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Nanoporous Materials for the Onboard Storage of Natural Gas

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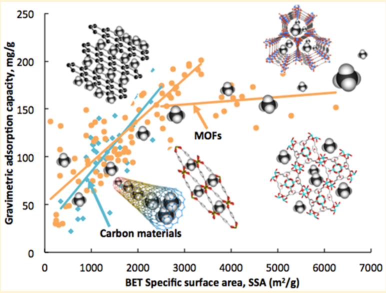
Supporting Information

ABSTRACT: Climate change, global warming, urban air pollution, energy supply uncertainty and depletion, and rising costs of conventional energy sources are, among others, potential socioeconomic threats that our community faces today. Transportation is one of the primary sectors contributing to oil consumption and global warming, and natural gas (NG) is considered to be a relatively clean transportation fuel that can significantly improve local air quality, reduce greenhouse-gas emissions, and decrease the energy dependency on oil sources. Internal combustion engines (ignited or compression) require only slight modifications for use with natural gas; rather, the main problem is the relatively short driving distance of natural-gas-powered vehicles due to the lack of an appropriate storage method for the gas, which has a low energy density. The U.S. Department of Energy (DOE) has set some targets for NG storage capacity to obtain a reasonable driving range in automotive applications, ruling out the option of storing methane at cryogenic temperatures. In recent years, both academia and industry have foreseen the storage of natural gas by adsorption (ANG) in porous materials, at relatively low pressures and ambient temperatures, as a solution to this difficult problem. This review presents recent developments in the search for novel porous materials with high methane storage capacities. Within this scenario, both carbon-based materials and metal−organic frameworks are considered to be the most promising materials for natural gas storage, as they exhibit properties such as large surface areas and micropore volumes, that favor a high adsorption capacity for natural gas. Recent advancements, technological issues, advantages, and drawbacks involved in natural gas storage in these two classes of materials are also summarized. Further, an overview of the recent developments and technical challenges in storing natural gas as hydrates in wetted porous carbon materials is also included. Finally, an analysis of design factors and technical issues that need to be considered before adapting vehicles to ANG technology is also presented.



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1. INTRODUCTION

The depletion of global oil reserves and concerns over climate change due to increasing CO_2 levels in the atmosphere prompt the need to find a new clean and abundant source of alternative energy for the future. A 2004 report from the European Union (EU) Commission stated that transportation is the main energy-consuming sector in the EU, accounting for 32% of energy use and 67% of final oil demand, as transportation is almost solely dependent on oil-derived products.[1] Projections in this report indicated that the EU dependence on imported oils might increase by 90% by 2020. According to this report, the per capita transport energy consumption increased in the EU at an annual average growth rate of 13% from 1990 to 2008. In 2008, road transport alone represented, on average, 81% of the total energy consumption in the transport sector, with cars representing almost 50% and road freight transport about 31%. Another EU report, from 2011, also mentioned that the CO_2 emissions from transportation increased by almost 24% from 1990 to 2008, with the transport sector alone representing 42%

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of total CO_2 emissions of final consumers.[2] Emissions from cars increased by 18% in the same period of time and, in 2008, contributed nearly 54% of the total emissions of the transportation sector. Projections indicate that CO_2 emissions due to transport alone grew by 50% between 1990 and 2007, with 90% of this coming from road transport.[3] Recently, the EU pledged in the Copenhagen Accord to reduce CO_2 emissions by 20−30% compared to the emission levels in 1990 by 2020.[4]

