities for activated
487 carbon at mild operating conditions (0.01–0.1 MPa CO_2 and 295–345 K) range between
488 3–154 mgCO_2/g activated carbon (D'Alessandro et al., 2010; Lee et al., 2008). This is
489 slightly lower than that of zeolites under similar operating conditions (Table 1). Himeno
490 et al. reported a systematic study of the adsorption of CO_2 on several Activated Carbons
491 at temperatures ranging from 273 to 333 K and at pressures up to 6 MPa. They
492 concluded that activated carbon MAXSORB had the highest adsorption capacity (1408
493 mg CO_2/g) at 3.2 MPa and 273 K) (Himeno et al., 2005). There are few reports on CH_4
494 adsorption on activated carbons. Again, Himeno et al. (Himeno et al., 2005) performed
495 CH_4 adsorption on various kinds of commercially available Activated Carbons and
496 reported adsorption capacities up to 224 mg/g at 4.6 MPa and 273 K.

497 Other modifications of activated carbon to improve their surface area and pore
498 structure, and thus their adsorption capacity, are under research. The physical
499 adsorbents can be modified after increasing alkalinity by chemical modification on the
500 surface by adding basic groups, such as amino groups and metal oxides (Cheng-Hsiu et
501 al., 2012).

16

502   Current research focuses on how to improve the CO_2 and CH_4 adsorption capacity
503   and selectivity by using carbonaceous materials. These are the most common sorbents
504   to adsorb CH_4 adsorption nowdays via the following mechanisms:

505   i) Improvement of the surface area and the pore structure of the carbonaceous
506   adsorbents by either using different precursors or by fabricating different structures such
507   as ordered mesoporous carbon, single-wall carbon nanotubes, multi-walled CNT (MW-
508   CNTs), graphene, etc.

509   ii) Modification of the activated carbons with Metal Oxide NPs or other nano-
510   compounds.

511   CNTs, carbon nanofibers, carbon nanospheres, nanodiamond and fullerene have
512   been progressively used due to their excellent physical, chemical and electronic
513   properties. More specifically, graphene, as a new member of carbon-based materials,
514   has emerged as a promising nano-platform with enormous potential for research in
515   various fields (Wang et al., 2013).

516   Regarding carbonaceous materials, this review focuses on: nanoporous carbon
517   materials, carbon nanotubes and graphene-based nanomaterials.

518

519   *3.5.1 Nanoporous carbon-based materials*

520   Since promising adsorption results for CO_2 capture by mesoporous carbon materials
521   have been reported, a series of nanoporous carbon materials of tunable mesopore size
522   have been synthesized (i.e. CMK-1, CMK-3 and CMK-5). These are quite promising
523   materials for the storage of natural gas due to: large pore volume, high specific surface
524   area, high thermal stability, high chemical stability, high mechanical stability, and
525   ordered pore structure. The sorption isotherms of CH_4 in the synthesized CMK-3-1.25
526   sample at 275 K of both the dry and wet samples showed that the highest sorptive
527   capacity at 112.3 mg/g was reached at 9.03 MPa on dry samples (Liu et al., 2006).

528

529   *3.5.2 Carbon nanotubes (CNT)*

530   Carbon nanotubes (CNT) are the most famous among nano-hollow structured materials
531   with dimensions ranging from 0.8 to 2 nm in diameter and from less than 100 nm to
532   several cm in length (De Volder et al., 2013). The enrichment of CH_4 using different
533   types of CNTs in a mixture of gases that initially contained CH_4, CO_2 and H_2S has been

reported. In general, CO_2 is preferentially adsorbed onto CNTs more than either CH_4 or H_2S (Esteves et al., 2008). However, Zhou et al. investigated the adsorption of CH_4 on dry and water-loaded MW-CNT with good results, and reported a CH_4 uptake of 80mg/g at 10 MPa and at 275º K (Zhou et al., 2005).

