Historical perspective

Gas adsorption properties of graphene-based materials

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Abstract

Clean energy sources and global warming are among the major challenges of the 21st century. One of the possible actions toward finding alternative energy sources and reducing global warming are storage of H2 and CH4, and capture of CO2 by using highly efficient and low-cost adsorbents. Graphene and graphene-based materials attracted a great attention around the world because of their potential for a variety applications ranging from electronics, gas sensing, energy storage and CO2 capture. Large specific surface area of these materials up to ~3000 m2/g and versatile modification make them excellent adsorbents for diverse applications. Here, graphene-based adsorbents are reviewed with special emphasis on their adsorption affinity toward CO2, H2 and CH4. This review shows that graphene derivatives obtained mainly via “chemical exfoliation” of graphite and further modification with polymers and/or metal species can be very effective sorbents for CO2 and other gases and can compete with the currently used carbonaceous or non-carbonaceous adsorbents. The high adsorption capacities of graphene-based materials are mainly determined by their unique nanostructures, high specific surface areas and tailorable surface properties, which make them suitable for storage or capture of various molecules relevant for environmental and energy-related applications.

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CO2 adsorption
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1. Introduction

In 1986 Boehm et al. [1] named a single graphite layer as graphene; the word graphene is a combination of the word graphite and the termination “ene” relating to polycyclic aromatic hydrocarbons. Due to the two-dimensional structure and band gap equal to zero, a single layer of graphene is almost transparent (transmittance 97.7%). Each additional layer reduces the transmittance value by about 2.3% [2]. Furthermore, a very high concentration of charge carriers (~1013 1/cm2) [3] and their extraordinary high mobility (15,000 cm2/Vs) make graphene an excellent material for electronic and optoelectronic applications [4]. It is speculated that the mobility could be enhanced to the value of 100,000 cm2/Vs [5]. High conductivity and the quantum Hall effect observed even at room temperature are characteristic features for graphene [6–8]. Graphene is undoubtedly one of the most durable materials in the world. Its Young’s modulus is equal to 1 TPa, which is five times higher than that of steel, 0.2 TPa [9].

A wide range of potential graphene applications includes computer industry to replace silicon in a new generation processors. Other possible electronic applications of graphene/graphene-based materials are touch screens, nanotransistors, microprocessors, LED—including
so-called flexible electronics. Besides electronic applications of graphene other its uses include: energy storage (supercapacitors, batteries, fuel and solar cells) [10–13], filters, adsorbents and detectors. Due to its high aspect ratio and unique physicochemical properties graphene is extremely valuable component for the development of various composite materials [14,15]. Also, it can be used in medicine, e.g., anticancer therapy, and as a drug carrier or bactericidal material [16,17]. Graphene is a potential material for aviation, automotive and aerospace industry applications. Also, possible military applications of graphene are very interesting, such as energy weapon defense (hybrid broadband absorbers), as a component of hydrophobic ballistic materials, static and dynamic camouflage systems and more.

Theoretical specific surface area of a single, defect free graphene sheet is equal to 2630 m²/g [18]. A three-dimensional porous graphene material could have the specific surface area even higher, which promises highly effective gas storage, especially hydrogen. The structures shown in Fig. 1 can possess the interlayered distances ranging from 0.7 nm to 1 nm [19]. Ganesan and Shajumon [20] synthesized graphene porous materials with the BET specific surface area of 3240 m²/g and total pore volume of 2.23 cm³/g. A similar specific surface area of 3355 m²/g has been obtained for a 3D graphene sample reported by Zhang et al. [21].

In general, porous graphene materials are very interesting because of their unique physicochemical properties such as high surface area, well-developed porous structure, possible modifications, and high thermal stability [20–22]. In addition, physical or chemical activation can be used to further develop their porosity [20–26]. Chemical activation is often used because it can be effectively performed at lower temperatures than those used in physical activation [23,27]. The latter is carried out at higher temperatures (600 °C–1200 °C) in the presence of CO₂, steam, air or a mixture of these gases. Chemical activation process involves mixing a carbonization product with activating agents such as NaOH, KOH, H₃PO₄, ZnCl₂ [23,28] followed by heating to a temperature between 450 °C and 900 °C under inert atmosphere. A combination of both methods known as physicochemical activation has been also applied [23]. The mechanism of KOH activation of graphene materials is analogous to that reported for porous carbons [29–31].

Experimental studies of gas adsorption on graphene oxide (GO) and reduced graphene oxide (rGO) materials published so far indicate that the CO₂, H₂ and CH₄ uptakes on GO and rGO are rather low. One of the possible ways to enhance adsorption properties of graphene materials is the enlargement of their surface area by activation, for instance by using KOH activating agent as indicated above. Activation of graphene generates a three-dimensional structure composed of interconnected and strongly defected graphene sheets with large surface area that is needed for boosting adsorption of gases. Activated reduced graphene oxide (a-rGO) showed H₂ uptake of 7.04 wt% at −196 °C and 40 bar [32]. Also, another activated graphene material, a-GDC (activated graphene-derived carbon) exhibited impressive adsorption properties: 3.8 wt% H₂ at −196 °C under 10 bar and 11.3 mmol/g CH₄ at room temperature and 35 bar [20]. In the case of methane and carbon dioxide adsorption, the presence of suitable micropores seems to be more important than surface area. For example, one of the best graphene-based adsorbents for CO₂ under ambient conditions (4.3 mmol/g) was highly microporous activated polymer-modified rGO [25]. Nevertheless, syntheses of these materials have some inherent drawbacks, especially related to the usage of harsh chemicals for activation, which is unfavorable from both environmental and economic viewpoints. Graphene can be also quite easily functionalized. Various approaches have been adopted for modification of graphene sheets. A lot of attention gained graphene doping with heteroatoms and its decoration with metal nanoparticles, which are used to generate various active sites for specific adsorption and chemisorption to increase the overall gas uptakes. For instance, Pd-decorated nitrogen-doped reduced graphene oxide (Pd/N/rGO) showed high H₂ adsorption capacity of 4.4 wt% at room temperature and 40 bar [33]. Unfortunately, a disadvantage of this composite sorbent is the use of expensive noble metal nanoparticles. Thus, further efforts toward development of effective and inexpensive graphene-based sorbents would be desirable. This review provides a critical appraisal of the existing literature on gas adsorption properties of graphene-based materials. Also, a brief comparison of adsorption properties of these materials is provided in relation to other kinds of sorbents such as conventional activated carbons and metal-organic frameworks.

2. Graphene-based adsorbents

Graphene-based materials have been extensively explored as adsorbents for removal of environmental pollutants e.g., heavy metal ions.

**Fig. 1.** Structural models of perforated graphene materials. Top: an example of 3D porous material (stacking of perforated graphene sheets). Bottom: different patterns of defected graphene sheet. [Reprinted with permission from reference [19]; copyright © 2015 Elsevier Inc.]
(Hg$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Co$^{2+}$, Cr$^{6+}$, As$^{3+}$, As$^{5+}$) [34–38], dyes [39–41], inorganic anionic pollutants [42,43], organic pollutants (pesticides, phenolic compounds, polycyclic aromatic hydrocarbons) [44–47] from water, and gaseous air pollutants (CO$_2$, CO, NH$_3$, SO$_2$, H$_2$S, C$_6$H$_6$, C$_2$H$_5$OH) [48–55]. Also, graphene-based materials have attracted a lot of attention as potential energy storage materials [33,53,56,57].