The type of fuel burned, combustion efficiency, and emissions of air pollution are intrinsically related. Finding a feasible and efficient alternative fuel source could solve both the oil import dependency, which threatens the diversified energy supply, and the environmental pressures from CO_2 and other emissions. In this sense, the Joint Research Centre of the European Commission suggested natural gas as a promising fuel for securing and diversifying the transportation energy demand in a more environmentally friendly way.[5] Natural gas has several advantages over conventional fuels, beginning with its availability and clean burning properties.[6,7] In terms of availability, statistical projections indicate that approximately 368 trillion cubic meters of natural gas could be recovered from all deposits of natural gas hydrate found worldwide.[8] Managing gas extraction of just 1% of these hydrate sources could flood the world with a clean-burning fuel thst yields, upon combustion, the lowest amount of greenhouse gases of any available fossil fuel.[8] Regarding the environmental impact of natural gas in vehicles, significantly lower amounts of harmful emissions such as NO_x, particulate matter, the greenhouse gas carbon dioxide, and toxic and carcinogenic substances (e.g., benzene and 1,3-butadiene) are released when compared to engines running on gasoline or diesel. A vehicle running on compressed natural gas (CNG) emits 70% less CO, 87% less non-methane organic gas, 87% less nitrogen oxide, and 20% less CO_2 than a vehicle running on gasoline.[9]

Additionally, a natural gas vehicle demands only slight modifications of the conventional spark- or compression-ignited engine, which can be realized with very little expense. Natural gas can be used in spark-ignited internal combustion engines, and such engines can be flexibly operated as dedicated engines (engines that run on only natural gas) or as bifuel engines.[10] Bifuel or dual engines are capable of running on two fuels, natural gas and gasoline, depending on the momentum and availability of the two fuels, switching back and forth from gasoline or diesel to natural gas either manually or automatically. The efficiency of bifuel engines is considerably lower than that of dedicated engines, as the engine parameters cannot be optimized due to the different fuel properties of gasoline and natural gas; in general, the power delivered while running on natural gas is typically 10−15% less because the compression ratio of engines is lower for gasoline engines.[11] Natural gas can also be used in compression-ignited internal combustion engines (diesel engines) that lack spark plugs. In this case, diesel is injected at the end of the compression stroke, thereby maintaining the original diesel-engine operating principle. Because of the low energy density of natural gas compared to diesel (see Table 1 in section 3), dual-fuel engines consume 10−15% more than diesel compression engines.[10] Dedicated natural gas engines designed for a high compression ratio (because of the fuel's high octane number, 120−130) are highly efficient and fuel-economical when compared to bifuel or dual engines, as the vehicle does not have to carry two types of fuel, thereby increasing the cargo capacity and reducing weight.

Despite this flexibility and additional advantages, natural gas vehicles still have some severe drawbacks. Even in developed countries, not enough refueling stations for natural gas are available, making such vehicles impracticable for cross-country drives. Additionally, the driving distance is lower than for gasoline-powered vehicles (the fuel tank would take more space in the trunk of the car, making onboard storage of natural gas a problem). Despite the advances in the use of natural gas in spark-ignited, compression-ignited, and bifuel engines, a vehicle run on natural gas would have a driving range of about 300 km with the current natural gas storage technologies. As a case report, the Honda Civic GX, which runs on compressed natural gas, can provide only 300 km before it needs refueling, which is considerably less compared than for the gasoline-powered Honda Civic GX, which has a driving range of 650 km.[12]

Considering the increasing trend in oil usage and emission rates, natural gas seems to be a promising alternative for oil and a long-term solution (at least for the next five to six decades) to overcome oil dependence. Thus, it is reasonable to expect support and motivation from governments, nongovernmental organizations, and scientists to target a rapid expansion of the number of natural gas fueling stations worldwide. Assuming that this scenario is realized in the near future, the main drawback when using natural gas vehicles still remains the low energy density of the fuel, which demands a refinement of existing technologies or finding a new technology/suitable system for storing an acceptable volume of natural gas to provide a reasonable driving distance.

A balloon of natural gas at room temperature and pressure would have to be nearly 1000 times larger than the container needed to deliver the same amount of energy with diesel fuel, which is certainly not a practical solution for use in a vehicle. Combustion of 1 L of natural gas at standard temperature and pressure (STP) will yield 0.033 MJ, whereas combustion of 1 L of gasoline will yield 34.2 MJ. The huge difference in energy density and the limited space availability in vehicles for onboard storage reduce the driving range of a vehicle running with a dedicated natural gas engine using a conventional storage system when compared to a vehicle running with gasoline or diesel. Extra storage tanks can increase the driving range, but the additional weight would displace payload capacity. Thus, to make natural gas a viable alternative fuel, a large amount of energy must be stored in a container of acceptable volume at a reasonable pressure.[13] This work presents an overview of the available technologies for storing methane in different classes of novel highly porous materials, which are able to deliver an amount of energy as near as possible to that of gasoline/diesel fuel.