Furthermore, CNTs have been investigated and used as composite fillers for various applications (Zhu et al., 2013). In particular, CNTs can be an effective additive to improve the kinetics of gas storage materials (Yoo et al., 2014). For instance, MW-CNTs@JUC32 nanocomposites (i.e. MOFs NPs synthesized in situ on MW-CNTs) showed enhanced adsorption for CO_2 and CH_4. The CO_2 and CH_4 uptake for MW-CNTs@JUC32 is 67.8 and 12 mg/g, respectively, at room temperature. This is 70% and 90% higher for CO_2 and CH_4, respectively, than the single MW-CNTs tested at the same conditions (Kang et al., 2015). Also, CNTs modified with 3-aminopropyl-triethoxysilane ($H_2NCH_2CH_2CH_2-Si(OCH_2CH_3)_3$, APTS) presented a CO_2 adsorption capacity equal to 96.3mg/g, which is 40% higher than non-modified CNT adsorbents (Lu et al., 2008).

However, in most of the cases, the few reports regarding CH_4 adsorption on CNTs-based materials, although promising, are still based on conceptual models (Tanaka et al., 2002; Zhang and Wang, 2002) and mathematical simulations. CNTs are ideal templates onto which NPs can be immobilized, allowing the construction of designed nano architectures that are extremely attractive as supports for heterogeneous catalysts (Nhut et al., 2002).

3.5.3 Graphene

Graphene is an ideal two-dimensional material and single-atom layer of graphite, and has attracted increasing interests in multidisciplinary research because of its unique structure and exceptional physicochemical properties (Wang et al., 2013). Therefore, there have been multiple reports on the structure, chemistry and the use of graphene, but very few on environmental concerns (Kemp et al., 2013). It is known that graphene-based materials can offer a large potential for environmental remediation and energy applications. This is due to their tremendous adsorption capacity and the excellent catalytic performances, especially during removal of pollutants from water, during gas upgrading and purification, and during hydrogen generation and storage (Wang et al.,

566 2013). Graphene, like other carbon-based materials, is lighter and cheaper to produce
567 than other solid-state gas adsorbent materials (D'Alessandro et al., 2010; Schlapbach
568 and Zuttel, 2001). For instance, nanoporous graphene materials have been applied as
569 sorbents for CO_2 sequestration, biogas upgrading, SO_2 pollution control, and air
570 dehumidification. In those processes, the physisorption of gas on the surface depended
571 on the electrostatic and dispersion interactions with adsorbates (Gadipelli and Guo,
572 2015).

573 Graphene has been modified with different compounds to enhance its properties.
574 Ning et al. produced nanomesh graphene (NMG) with porous MgO layers which
575 present great storage capacities for CH_4 and CO_2 (Ning et al., 2012). Also, the
576 preparation of Mg–Al Layered double hydroxides (LDHs) onto negatively charged
577 graphene oxide (GO) has been reported (Garcia-Gallastegui et al., 2012). The inclusion
578 of GO (7 wt%) led to an enhancement in adsorption capacity, which was 2.5 times
579 higher than that of the pure LDH (62% at 573 K and $P(CO_2) = 0.02$ MPa). In addition, it
580 led to stability upon recycling and increased the active/effective LDH surface area
581 (Kemp et al., 2013).

582 Although it has been shown that graphene-based materials can be utilized as
583 adsorbents for gas storage, the majority of the studies are based on conceptual models.
584 Among them, it is worth to mention the study reported by Liu et al., which has shown
585 that graphite defect sites can react with CH_4 (Liu et al., 2012). This study showed that a
586 CH_4 molecule is activated at certain mono-vacancy sites on the graphite surface. This
587 activation can lead to chemisorption that occurs as the CH_4 ruptures into CH_2 and 2H
588 which then chemisorb at the vacancy sites. Furthermore, graphene materials could also
589 be non-covalently decorated with MNPs (e.g., Au, Ag, Pt, Ni, Ru) through different
590 synthetic procedures such as in situ reduction, electro-deposition, or thermal
591 evaporation (Wang et al., 2016). However, they have not been yet widely used for CO_2
592 or CH_4 adsorption but for hydrogen storage and catalysis (Huang et al., 2011; Wang et
593 al., 2012).