Adsorption efficiency of a material is primarily determined by nanoporous structure, specific surface area and presence of active sites (functional groups, heteroatoms). For example, physisorption of NH$_3$ under standard conditions takes place mainly in pores of similar sizes to the size of NH$_3$ molecule (0.3 nm); consequently, an effective adsorbent should have ultramicropores. Furthermore, functional groups attached to its surface can increase the adsorbed amount of NH$_3$ via specific interactions such as acid-base interactions and complexation [48,49,58].

There are two main strategies to obtain graphene-based materials: exfoliation of graphite through overcoming weak van der Waals forces or the use of alternative forms of carbons. The former strategy usually involves oxidation of graphite to obtain graphite oxide, its exfoliation to graphene oxide (GO) followed by reduction giving the reduced GO (rGO) [see review [59] and references therein]. Note that the exfoliated GO is often used to prepare hybrid/composite materials that are efficient gas adsorbents.

“Chemical exfoliation” of graphite is a relatively simple and inexpensive method for preparation of graphene oxide (GO) that can be further modified by doping with various heteroatoms, decorated with various inorganic and/or organic species, and/or activated as shown in Fig. 2 [60]. Multilayer GO is a stack of defected layers (<10) with interlayer distances that are typically in the range of 0.34 nm to 0.4 nm [61]; whereas the distances between graphite oxide layers are in the range from 0.6 nm to 1.2 nm depending on the humidity, which affects the intercalation of water molecules [62]. Graphite oxide is hydrophilic and able to create stable aqueous suspensions. The oxidized graphite layers dispersed in water have negative surface charge. Dry graphite oxide has dark brown color caused by the presence of many, covalently attached functional groups: OH, C—O—C, C=O and COOH [56,63,64]. For details on the preparation of graphene-based adsorbents one is encouraged to look at review articles [65,66] and the references therein.

3. CO$_2$ capture

There is a great interest in the development of new, efficient and cost effective methods for capture of CO$_2$ and other greenhouse gases in the era of rising energy demand [67]. The average CO$_2$ concentration in atmosphere was 315 ppm in 1958, 354 ppm—30 years later in 1990, and 400 ppm—in 2015 [68]. Therefore, the reduction of emissions of greenhouse gases is needed and can be achieved by replacing fossil fuels with other energy sources, such as hydrogen or methane.

One of the most common industrial CO$_2$ capture system uses aqueous amines such as monoethanolamine (MEA) as absorbers. A viable alternative to this energy-consuming system are technologies employing solid adsorbents for CO$_2$ capture. If the working capacity of an adsorbent approaches or exceeds 3 mmol/g of CO$_2$, then the required energy for post-combustion capture would be reduced by 30–50% as compared with amine absorption [69]. Therefore, the current research in this area is focused on five different classes of materials for CO$_2$ capture from flue gases: activated carbons, graphene-based materials, zeolites, hydroxalicates (known as layered double hydroxides, LDHs) and metal-organic frameworks (MOFs). Although MOFs can be easily prepared with desired properties, their synthesis requires complex organic linkers, and the resulting materials are often susceptible to degradation under humid conditions, which make them less suitable for industrial CO$_2$ capture. In contrast activated carbons as well as graphene-based adsorbents are stable under such conditions and can be easily regenerated and reused. Also, their activation allows for fine tuning their microporosity and surface area.

Numerous experimental studies proved that porous solids can be highly useful for CO$_2$ capture [70–101]. Especially, carbonaceous solids with pores smaller than 0.7 nm (ultramicropores) are most effective for CO$_2$ adsorption at atmospheric pressure [84]. At higher pressures
CO₂ is also adsorbed in supermicropores (0.7–2 nm). It is well known that the CO₂ adsorption capacity decreases drastically with increasing temperature. Therefore, there is a great interest in the design of sorbents with high affinity and selectivity toward CO₂. This can be achieved by developing porous networks with large volume of suitable micropores, modifying their surface chemistry and/or forming hybrid/composite sorbents.

The most popular graphene material—reduced graphene oxide (rGO) in a powder form, is a stack of defected graphene sheets. Usually the CO₂ adsorption capacity of rGO obtained by simple thermal/chemical reduction of GO is lower than 1.5 mmol/g at ambient conditions [70], while a hydrothermally reduced GO adsorbs up to 2.4 mmol/g at 0 °C and ambient pressure [99]. Graphene sheets known as HEG are obtained by thermal exfoliation of graphite oxide at ~200 °C under hydrogen atmosphere. The exfoliated-reduced graphene oxide materials exhibit high CO₂ adsorption capacities at high pressures; for instance, 21.6, 18 and 12 mmol/g at 11 bar and 25, 50, 100 °C, respectively [72,73]. This capacity can be further enhanced by heteroatom doping. Oh et al. [70] performed a comparative study of CO₂ adsorption properties of rGO and boron-doped rGO (B/rGO). The doping of boron atoms improved the adsorption properties from ~1.3 mmol/g to ~1.8 mmol/g at room temperature and 1 atm pressure. The calculated isosteric heat of CO₂ adsorption for B/rGO was in the range from 31.6 kJ/mol to 3.5 kJ/mol. Computer simulations showed that the adsorbed CO₂ molecules assume a parallel orientation toward pristine graphene sheets. For an optimized configuration, the distances between CO₂ and pristine graphene sheets are 0.345–0.361 nm, which is typical for van der Waals interactions (Fig. 3) [70].

It is generally known that introduction of nitrogen atoms into carbon-based structures improves the CO₂ adsorption properties mainly due to the acid-based interactions. Different methods have been reported to prepare nitrogen-doped graphene materials, such as post-synthetic ammonia treatment and the most popular is direct synthesis with usage of nitrogen-containing precursors. To the best of our knowledge, one of the most efficient CO₂ adsorbents reported so far is the PANI/HEG (polyaniline/hydrogen exfoliated graphene) nanocomposite [71]. This material adsorbed 75 mmol/g of CO₂ at 25 °C and 11 bar (Fig. 4), almost 3.5 times more than unmodified HEG (21.6 mmol/g). FTIR (Fourier Transform Infrared) spectroscopy was used to identify physicochemical CO₂ capture by PANI/HEG. The FTIR spectrum in Fig. 5 shows two peaks at 1384 and 1751 cm⁻¹, which confirm chemical interactions of CO₂ molecules with nitrogen containing groups of the material. While the presence of low intensity peak at 2333 cm⁻¹ indicates that also physical adsorption of CO₂ took place (Fig. 5). The PANI/HEG sorbent showed good cyclability; namely, the capacity of reused sorbents was only 2–3% lower than that of the fresh sorbent.