In what follows, it is assumed that natural gas and methane are synonymous, but it should be mentioned that natural gas contains appreciable quantities of minor compounds that can affect the performance of vehicles fueled with adsorbed natural gas (ANG), as discussed in later sections.

2. CONVENTIONAL METHODS FOR THE STORAGE OF NATURAL GAS

Natural gas is conventionally stored in high-pressure tanks made of very thick steel that are tested up to 30 MPa and filled up to 18−25 MPa at room temperature. To deliver the energy equivalent to 1 gal of diesel fuel, over 4 gal of compressed natural gas (CNG) at 18−20 MPa would be needed, which is impractical for a conventional vehicle. Thus, a typical 63 kg natural gas fuel tank filled with compressed gas at 18−20 MPa

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holds the energy equivalent of only about 4 gal of gasoline, which limits the driving range to about 140−190 km. The driving range can be improved by adding extra tanks, but this will also add weight and decrease the payload capacity of the vehicle. The use of CNG implies more practical problems, some of which are as follows: (i) The quality of the fuel is difficult to maintain because the composition of natural gas changes with region and time. (ii) The compression of natural gas increases the concentration of moisture and non-methane hydrocarbons, which could significantly affect the engine components, as well as the overall engine's performance. (iii) Natural gas requires a multistage compressor and a specific refueling system, which varies with the type of refueling method (fast or slow refill). In addition, specific cylindrical or spherical heavy steel or expensive composite storage tanks and complex valves are needed to ensure safety, because of the very high operating pressures and the resulting hoop and axial stresses generated within the vessel.

Alternatively, natural gas could be stored as liquefied natural gas (LNG) by cooling it to below its boiling temperature (110 K), increasing its energy density at moderate pressures of 0.2−0.6 MPa. For comparison, the energy density of LNG (22.2 MJ/L) is 2.4 times greater than that of CNG (9.2 MJ/L at 250 bar), 59.5% of that of diesel fuel (37.3 MJ/L), and 65% of that of gasoline (34.2 MJ/L). Despite of its higher energy density, LNG demands large, heavy, and highly insulated storage tanks to keep the fuel cold, which adds to the cost of the vehicle by a significant amount. These harsh operating conditions make it harder to implement this technology for the onboard storage of methane in domestic cars or even in heavy-duty vehicles. LNG also has the disadvantage of fuel boil-off induced by heat transfer if the vehicle is parked indoors or outdoors over a period of time, which, in turn, will alter the composition of the fuel.[14] Among currently available technologies, LNG is not feasible for passenger vehicles, and its application is limited to only heavy-duty vehicles, where the fuel is completely exploited in daily runs, rather than in light-duty vehicles or passenger cars. LNG also seems to be a promising fuel option for the aviation industry. A 2012 report by Boeing stated that LNG could fuel aircraft in the future and thus reduce fuel burn by as much as 62% over current aircraft, with lower emissions.[15]

3. ADSORBED NATURAL GAS (ANG)

The standard practice is to express adsorption as a Gibbs surface excess quantity, which is the amount of adsorbate present in the adsorbed layer within a pore volume in excess of the bulk gas density. Conventionally, the surface excess amount is the quantity measured in standard volumetric or gravimetric adsorption equipment; it is also the value used in the large majority of scientific articles published on methane storage. Nevertheless, the absolute adsorption, which cannot be measured directly in adsorption experiments, does frequently appear in the literature. Absolute adsorption values involve an additional parameter that considers the void spaces within the vicinity of the solid potential field and the space outside the potential field of the solid. Unless otherwise specified, all storage capacity values reported in this review correspond to Gibbs excess adsorption. Of course, this means that the values given in this text are lower than the actual volumes of methane inside real systems (container plus the adsorbent plus the methane), but they correspond to the experimental values measured in conventional volumetric adsorption equipment and are published as such. Additionally excess adsorption gives a practical and reliable measure of the functional usability of the material to store or deliver methane from porous materials.