594 The sorption of gas-phase molecules on the surface of graphene-based materials
595 strongly depends on the electrostatic attraction, dispersion interactions, van der Waals
596 interactions or charge transfer (Du et al., 2011; Leenaerts et al., 2008; Leenaerts et al.,
597 2009; Wang et al., 2013).

19

Overall, Table 3 shows a summary of the most representative nanomaterials for CO_2 and CH_4 sorption.

(Table 3 here)

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 those materials.

4. Techno-economic views on nanomaterials as CO_2 and CH_4 sorbents

Apart from achieving high CO_2 and CH_4 capture efficiencies in the laboratory, the economic viability of the sorption processes at field scale is important. The cost of a complete CO_2 removal process includes cost of sorbents, cost of process installation and commissioning, operation and maintenance costs, additional fuel resources, and CO_2 compression, and the cost of transport and storage. To develop a sustainable CO_2 removal system, many factors should be considered such as high CO_2 capture capacity, sustainability of the sorbent throughout multiple sorption/desorption cycles and the low production cost. Thus, it is prefered to have a low-cost, widely available raw material and a simple synthesis process. For instance, lithium salts have been reported to be good sorbents for CO_2 removal. However, the high price of the pertinent raw materials makes them unattractive compared to other metal salts. According to Abanades et al. (Abanades et al., 2004), the cost of lithium carbonate (Li_2CO_3) was \$4.47 per kg, whereas the cost of $CaCO_3$ (raw material for CaO), at the same time, was only \$0.005 per kg.

Another example are the carbonaceous adsorbents. For instance, CNTs with a specialized structure are only available at extremely high prices (i.e. \$5/g) compared to granular activated carbon (GActivated Carbon), which typically costs around \$1/kg. Also, reusability of the captured CO_2 would also be an added advantage in order to make the CO_2 removal process economically feasible (Lee et al., 2012). Moreover, a

630 CO_2 removal system that operates close to flue gas emission temperatures would be

631 ideal as no extra energy would be needed.

632 Based on the above, the challenges are to decrease the cost of capture and to scale-

633 up the technologies to the size required so that to minimize large-scale power generation

634 emissions. For example, a large coal plant of 1000 MW will typically generate about

635 8000 tons of CO_2 per day or about 3 million tons of CO_2 per year, provided that it runs

636 at base load. This is more than one order of magnitude larger than the capacities of

637 existing separation technologies. From the point of view of cost, the current

638 technologies, if applied, would cost between €20 and €50 per ton of CO_2 separated,

639 which would increase the cost of the electricity produced by 30% for a large coal plant.

640 Fossil fuel based power generation with CO_2 capture and storage technologies would be

641 competitive if these costs are properly addressed and reduced (CO_2 capture,

642 https://ec.europa.eu/research/energy/pdf/synopses_co2_en.pdf).

643 Nanomaterials are promising sorbents to overcome many limitations of the CO_2

644 capture processes. They have relatively high CO_2 capture capacities, they are reusable

645 throughout multiple sorption/desorption cycles, and some of them have relatively low

646 energy requirements. However, to tailor and control their sizes and dimensions,

647 synthesis of nanomaterials usually needs costly materials, while the application methods

648 are complicated. Besides screening and identifying an ideal nanomaterial sorbent, future

649 research should focus on designing simple and low-cost production routes for those

650 nanomaterials. This should be followed by a scale-up and process study for the sorbent.