Another highly efficient CO₂ adsorbent is reduced graphene oxide containing Fe₃O₄ nanoparticles (Fe₃O₄/HEG) [72]. Despite small values of the basic porous structure parameters (specific surface area = 98 m²/g, pore volume = 0.31 cm³/g) this material showed high CO₂ capture capacity of 60 mmol/g, 35 mmol/g and 24 mmol/g of CO₂ at 11 bar and 25 °C (Fig. 4), 50 °C and 100 °C, respectively. These CO₂ uptakes are higher than those obtained for HEG (hydrogen exfoliated graphene), having four time higher specific surface area (443 m²/g) [72]. This fact indicates chemical interactions between CO₂ molecules and Fe₃O₄ nanoparticles, as confirmed by FTIR spectroscopy. Fe₃O₄/HEG nanocomposite featured mesopores with average pore diameter of about 3.8 nm. Thus, the aforementioned high uptake was mainly achieved due to its specific interactions with CO₂. One should note that in the case of strong specific interactions chemisorption can take place, which is irreversible process that may strongly affect cyclability of the sorbent studied. This issue was not discussed in [72], thus further studies on the feasibility of Fe₃O₄/HEG for CO₂ capture would be desirable.

Metal-organic frameworks (MOFs) are composed of metal ions/clusters and coordinating organic linkers, which create porosity in the MOF structures. MOFs were shown to be effective materials for gas storage and gas separation. For instance, Furukawa et al. [74] demonstrated that MOFs have a great potential as adsorbents for CO₂ capture. One of the best MOF samples showed the CO₂ uptake of 54.5 mmol/g at room temperature and 50 bar pressure. Despite high applied pressure, the material did not reach CO₂ capture capacities of the polymer/metal oxide modified graphene materials (up to 75 mmol/g at 11 bar) [71,72]. Huang et al. [75] reported the synthesis of a composite adsorbent consisting of MOF and reduced graphene oxide (Cu-MOF/rGO-1) (Fig. 6). This composite showed high CO₂ capture at ambient conditions (8.19 mmol/g) (Fig. 7a) and also good CO₂/CH₄ selectivity. The Cu-MOF/rGO material contained only 1 wt% of rGO and had a specific surface area of 1677 m²/g. Similar CO₂ adsorption properties were reported for a Cu-MOF/rGO-2 nanocomposite (8.26 mmol/g) having 9 wt% of rGO [76]. For comparison, Cu-MOF without rGO showed CO₂ adsorption capacity of 7.23 mmol/g under the same conditions [77]. These data indicate that even a relatively small amount of rGO in the rGO-MOF composite is beneficial for CO₂ sorption. Recently, Xu et al. synthesized rGO and Cu-MOF composite (Cu-MOF/rGO-3) with high CO₂ adsorption capacity of 9.02 mmol/g at 1 bar and 0 °C and CO₂/N₂ selectivity of 186 [78]. A thorough analysis of the composite indicated the existence of narrow slit-like micropores, which are beneficial for adsorption of small gas molecules. MOF materials selectively absorb some species thanks to the presence of specific functionalities. Many different metal-ligand combinations have been reported so far. A proper coupling of the MOF

![Fig. 3. Distances between adsorbed CO₂ and pristine graphene sheet.](Adapted with permission from reference [70]; copyright © 2014 Elsevier Inc.)

![Fig. 4. CO₂ adsorption isotherms measured on PANI/HEG and Fe₃O₄/HEG materials at 25 °C.](PANI/HEG adapted with permission from reference [71]; copyright © 2012 Royal Chemical Society; and Fe₃O₄/HEG adapted from reference [72]; copyright © 2014 AIP Publishing LLC)
structures with graphene sheets or other carbon-based materials such as fullerenes, carbon nanotubes could be the key to obtain hybrid materials with desired porosity, surface functionality and excellent adsorption properties [79,80]. MOFs and their composites with graphene oxide can exhibit better CO₂ adsorption properties at ambient conditions than graphene materials alone.

Hybrid materials consisting of graphene and polymers were shown to be good CO₂ adsorbents under ambient conditions too (25 °C, 1 bar) [25,26,77,82]. Chandra et al. [25] reported a chemically activated polypyrrole/reduced graphene oxide nanocomposite (a-PPy/rGO). The nitrogen-containing polymer was added to GO solution at the mass ratio of 4:1. The nanocomposite had CO₂ capture capacity of 4.3 mmol/g under ambient conditions (Fig. 7b). Nitrogen doping also highly improves the CO₂/N₂ selectivity of carbon materials. The aforementioned a-PPy/rGO material showed high selectivity of CO₂ over N₂ of 34 at 25 °C calculated from the ratio of the initial slopes CO₂ and N₂ isotherms. In addition, the adsorbent exhibited a good stability during cycling experiments (CO₂ adsorption was only 10% smaller after 9 cycles), which is highly important for industrial applications. Similar CO₂ adsorption (4.13 mmol/g) was obtained for polyethyleneimine/graphene nanocomposite (PEI/G) [81]. These values are analogous to those obtained on microporous carbons prepared from different polymers such as polypyrrole, sulfonated styrene-divinylbenzene resin and so on. The best sample (polypyrrole-derived activated carbon, a-PPy/C) showed CO₂ uptake of 4.15 mmol/g and 6.88 mmol/g at 25 °C and 0 °C (1 bar), respectively (Fig. 7) [83]. Wickramaratne and Jaroniec [84] synthesized carbon spheres characterized by a large fraction of ultramicropores and high specific surface area (2284 m²/g), which adsorbed 4.55 mmol/g and 8.05 mmol/g of CO₂ at 25 °C and 0 °C (1 bar), respectively (Fig. 7a).

For comparison, carbon monoliths belong to the best adsorbents for CO₂ capture at ambient conditions. For instance, carbon molecular sieve monolith reported by Wahby et al. adsorbed 8.6 mmol/g under ambient conditions [85]. Porous N-doped carbon monolith prepared by Nandi et al. exhibited CO₂ uptake of 11.51 mmol/g at 0 °C and ambient pressure [86]. This nitrogen-doped monolith was synthesized by carbonization and CO₂ activation of mesoporous polyacrylonitrile monolith. The efficient CO₂ adsorbents possess micropores smaller than 1 nm, which are responsible for high CO₂ uptake at 1 bar. Despite the fact that many of the reported graphene materials had well developed porosity, the adsorbed amounts of CO₂ were relatively low under ambient conditions in comparison to the best carbons or MOFs.

As alternative CO₂ adsorbents, magnesium-aluminum layered double hydroxides (MgAl-LDHs) [87,88] have been used. LDHs are two dimensional nanostructured materials composed of M²⁺/(OH)₂ layers. Divalent cations are partially substituted by trivalent cations. Positive charge is compensated by anionic groups and water located in the interlayer space. Naturally charged LDHs structure can be described by the following formula: \( (M_2^{2+} - M_2^{3+} (OH)_2)^{x^-} (A_m^{m^-} - nH_2O)^{x^-} \), where M²⁺, M³⁺, A⁻ⁿ⁻ represent Mg²⁺, Al³⁺ and CO₃⁻, respectively. Addition of a small amount of graphene oxide separates the LDH layers via electrostatic interactions, increasing the specific surface area [89] and CO₂...
capture capacity. A nanocomposite containing Mg-Al-NO3 LDH and 6.54 wt% of GO showed twice better CO2 capacity than Mg-Al-NO3 LDH without GO. The CO2 capture capacity of such nanocomposite can be further increased up to 0.6 mmol/g at 200 °C and 1 atm by synthesizing material with 15 wt% of K2CO3 [88].