651 Regarding CH_4, the storage capacity and the adsorption/desorption cycle durability

652 of existing adsorbents should be improved. The study of superior adsorbents for CH_4

653 storage requires the implementation of techno-economical systems. So far, it is

654 significant that a large amount of data has been collected using adsorption reactors and

655 gas storage systems. In addition, because of the progress of nanoporous adsorbents for

656 CH_4 storage, it is expected that improved techno-economical systems will enhance the

657 adsorption performance of CH_4 gas. Consequently, it is expected that nanoporous

658 carbonaceous materials for CH_4 storage will be extensively developed and used in the

659 future (Pil-Seon et al., 2016).

In summary, although some discrete adsorption capacity values can be found for CO_2, there is a lack of rigorous technical and economical data for CH_4. This clearly hampers the implementation of such capture systems for methane at field scale.

5. Conclusions

The conclusions drawn from this review are:

- The introduction of nanomaterials for the capture of CO_2 and CH_4 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.

- Although IRMOF-6, ordered mesoporous carbon, MOF-177 and MOF-5 have shown the highest adsorption capacities for CH_4, their adsorption capacities values were low in real scale applications compared to graphene or graphene-based NPs.

- 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/CH_4 emission free.

- Further research is needed to prove the long-term efficacy of the 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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Table 1. Summary of characteristics of conventional adsorbents for CO_2 and CH_4

Sorbent	CO_2 adsorption capacity (mg CO_2/g sorbent)	CH_4 adsorption capacity (mg CH_4/g sorbent)	Experimental conditions	Process scale	Key strengths	Main Drawbacks
NaXzeolite (Li et al., 2013)	263	50.7	0.1 MPa, 303 K	Lab scale		
Zeolite 5A (Saha et al., 2010)	222.7	143.1	1.4 MPa for CO_2, 10 MPa for CH_4, 298 K	Lab scale	• Good adsorption kinetics • Good performance at mild conditions	• Impurities • Elevated Temperatures for regeneration
Zeolite 13X (Cavenati et al., 2004)	324.37	91.50	3.2 MPa for CO_2, 4.7 MPa for CH_4, 298 K	Lab scale		
Activated Carbon (MAXSORB) (Cheng-Hsiu et al., 2012;	1408	224	3.2 MPa for CO_2, 4.6MPa for CH_4,273 K	Lab scale	• High thermal stability. • Good adsorption kinetics. • Cheap raw material	• Low capacity at mild conditions • Low selectivity • Impacted by NOx, SOx.

Himeno et al., 2005)					• Large adsorption capacity at elevated pressures. • Easy regeneration	
K_2CO_3/TiO_2 (Lee et al., 2006)	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 (Ochoa-Fernández et al., 2005)	220	--	Patm, 873 K	Lab scale & simulation	• Unique thermal stability • 20 absorption / regeneration cycles • Small volume change during cycles	• Slow absorption kinetics

1091   Patm: atmospheric pressure

Table 2.Summary of characteristics of novel adsorbents for CO$_2$ and CH$_4$

Sorbent	Maximum CO$_2$ capacity (mgCO$_2$/g sorbent)	Maximum CH$_4$ capacity (mgCH$_4$/g sorbent)	Experimental conditions	Process scale	Key strengths	Main Drawbacks
Zeolites N-doped C (Xia et al, 2011)	304.5 192.7	-- --	0.1 MPa, 273 K 0.1 MPa, 298 K	Lab scale Lab scale	• High selectivity for CO$_2$ • Excellent recyclability and regeneration stability • Ease of preparation	• Low content of N could not determine the interaction of CO$_2$ and carbon material
Zeolite (analcime) (Espejel-Ayala et al., 2014)	74.71	--	0.101 MPa, 323.1 K,	Lab scale	• Can be used in the purification of gas. • Production of energy without increasing atm. CO$_2$ concentrations	• Leaching of calcium in the treatment of PSA. • Costly using synthesized zeolite. • Emission of GHGs
Phenol based activated carbon (Lee et al., 2007)	--	128.90	3.7 MPa, 293.1 K	Lab scale & simulation	• Production of monolith using RP-20 • Increase the adsorption capability of methane on a volume basis	• Low surface area and high packing density using monolith on a mass basis

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Material			Conditions	Scale	Advantages	Disadvantages
MW-CNT preloaded with H_2O (Zhou et al., 2005)	--	85	10 MPa, 275 K	Lab scale	• Five times higher sorption capacity than dry CNT	• Limited surface area and pore volume to use CNT as energy carriers
NH_3-CWZ-35 Activated carbon (Przepiórski et al., 2004	76.0	--	0.1 MPa, 309.1 K	Lab scale	• High stability of N-containing groups used for CO2 adsorption.	• High temperatures of ammonia treatment (200ºC-1000ºC). • Formation of cyanide groups.
NH_2 functionalizedme soporous silica (PEI50%-KIT-6) (Kim et al., 2008)	78.8	--	298 K	Lab scale	• Strong ald simple introduction of amine groups using anionic surfactants. • Success for 10 adsorption-desorption cycles	• High temperatures of ammonia treatment (200ºC-1000ºC). • Formation of cyanide groups.
KIT-6-PEI 50 mesoporous silica (Son et al., 2008)	135	--	348 K	Lab scale	• Fastest response time • Success for 3 adsorption-desorption cycles	• Information of the meaningful textural properties cannot be obtained from the N_2 adsorption–desorption isotherms for PEI loadings.

Table 3.Summary of characteristics of nanomaterial based sorbents for CO_2 and CH_4

Sorbent	Maximum CO_2 capacity (mg CO_2/g sorbent)	Maximum CH_4 capacity (mg CH_4/g sorbent)	Experimental conditions (P,T)	Process scale	Key strengths	Main Drawbacks
DD3R nano zeolite (Himeno et al., 2007)	123	26.6	3MPa, 273-348 K	Lab scale	• High selectivity for CO_2. • 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 (Jiang et al., 2013)	176.4	--	0.1 MPa, 288 K	Lab scale	• Potential application in the natural gas purification process. • Recyclability • Applicability for post-combustion CO_2 separation.	• More than 100h to synthesize the T-type zeolite. • Decrease of the adsorption capacities with increasing temperature from 288-313 K.
Zeolite NaA nanocrystals (Shakarova et al., 2014)	215.6	--	0.1 MPa, 293 K	Lab scale	• Use of a cost-effective method for the synthesis of highly active nanosized zeolites. • 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 (Liu et al., 2006)	--	412	<7MPa, 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-	347.6	--			• Inexpensive material	• Lack of the selectivity factor for

mesoporous silica (Qi et al., 2011)			P_{atm}, 348 K	Lab scale	• Can be regenerated • Easy to operate • Fast CO_2 adsorption kinetics	both CO_2 and H_2S
TRI-PE-MCM-41 (Belmabkhout et al., 2009)	112.6	--	0.1 MPa, 298 K	Lab scale	• Potential application in purification of biogas • Separation of biogas	• Low CH_4 adsorption
MOF-177	a) 1452 (Millward and Yaghi, 2005) b) 396.9 (Saha et al., 2010)	c) 220.3 (Saha et al., 2010)	a) 4.5 MPa, RT b) 1.4MPa, 298 K c) 10 MPa, 298 K	Lab scale	• High thermal stability • Extra high porosity • High adsorption capacity at elevated pressures • Easily tunable pore and chemical characteristics.	• Negatively impacted by NOx, SOx, and H_2O. • Low selectivity in CO_2/N_2 gas streams. • Lack of experimental data on performance after multiple cycles. • Desorption approaches have not been adequately researched. • Chemical instability upon time. • High pressures
MOF-5 (Saha et al., 2010)	480	171.5	1.4 MPa for CO_2, 10MPa for CH_4; 298 K	Lab scale		
Ni_2(dhtp) MOF (Wu et al., 2009a)	--	283.4	3.5 MPa, 298 K	Lab scale		
Mg_2(dhtp) MOF (Wu et al., 2009a)	--	363	3.5 MPa, 298 K	Lab scale		
IRMOF-6 (Düren et al., 2004)	--	409	3.500 MPa, 298 K	Lab scale & Simulation		