Table 1 summarizes various graphene-based CO2 sorbents reported in [20,25,70–72,75,76,81,82,88,90–101]. As can be seen from this table the CO2 uptake obtained for reduced graphene oxide at ambient conditions is rather low [70,96]. Although porous graphene structures show much higher CO2 uptakes at ambient conditions [96,99], they are still much lower as those obtained on microporous carbons including monoliths, which can exceed 11 mmol/g at 0 °C and 1 bar (see for instance data in [86]). However, graphene materials seem to perform well as CO2 sorbents at high pressures (e.g., see data in [20,90,91] and further studies in this direction would be desirable. Coupling graphene sheets with suitable polymers such as polypyrrole (PPy), polyethylenimine (PEI) and polyaniline (PANI) give higher CO2 uptakes at ambient conditions, which are comparable with the values obtained for microporous carbons (e.g., see data in [25,81,82]).

However, combining MOFs with GO seems to be useful because the CO2 uptakes at both ambient and high pressures are high (e.g., see data in [75,76,93,94]). No much data for CO2 sorption are available for hybrid materials composed of GO or rGO and metal oxides, although the reported CO2 sorption uptakes for hybrid sorbents consisting of metal oxides and GO or rGO at both ambient and high pressures (Table 1) are promising [72,95], which is encouraging finding for further studies of this type of systems. Overall, the CO2 uptakes summarized in Table 1 show that there are good prospects for the development of effective sorbents for CO2 sorption at both ambient and high pressures by combining graphene oxides with MOFs, functional polymers and metal oxide nanoparticles; therefore, further studies in this area would be desirable.

4. H2 Storage

Molecular hydrogen has very advantageous properties, which make it an important fuel in the near future. Hydrogen molecule consists of the lightest known element, has high combustion heat (per mass; about 3 times higher than liquid hydrocarbons such as gasoline) and its combustion product is only pure water. A major problem of using hydrogen as a fuel is related to its storage. Although hydrogen storage technologies for transport applications are already available, they require high density of stored fuel at the operating temperatures from 0 °C to 150 °C and respectively rapid load/unload of the storage systems. Hydrogen storage in solid materials has potential to surpass the densities of compressed hydrogen. It is worth noting that the efficiency of storage is predominantly measured by two parameters: the volumetric density—the stored hydrogen mass per unit volume of the system (kg H2/L system) and the gravimetric density—the weight of stored hydrogen per the total weight of the system, namely hydrogen + container (kg H2/kg system). The U.S. Department of Energy (DOE) has set targets, which are expressed in terms of both parameters. In the case of onboard hydrogen storage systems for light-duty fuel cell vehicles, the DOE targets projected on 2020 are: 0.040 kg H2/L system for the volumetric capacity,

![Figure 7. CO2 adsorption isotherms measured on a) various materials: Cu-MOF/rGO, a-Ppy/C and carbon spheres at 0 °C.
Cu-MOF/rGO adapted with permission from reference [75]; copyright © 2014 American Chemical Society; a-Ppy/C adapted from reference [83]; copyright © 2015 Oddział Doświadczalno-Polityczny Polskiego Zrzeszenia Inżynierów Techników Sanitarnych; and carbon spheres adapted from reference [84]; copyright © 2013 American Chemical Society; b) Chemically activated materials: a-Ppy/rGO and a-Ppy/C measured at 25 °C [a-Ppy/rGO adapted with permission from reference [25]; copyright © 2012 Royal Chemical Society].

Table 1. CO2 adsorption capacities of various graphene-based materials.

<table>
<thead>
<tr>
<th>Graphene material</th>
<th>Pressure, bar/temperature °C</th>
<th>CO2 adsorption, mmol/g</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>rGO</td>
<td>1/0</td>
<td>0.82</td>
<td>[96]</td>
</tr>
<tr>
<td>Spongy graphene</td>
<td>1.01/0</td>
<td>0.86</td>
<td>[100]</td>
</tr>
<tr>
<td>Nanoporous graphene</td>
<td>1.0</td>
<td>2.89</td>
<td>[96]</td>
</tr>
<tr>
<td>H2 exfoliated graphene</td>
<td>1/0</td>
<td>2.4</td>
<td>[99]</td>
</tr>
<tr>
<td>Graphene nanoplastes</td>
<td>30/25</td>
<td>56.4</td>
<td>[90]</td>
</tr>
<tr>
<td>Nanomesh graphene</td>
<td>31/1</td>
<td>31.1</td>
<td>[91]</td>
</tr>
<tr>
<td>Porous graphene framework</td>
<td>1.01/°78</td>
<td>25.45</td>
<td>[92]</td>
</tr>
<tr>
<td>N-doped graphene aerogel</td>
<td>1/0</td>
<td>2.57</td>
<td>[97]</td>
</tr>
<tr>
<td>3D interconnected GO</td>
<td>25/0</td>
<td>2.7</td>
<td>[27]</td>
</tr>
<tr>
<td>B-doped rGO</td>
<td>1/25</td>
<td>1.8</td>
<td>[70]</td>
</tr>
<tr>
<td>Polymerized ionic liquid/HEG</td>
<td>1/25</td>
<td>0.51</td>
<td>[101]</td>
</tr>
<tr>
<td>PANI/HEG</td>
<td>11/25</td>
<td>75</td>
<td>[71]</td>
</tr>
<tr>
<td>PANI/GO</td>
<td>1.01/25</td>
<td>2.7</td>
<td>[82]</td>
</tr>
<tr>
<td>PEI/C</td>
<td>1.01/25</td>
<td>4.13</td>
<td>[81]</td>
</tr>
<tr>
<td>3D PEI/GO</td>
<td>1/0</td>
<td>2.54</td>
<td>[98]</td>
</tr>
<tr>
<td>a-Ppy/rGO</td>
<td>1.25</td>
<td>4.3</td>
<td>[25]</td>
</tr>
<tr>
<td>Polyindole-modified GO</td>
<td>1.01/25</td>
<td>3.0</td>
<td>[26]</td>
</tr>
<tr>
<td>ZIF/N/rGO</td>
<td>1.01/25</td>
<td>3.55</td>
<td>[95]</td>
</tr>
<tr>
<td>Fe3O4/HEG</td>
<td>11/25</td>
<td>60</td>
<td>[72]</td>
</tr>
<tr>
<td>Cu-MOF/rGO-1</td>
<td>1/0</td>
<td>8.19</td>
<td>[75]</td>
</tr>
<tr>
<td>Cu-MOF/rGO-2</td>
<td>1.01/0</td>
<td>8.26</td>
<td>[76]</td>
</tr>
<tr>
<td>MIL/GO</td>
<td>25/25</td>
<td>22.4</td>
<td>[93]</td>
</tr>
<tr>
<td>ZIF/GO</td>
<td>1/01/78</td>
<td>16.36</td>
<td>[94]</td>
</tr>
<tr>
<td>LDH/GO</td>
<td>1/200</td>
<td>0.6</td>
<td>[88]</td>
</tr>
</tbody>
</table>

and 0.055 kg H₂/kg system for the gravimetric capacity, which correspond to the net useful energy per system mass of 1.8 kWh/kg [102]. Physical H₂ adsorption, which take place on nanoporous carbon materials is advantageous due to reversibility of the process and good adsorption kinetics. Hydrogen gravimetric uptake plotted against the specific surface area shows an approximately linear relation for various adsorbents due to the weak physical interaction between H₂ and solid surfaces. A disadvantage of H₂ physisorption is that low temperatures (−196 °C) and high pressures are usually required to store sufficiently high quantities of this gas. Therefore, to achieve a reasonable storage of H₂ by physisorption the aforementioned conditions are required. Chemisorption in turn relay on the chemical binding, which seems to be more suitable for storage and transport of hydrogen for longer time. In this case, higher temperatures are required as compared to physisorption.