Material					Advantages	Disadvantages
MgO/SBA-15 (Bhagiyalakshmi et al., 2010)	80	--	Patm, 298 K	Lab scale	• Thermally stable NPs. • Can be regenerated. • High selectivity to CO_2 • Can be used in different technologies applications for CO_2 separation.	• Slight decrease of surface area and pore volume.
CaO nanopods (Yang et al., 2009)	770	--	Patm, 873 K	Lab scale	•Can be regenerated during 50 cycles • Better than commercial CaO	•High temperatures
Fe_2O_3 on AC (Hakim et al., 2015)	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 (Kang et al., 2015)	67.8	12	Patm, 273 K	Lab scale	• 70% and 90% higher than non-modified MW-CNTs • Increase the CO_2 adsorption enthalpy	
APTS-CNTs (Lu et al., 2008)	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 (Mishra and Ramaprabhu,	2640	--	1.1 MPa, 298 K	Lab scale	•Easy synthesis •Can be reused	•High pressures

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2014)						
Graphene (Mishra and Ramaprabhu, 2011)	950.4	--	1.1 MPa, 298 K	Lab scale	•High adsorption capacity compared to other carbon nanostructures. •Possible use for industrial applications	•High pressures

1094   Patm: atmospheric pressure

Figure Captions

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1097 **Figure 1.** CO_2 uptake capacity using porous carbon materials templated from
1098 zeolite [where CEMFAET is the free N-sample, and CEM700, CEM750, and CEM800
1099 are the N-doped samples prepared at chemical vapor deposition temperatures of 700,
1100 750, and 800 °C, respectively] (Xia et al., 2011).

1101 **Figure 2.** Adsorption capacities of CO_2, CH_4, N_2O, and N_2 using MOF-5, MOF-
1102 177, and zeolite 5A at 298 K and 0.1 MPa (Saha et al., 2010).

1103 **Figure 3.** Comparison of the total gravimetric and total volumetric adsorption
1104 capacities of CH_4 at 10 MPa and at 298 K (adapted from Mason et al., 2014).

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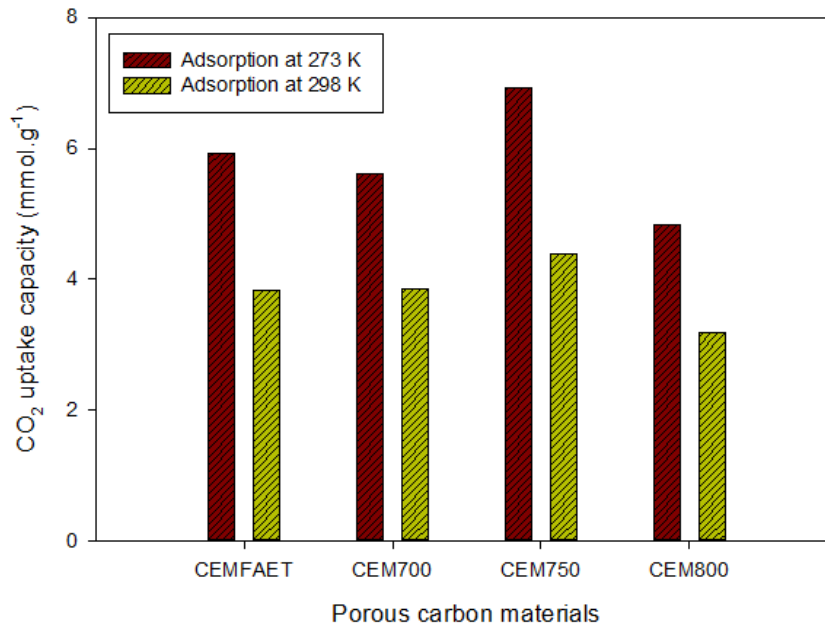
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1127 **Figure 1**