Adsorption properties of various solids including graphene-based materials in relation to H₂ storage have been broadly studied [103–126]. The volumetric density is not well defined for a single graphene layer, thus the estimation of hydrogen storage capabilities should be considered for multilayer or three-dimensional graphene structures. The maximum gravimetric density achievable by chemisorption in a graphene layer is calculated to be 8.3 wt%, corresponding to a completely saturated graphene sheet with one hydrogen atom per carbon atom (graphene) [103,104]. The simulated adsorption isotherms in carbon slit-like pores suggest the maximum excess uptake of about 8 wt% at −196 °C and 40 bar for an optimal spacing between graphene layers of about 2 nm [105].

Experimental studies of H₂ adsorption on a so-called “pristine single-layer graphene sheet” (the specific surface area of 156 m²/g) show that the adsorption capacities are rather small, i.e., about 0.4 wt% and 0.2 wt% at 77 K under 1 bar and at room temperature under 60 bar, respectively [124]. Graphene materials prepared by thermal exfoliation of graphite oxide exhibit hydrogen uptakes of about 3.1 wt% (in the case of single-layer graphene) at 25 °C and 100 bar [106]. In contrast, graphene nanosheets obtained by reducing the exfoliated graphite oxide with glucose showed the relatively high hydrogen storage capacity of 2.7 wt% at 25 °C and 25 bar. This material possessed the specific surface area of 1206 m²/g [107]. In order to enhance H₂ adsorption properties of graphene and graphene derivatives various approaches including functionalization and activation routes were proposed. One of the best H₂ adsorbents under broad range of pressures (−0–120 bar) is the chemically activated reduced graphene oxide (a-rGO) [32]. After additional activation of rGO with KOH, highly defected graphene layers formed a three-dimensional structure (Fig. 8). The H₂ uptake of 7.04 wt% was obtained for this material at −196 °C under 40 bar [Fig. 9a] and 4.23 wt% at −80 °C under 120 bar. These enhanced adsorption properties were retained even after the prolonged air exposure (9 days) and were reversible for several cycles. The reported activated rGO (a-rGO) featured high specific surface area BET of 3230 m²/g and extraordinarily high pore volume of 2.22 cm³/g, which are superior values as compared to other carbon materials.

Ganesan and Shajuomon [20] synthesized a highly porous activated graphene-derived carbon (a-GDC), which exhibited the H₂ uptake of 3.82 wt% at relatively low pressure conditions (10 bar) and cryogenic temperature (Fig. 9b). Description of this a-GDC material can find in the next paragraph. In contrast, an activated polymer-based carbon and a MOF material exhibited similar hydrogen uptakes of 3.75 wt% and 2.54 wt%, respectively, at −196 °C but under ambient pressure instead of 10 bar [108,109] (Fig. 9b). Yushin et al. [110] suggested that the pore size of 0.6 nm could be the most optimum for hydrogen storage.

Under high pressures (20 bar) MOFs (MOF-174-Mg) reported by Oh et al. [111] featured the excess hydrogen storage capacities of 4.33 wt% and 0.15 at wt% −196 °C and 25 °C, respectively. The specific surface area (SSA) of MOF-174-Mg was 2470 m²/g. Another sample (MOF-184-Mg) had higher SSA (3150 m²/g) but slightly lower H₂ capacity (4.01 wt%) under the same conditions. The observed increase in SSA is probably a result of using longer linker during the synthesis. The both samples had the same usable H₂ capacities of 3.7 wt%, when loading was at −196 °C and 20 bar, unloading at −156 °C and 2 bar. One should note that under 10 bar (−196 °C) H₂ uptakes on MOF-174-Mg and a-GDC are quite similar (almost 4 wt%), but lower than that on a-rGO (−5 wt%, see Fig. 9) [20,32,111].

Nitrogen has an extra valence electron in comparison to carbon, thus introduction of nitrogen to pristine graphene increases local π-electron density. This asymmetry in the electron density enhances interactions

![Fig. 8. Scanning electron microscopy (SEM) images of the a-rGO material with the specific surface area of 3230 m²/g. The images a) and b) show hierarchical porous structure network; c) and d) images show the layered structure with the broken grain edges.](image-url)
between graphene and hydrogen by increasing the polarization of H₂ molecules. It was shown that heteroatoms such as nitrogen reduce hydrogen dissociation energy in the heteroatom-doped carbon nanotubes (CNTs) as compared to that of parent CNTs [112]. Nitrogen doping of graphene sheets enhances the hydrogen uptake capacity by 66% at 25 °C and 20 bar [33]. In the case of metal/metal oxide modifications, Hong et al. [113] demonstrated, that transition metal oxide nanoparticles wrapped with single- or few-layered graphene oxide nanosheets are better H₂ adsorbs than pristine transition metal oxide or graphene oxide (GO) alone. The aforementioned wrapping with GO causes an enhancement of the hydrogen storage capacity by about 1.2 wt% for V₂O₅/GO composite and by about 0.7 wt% for TiO₂/GO material at − 196 °C.

Decoration of graphene with transition metal nanoparticles can be crucial for the enhancement of the hydrogen uptake capacity. The metal catalyst can actively anchor hydrogen and reduce the activation energy barrier to dissociate H₂ molecules. After dissociation, the ejected hydrogen atoms have sufficient kinetic energy to migrate onto neighboring graphene sheets via surface diffusion (so-called spillover mechanism) [Fig. 10] [114]. Some transition metals such as Ti bind strongly with H atoms, which preclude their migration. Consequently, the nanoparticle is saturated with hydrogen atoms and becomes inactive for further accumulation of H₂. In contrast, transition metals like Pd or Pt bind H atoms relatively weakly allowing their migration onto graphene sheets. In that context, graphene-based materials decorated with Pt or Pd nanoparticles are reported to be very good adsorbents for H₂ storage. Recently, Zhou et al. [115] reported a Pd-decorated graphene material (1 at%) with a gravimetric density of 4.83 wt% at a hydrogen charging pressure of 40 bar and room temperature. Further, at 25 °C and 60 bar, this nanocomposite system was able to capture 8.67 wt% of H₂. Those values exceed the DOE target for 2020. The Pd nanoparticles had spherical shape and their size was in a range of 5−45 nm. For comparison, a Ni-decorated graphene material (5 at%) exhibited hydrogen gravimetric density of 1.2 wt% at 25 °C and 60 bar pressure [116].

However, decoration graphene with transition metal nanoparticles creates additional challenges such as poor reversibility and issues with structural stability of dispersed nanoparticles. Metal nanoparticles tend to aggregate easily due to strong metal cohesion forces. In the case of graphene these particles can be bonded to defects, edges and functional groups of graphene sheets, which effectively prevent their aggregation. For example, nitrogen doping of graphene sheets can cause stronger metal binding with defect sites and therefore, decreases possibility of metal-metal cohesion. Theoretical calculations show that also boron doping of graphene enhances the adsorption strength for both metal and H atoms on the graphene sheets. Therefore, the incorporated heteroatoms minimize the detachment of Pt nanoparticles and also can enhance adsorption of hydrogen on B-doped graphene under ambient conditions as compared with bare graphene [117]. High H₂ adsorption capacity under high pressures was observed for a Pd-decorated nitrogen-doped graphene material (Pd/N-rGO) [Fig. 9a] [33]. The maximum H₂ adsorption capacity for this material was 4.4 wt% at room temperature and 40 bar. This high capacity was possible due to the high dispersion of Pd nanoparticles as shown in Fig. 11a. The XRD spectra of this composite and related rGO samples show characteristic peaks for Pd and Pd nanoparticles (Fig. 11b). The dispersion of metal nanoparticles on graphene sheets is essential for efficient hydrogen storage on metal-decorated graphene. Contescu et al. [125] demonstrated that it is possible to obtain atomic dispersion of Pd on high surface area carbon materials. It was shown that in the presence of Pd catalyst, at high pressures and prolonged exposure to H₂, new bonds are formed between atomic hydrogen and unsaturated carbon atoms of the Pd-containing carbon adsorbents. Thus, the ability to stabilize Pd atoms on the monolayer or multilayer graphene can be utilized to further enhance H₂ adsorption properties of these materials [125–127]. In addition, Blanco-Rey et al. performed ab initio molecular dynamics simulations to analyze the validity of spillover mechanism for explaining the improvement of H₂ storage capacities in porous carbons doped with transition metal nanoparticles [128].

Table 2 presents a summary of H₂ adsorption properties for various graphene-based materials. A comparison of various materials ranging from graphene, GO and activated rGO to graphene-based composites with metal and metal oxides nanoparticles shows that the best H₂ capacities were reported for activated rGO samples [19,32] and rGO composites with incorporated Pd nanoparticles [33,115,118]. In both cases high pressures (about 40 bar) were used to achieve high values of H₂ adsorption; namely about 5.5−7 wt% of H₂ was adsorbed in activated rGO materials, and about 4.4−4.8 wt% in rGO composites with incorporated Pd nanoparticles. Note that higher percentages of adsorbed H₂ were obtained for activated rGO but at low temperatures (−196 °C), while still high percentages of H₂ were achieved for Pd-graphene composites at much higher temperature (25 °C). Although the latter system seems to be better suited for practical applications, its major disadvantage is the use of expensive noble metal (Pd) nanoparticles. Thus, further search for effective and inexpensive sorbents for H₂ adsorption would be desirable.
5. CH₄ storage

A continuous decrease of the easily accessible fossil fuels and climate change are nowadays important societal issues. One of the alternative energy sources is biogas [129]. For ecological use of this fuel, mainly composed of CH₄ and CO₂, it is necessary to develop an effective technique for CO₂/CH₄ separation [130,131]. In natural gas, CH₄ is about 90% with concentration of other contaminants of about 10 wt%; thus, to convert natural gas storage to CH₄ storage, a separation process is needed. Methane has 2.85 times higher heat value than fossil fuel. Moreover, the combustion of methane produces the smallest amount of carbon dioxide per unit of heat among all fossil fuels. Materials with high porosity and large surface areas are promising for CH₄ storage. The intermolecular forces between CH₄ molecule and an adsorbent are primarily induced by instant polarization because of high symmetry of CH₄ molecule. A key factor determining the interaction of CH₄ with the pore wall is the pore size. A large surface area of an adsorbent would result in high gravimetric CH₄ uptake, while high density is needed to achieve high volumetric CH₄ uptake. The packing density should be considered as one of the important factors for achieving high final volumetric storage capacities of materials. A drawback of any powdered storage medium is the packing density limitation: 0.3 g/cm³ for typical and 1 g/cm³ for an ideal bulk sample. The packing density calculated by compressing the powder represents the bulk density of the material.

The volumetric storage capacity is often estimated from the bulk density of non-monolithic materials, which results in unrealistic outcomes due to the voids in a powder packing. Furthermore, in many reports this capacity is calculated on the basis of single-crystal density. In practice, if there is no a structure change, the packing density is much lower that the crystal density. For instance, MOF materials are not very good for compressing because their structures can be damaged. Therefore, the volumetric capacity of methane storage is often estimated by using the packing density.

The Advanced Research Projects Agency—Energy (ARPA-E) of the U.S Department of Energy (DOE) indicates that the CH₄ storage values should be higher than 0.5 g (CH₄)/g (sorbent) for the gravimetric density and 12.5 MJ/L (sorbent) for the volumetric energy density in the range of temperatures between −40 and 85 °C for a vehicle in real applications [132]. Furthermore packing losses about 25% and the sorbent price <10 $/kg should be also taken into account [132]. Numerous works have been published on methane adsorption on solids, especially in recent years [133–158]. Peng et al. [133] estimated that the DOE gravimetric target could be reached by a MOF with apparent surface area of 7500 m²/g and pore volume of 3.2 cm³/g. Values of the structural parameters suggest that this MOF should exhibit 195 cm³ (STP)/cm³ (where cm³ STP refers to the volume of CH₄ at the standard temperature—0 °C and pressure—1 bar, per volume of the adsorbent). A commercially available MOF, known as HKUST-1, can reach the CH₄
Also, various porous adsorbents for CH4 are compared elsewhere [137, 138]. The porosity of the aforementioned graphene material was not optimized. The micropore volume is higher for carbon black. One should notice that micropore volume than that of graphene. In contrast, strong adsorption (chemisorption) for this type of synthesis is a high consumption of valuable gaseous hydrocarbons. Mahmoudian et al. [145] introduced a three-dimensional nanoporous graphene material (a-3D-G), which exhibited the CH4 adsorption capacity of 12.03 mmol/g at 25 °C and under lower pressure (35 Bar). The main carbon source of a-3D-G was bagasse powder obtained by calcination of raw bagasse. The specific surface area of 2720 m²/g and total pore volume of 1.45 cm³/g were obtained by KOH activation of graphene-based structure. Another efficient, chemically activated graphene-based CH4 adsorbent a-GDC (graphene-derived carbon) was obtained by Ganesan and Shaijumon [20]. The material adsorbed 11.3 mmol/g of CH4 at room temperature and 35 Bar. Besides the molecule–graphene distance lower (0.206 nm) in comparison to the corresponding values obtained for pristine graphene. Kandagal et al. [141] predicted that the edge-functionalization of graphene can also promote adsorption of CH4.

Physiosorption of CH4 on modified graphene slightly depends on the orientation of methane molecules and the electronegativity of dopant atom as well. For instance, doping graphene with boron reduces adsorption energy of CH4, while nitrogen doping increases this energy [142]. However, more experimental studies in this area are needed to better understand adsorption properties of doped/decorated graphene materials. The measured methane adsorption capacity of an activated S-doped reduced graphene oxide was reported to be only 0.5 mmol/g at 0 °C and 1 bar [143], whereas nitrogen doping of graphene aerogel enhanced its CH4 uptake capacity from 1.4 mmol/g to 1.7 mmol/g at the same conditions [97].