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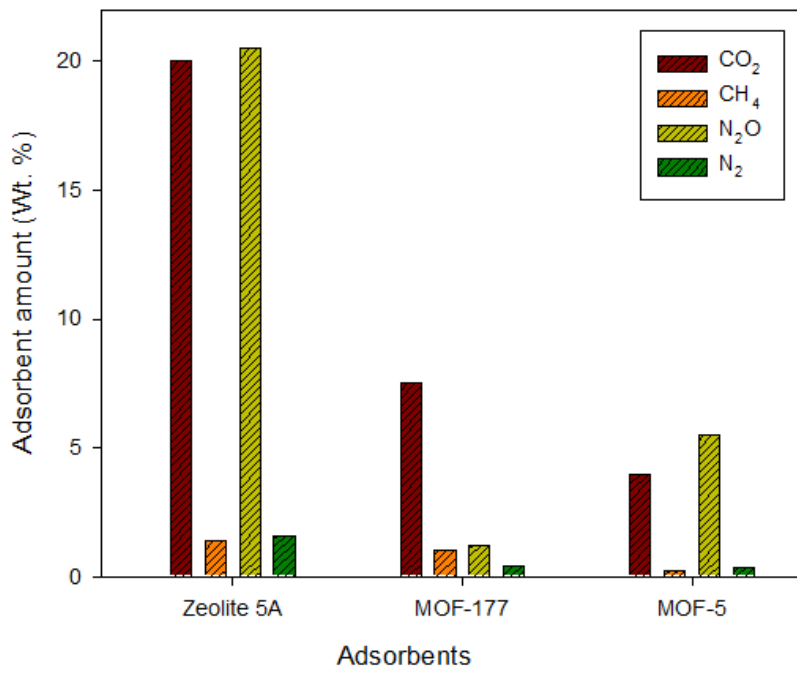1138

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1147   **Figure 2**

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1167   **Figure 3**

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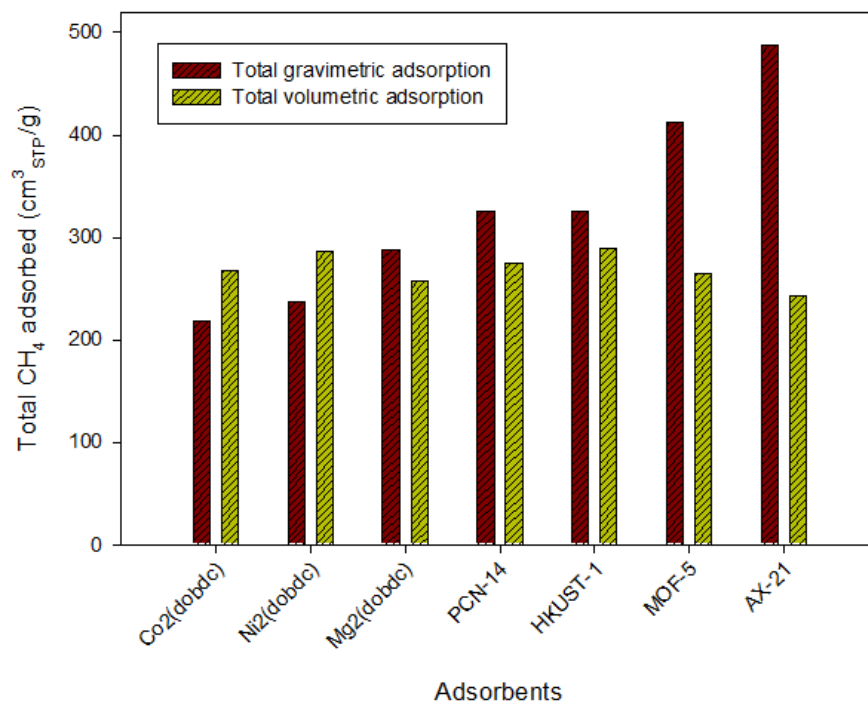1173

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