At ambient pressure and 0 °C a graphene material named “graphene nanoribbon framework” exhibited rather low CH4 capture capacity of 0.72 mmol/g. That might be a consequence of comparatively low specific surface area (680 m²/g) as well as small micropore volume (0.16 cm³/g) [144]. To achieve higher values of adsorbed CH4, higher pressures are needed. Ning et al. [91] reported a “graphene nanomesh” material characterized by high CH4 volumetric total uptake of 200 cm³/(STP)·cm⁻³ (bulk density 0.4 g/cm³) and excess methane uptake of 14.8 mmol/g at 1 °C and under high pressure (90 bar). This material was synthesized by “chemical vapor deposition” (CVD) using porous MgO sheets as a template and had high specific surface area of 2038 m²/g with the micropore distribution centered around 1 nm. Moreover, when the bulk density of graphene nanomesh tablet was increased to 0.5–1.0 g/cm³ by pressing, the volumetric methane uptake capacity reached 236 cm³ (STP)/cm³ at 1 °C and 90 bar. A drawback of this kind of synthesis is a high consumption of valuable gaseous hydrocarbons.

Table 2

<table>
<thead>
<tr>
<th>Graphene material</th>
<th>Pressure, bar/temperature °C</th>
<th>H₂ adsorption, wt%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>100/25</td>
<td>3.1</td>
<td>[106]</td>
</tr>
<tr>
<td>Nanomesh graphene</td>
<td>91/1</td>
<td>1.53</td>
<td>[91]</td>
</tr>
<tr>
<td>Spongy graphene</td>
<td>1.01/– 196</td>
<td>0.48</td>
<td>[100]</td>
</tr>
<tr>
<td>Porous graphene framework</td>
<td>20/– 196</td>
<td>1.9</td>
<td>[92]</td>
</tr>
<tr>
<td>Graphene nanosheets</td>
<td>25/25</td>
<td>2.7</td>
<td>[107]</td>
</tr>
<tr>
<td>Graphene flakes</td>
<td>58/– 196</td>
<td>2.01</td>
<td>[122]</td>
</tr>
<tr>
<td>GO</td>
<td>1/– 196</td>
<td>1.7</td>
<td>[121]</td>
</tr>
<tr>
<td>Thermally reduced GO</td>
<td>50/– 196</td>
<td>2.07</td>
<td>[120]</td>
</tr>
<tr>
<td>Chemically reduced GO</td>
<td>50/– 196</td>
<td>0.54</td>
<td>[120]</td>
</tr>
<tr>
<td>Porous GO/diboronic acid</td>
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<td>0.8</td>
<td>[122]</td>
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<tr>
<td>Activated reduced GO</td>
<td>40/– 196</td>
<td>7.04</td>
<td>[92]</td>
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<tr>
<td>Activated reduced GO²</td>
<td>30/– 196</td>
<td>5.5</td>
<td>[19]</td>
</tr>
<tr>
<td>Activated graphene-derived carbon</td>
<td>10/– 196</td>
<td>3.82</td>
<td>[20]</td>
</tr>
<tr>
<td>N-doped rGO</td>
<td>40/25</td>
<td>1.74</td>
<td>[33]</td>
</tr>
<tr>
<td>Pt/HEG</td>
<td>30/25</td>
<td>1.4</td>
<td>[114]</td>
</tr>
<tr>
<td>Pd-decorated graphene sheets</td>
<td>40/25</td>
<td>4.8</td>
<td>[115]</td>
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<tr>
<td>Pd-decorated N-doped rGO</td>
<td>40/25</td>
<td>4.3</td>
<td>[118]</td>
</tr>
<tr>
<td>Pd nanoparticle N-doped rGO</td>
<td>40/25</td>
<td>4.4</td>
<td>[33]</td>
</tr>
<tr>
<td>Ni-B/G</td>
<td>1.06/– 196</td>
<td>2.81</td>
<td>[119]</td>
</tr>
<tr>
<td>Fe-decorated graphene sheets</td>
<td>50/– 196</td>
<td>2.16</td>
<td>[120]</td>
</tr>
<tr>
<td>Fe₃O₄/rGO</td>
<td>1/– 196</td>
<td>2.1</td>
<td>[121]</td>
</tr>
<tr>
<td>V₂O₅/rGO</td>
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<td>[113]</td>
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<td>1.26</td>
<td>[113]</td>
</tr>
<tr>
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<td>42.56/– 196</td>
<td>3.58</td>
<td>[76]</td>
</tr>
</tbody>
</table>

1, 2—KOH activated, thermally reduced graphene oxide (800 °C), respectively.

volumetric capacity of 267 cm³ (STP)/cm³ at 25 °C and 65 bar, when the single-crystal density is used for its calculation. However, the gravimetric capacity of the MOF was found to be low [133,134]. A big concern of this material is its poor mechanical stability. After mechanical compaction, both volumetric and gravimetric capacity of HKUST-1 are significantly decreased. Recently, Spanopoulos et al. [135] reported similar material (Cu-tbo-MOF), which showed high gravimetric and volumetric CH4 uptakes of 16.58 mmol/g and 221 cm³(STP)/cm³ (using crystal density 0.595 g/cm³), respectively, at 25 °C and 85 bar. This MOF was synthesized by using highly aromatic and rigid organic linker with intrinsic strong CH4 adsorption sites, its BET surface area reached 3971 m²/g. Zhu et al. [136] performed a comparative study of CH4 adsorption on typical carbon-based materials: graphene sheets, activated carbon and carbon black. This study shows that the adsorbed amount of CH4 does not proportionally change with the specific area of the adsorbent, e.g. at 0 °C and 20 bar. The absolute adsorption on the activated carbon was 6 mmol/g, in comparison with 1.25 mmol/g on the graphene sheets and 0.6 mmol/g on the carbon black at above conditions. However, the specific surface area of the activated carbon (1118 m²/g) was about 3.7 times and 14.6 times higher than that of graphene sheets (300 m²/g) and the carbon black (76 m²/g), respectively. Similar conclusion can be extracted by comparing the specific pore volumes of the adsorbents. Graphene sheets had larger specific pore volume than that of carbon black, but it did not result in greater storage per unit surface area, which is highest for carbon black. One should notice that microporosity of the aforementioned graphene material was not optimized. Also, various porous adsorbents for CH4 are compared elsewhere [137, 138].

Methane–graphene interaction was profoundly described by Thierfelder et al. [139]. The presented calculations indicate that a CH4 molecule is oriented with hydrogen tripod down about 0.33 nm above graphene sheet with the adsorption energy of 0.17 eV. Recently, Rad et al. [140] reported that the equilibrium graphene–methane distance of 0.31 nm and the corresponding adsorption energy of —11.5 kJ/mol, and confirmed weak interaction (physiosorption) between CH4 and graphene. In contrast, strong adsorption (chemisorption) for this molecule was reported after decoration of graphene with Pt, when CH4 molecule was placed above Pt atom on the graphene sheet. In this case, the calculated energy was about 4 times higher (~46.8 kJ/mol)
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this, a-GDC was shown to be also promising adsorbent for CO2 (21 mmol/g at 25 °C and 20 bar) and H2 (3.8 wt% at −196 °C and 10 bar). The well-developed porous structure of this material having the BET specific surface area of 3240 m2/g with highly interconnected network of micro- and mesopores (average pore size of 2.75 nm) can explain its excellent adsorption properties. Additionally the a-GDC material showed good adsorption/desorption kinetics and low heat of adsorption, which indicate van der Waals interactions between the adsorbent surface and gas molecules. The pore sizes of this type materials ranged from 1 nm to 4 nm, while the calculated optimum pore size for the most effective CH4 capture at ambient temperature and 35 bar was estimated to be about 0.8–1.2 nm [146,147].

Fig. 12 shows a comparison of the methane adsorption capacities of some activated graphene materials at 25 °C and 35 bar in relation to the corresponding average pore sizes and specific surface areas (SSA) [20, 145,158]. The structure parameters were calculated on the basis of low-temperature nitrogen adsorption isotherms. The effect of SSA on the CH4 uptake is not clearly visible, which can be due to the differences (such as the range of adsorption data) in the procedures used for the evaluation of the BET surface area. The same comment refers to the effect of pore diameter. However, based on the available adsorption data one can suggest that the size of pores seems to be more important factor than SSA. In the range of average pore diameters from ~2.0 to ~2.8 the graphene adsorbents shown in Fig. 12 exhibited similar CH4 adsorption capacities, ranging from ~10.9 to ~12.0 mmol/g, despite quite significant difference in their SSA (1900–3200 m2/g). In addition to the proper size of micropores, their large volume and a certain volume of mesopores are required to achieve high CH4 storage and efficient adsorption/desorption kinetics. The pore size distribution centered at around 1 nm enables accommodation of two or three CH4 molecules, resulting in high packing density of the adsorbed phase [146–148]. Casco et al. [148] calculated the density of methane in micropores and micro-mesopores at pressures up to 100 bar using experimental data, and indicated a significant effect of pores below 1–2.5 nm on the methane adsorption capacity of activated carbons at high pressures.

A comparison of methane adsorption for various porous materials such as activated carbons, MOFs and graphene materials in relation to their SSA was collated by Mahmoudian et al. [145]. In the case of MOFs a sort of saturation was reported for materials with SSA exceeding 3000 m2/g, which means that a further increase in SSA of MOFs (even up to 6000 m2/g) did not result in better CH4 adsorption properties. Nowadays, metal-organic framework (MOF) and reduced graphene oxide (rGO) porous composites attract more and more attention [49,50,78,145–158]. Methane adsorption is usually measured at high pressure conditions (>20 bar). One should notice that values of the adsorption

Fig. 13. SEM images of: a) MOF, b) MOF/rGO. [Reprinted with permission from reference [78]; copyright © 2016, Elsevier Inc.]

Fig. 14. CH4 adsorption isotherm measured on a) a-GDC and MIL/rGO materials at 25 °C and CH4 isotherm measured on zeolite 13X at 30 °C. [a-GDC adapted with permission from reference [20]; copyright © 2016, Elsevier Inc., MIL/rGO from reference [94]; copyright © 2015, Elsevier Inc., and zeolite 13X from reference [156]; copyright © 2016, Elsevier Inc.].

obtained at room temperature and 25 bar (Fig. 14). The simulation performed for this system showed high CO2/CH4 selectivity (15.0) at 1.5 bar for equimolar CO2 and CH4 mixture, while the experimental selectivity for a mixture composed of 10% CO2 and 90% CH4 was of about 32 at 1.5 bar.

Activated carbons are also considered as potential CH4 storage materials. For instance, activated carbons prepared from mesophasic pitch adsorbed up to 160 cm3(STP)/cm3 (packing density 0.62 g/cm3) at 25 °C under 35 bar [154]. A KOH-activated carbon exhibited 12.33 mmol/g at 20 °C and 50 bar [152]. A very high CH4 uptake of 10.25 mmol/g (147 cm3/cm3) at 25 °C and 20 bar was obtained for poly(vinylidene chloride)-based carbon, which is one of the best uptakes reported for activated carbons with high surface areas under relatively low pressures [153]. Other activated carbons were characterized by following CH4 adsorption properties: 9.34 mmol/g (130 cm3(STP)/cm3) and 8.62 mmol/g (120 cm3(STP)/cm3) at 25 °C and ~30 bar, respectively [154,155]. Zeolite 13X is often used as adsorbent because of its polar surface, high surface area and pore volume. The CH4 adsorption capacity of the zeolite 13X was shown to be ~2.8 mmol/g at 30 °C and 10 bar (Fig. 14); its CO2/CH4 selectivity was about 26 at 30 °C and 4 bar [156]. Table 3 shows a short summary of CH4 adsorption properties of various graphene-based materials. While adsorption of CO2 and H2 on graphene-based materials was quite extensively studied (see Tables 1 and 2), the number of reports on CH4 adsorption on these materials is smaller [20,75,76,91,93,97,100,143–145,157,158]. Methane adsorption is usually measured at high pressure conditions (> 20 bar). One should notice that values of the adsorption...
at ambient pressure are extracted from works devoted to gas separation. At high pressures graphene materials alongside MOFs are the most promising methane adsorbents for eventual commercial applications. For example, activated graphene derivatives show high CH4 uptakes up to 12 mmol/g at 25 °C and under 35 bar [145]. Further studies of CH4 adsorption on graphene-based materials are desirable, especially on activated graphene materials, which showed high uptakes for CO2 and H2.

6. Conclusions

The observed depletion of the available fossil fuels and the anticipated threat of global warming are among the major challenges in the coming years. Therefore, new and feasible solutions of these issues are of great importance. In particular, the development of cost-effective methods for using clean energy carriers such as H2, as well as CO2 effective capture and storage solutions are required. Reduced graphene oxide is potentially one of the promising candidates for the development of sorbents for efficient gas storage applications. The environmentally-friendly methods suitable for large-scale production of graphene-based materials with desired adsorption properties are needed for effective storage of energy-relevant gases and CO2 capture. The gas uptakes obtained for unmodified graphene oxides (GO or rGO) alone are rather low; however, a significant progress has been made in recent years in this area, especially in the development of new graphene-based composite materials toward improving their adsorption properties. Graphene oxides can be doped with heteroatoms (e.g., B, N, S) and decorated with polymers and nanoparticles (e.g., Fe, Pd, Fe3O4, V2O5). Furthermore, these two-dimensional (2D) nanosheets can be used to design and prepare 3D structures with large surface area and well-developed porosity. In the case of some metal- or metal oxide-decorated graphene materials, an enhanced chemisorption and/or specific gas adsorption may take place in addition to physisorption resulting in an enhanced sorption capacity. For instance, the best H2 capacities were reported for activated rGO samples and rGO composites with incorporated Pd nanoparticles. However, in both cases high pressures (about 40 bar) were used to achieve high values of H2 adsorption; namely, about 5.5–7 wt% of H2 was adsorbed on activated rGO materials, and about 4.4–4.8 wt% on rGO composites with incorporated Pd nanoparticles. In the case of CO2 uptake, graphene materials also seem to perform well at high pressures. Moreover, coupling graphene sheets with suitable polymers such as polypropylene or polyethylene give high CO2 uptakes at ambient conditions, comparable with those obtained for microporous carbons. Also, high CO2 and CH4 uptakes have been reported for composite sorbents prepared by combining metal-organic frameworks (MOFs) with GO. In general, graphene materials combined with MOFs are the most promising methane adsorbents. For instance, activated graphene derivatives reached CH4 uptakes up to 12 mmol/g under 35 bar. This review shows that CO2, H2 or CH4 graphene-based adsorbents often surpass other materials, especially at high pressure conditions. Although graphene materials have promising performance as gas capture/storage sorbents, further studies should be carried out toward development of these materials for commercial applications.

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