Storing methane at relatively low pressures and room temperature by adsorption could overcome some of the disadvantages of CNG and LNG; thus, adsorption has been considered as a promising storage method for vehicle transportation. Adsorption in porous materials offers the possibility of reaching energy densities similar to that of CNG at 20−25 MPa and almost one-third that of liquid (LNG) at a much higher temperature, where both of these aspects are advantageous for transportation. Researchers at Brookhaven National Laboratory tested several adsorbents for their storage capacities in the early 1990s and found that, at 4.37 MPa, storage by adsorption in a nanometer-sized carbon pore increases the gas density by nearly 5 times.[14] This implies that the CNG density at 20 MPa (0.1572 g/mL) could be attained by ANG at roughly one-fifth of the gas pressure of CNG, thus simultaneously increasing the comfort factor and reducing the storage cost per unit volume of gas. The theoretical works of Matranga et al.[16] and Tan and Gubbins[17] suggested that, at 3.5 MPa and 298 K, a methane density of up to 0.223 g/mL could be reached in a carbon pore with an effective pore width of 0.78 or 0.8 nm. Experimental data confirmed that a methane density of up to 0.21−0.23 g/mL could be obtained with carbons that contain only narrow micropores.[18]

Because ANG operates at lower pressures than CNG, it alleviates the need for thick vessels to withstand high storage pressures (which are bulky and costly) and the need for multistage compressors required to fill CNG tanks. Additionally, the reduced operating pressure increases the safety for personnel and equipment in the case of collisions. Other important advantages include space aesthetics because ANG is compatible with a flat tank. Thus, it is possible to install multiple storage tanks to fit the space available in a vehicle efficiently without sacrificing passenger or cargo space, which would ultimately increase the driving distance. In recent years, ANG has emerged as the most promising method for providing safety and the desired volumetric storage capacity for a reasonable driving range.

The crucial factor when designing storage materials is considering the space occupied by the porous material in the storage container, and the space wasted by poor packing of porous materials should be kept to a minimum,[19] as the mileage per unit volume of a tank of natural gas is already only 0.10% of that of gasoline. A commonly invoked benchmark for the adsorption capacity required to obtain a reasonable driving range in automotive applications was provided by the U.S. Department of Energy (DOE), which set a target for storage capacity at 3.5 MPa and 298 K of 150 v/v (volume of methane adsorbed per unit volume of adsorbent material) for the year 1995 and an even higher value of 180 v/v (or 118 g/L of carbon) for 2000.[14,20] This represents the volume of methane delivered (not the storage capacity) at standard temperature and pressure (STP) per unit volume of the vessel. This value is independent of the gas adsorbed and the gas that remains in the gaseous state in equilibrium with the bulk gas phase;[21] that is, it corresponds to the experimentally measured values in conventional adsorption equipment. The deliverable capacity corresponds to the difference between the amount adsorbed at the storage pressure and the amount of methane remaining after the desorption step at ambient temperature and pressure, both corresponding to experimentally measured values. Often, the discharge capacity is directly estimated from the adsorption isotherms, assuming that the enthalpies of adsorption (ΔH_{ads}) and desorption (ΔH_{des}) are constant, which is valid for a system operating under isothermal conditions. In recent years, the value of 180 v/v has been taken by researchers as a landmark for the storage capacity rather than the deliverable capacity, and it is often considered as a yardstick for comparing the performances of adsorbents. Historically, the pressure of 3.5 MPa was selected arbitrarily to compare the performance of sorbent materials for methane storage. Furthermore, this pressure is about one-sixth or one-seventh of the maximum loading pressure of commercial CNG tanks in many countries, and it does not require heavy, thick-walled cylindrical tanks or multistage compressors.[21] Online commercial advertisements from different sources indicate that there are several single-stage natural gas compression units available on the market for home installation, in the range of US$ 500−3000 delivering a maximum pressure between 2 and 5 MPa. More generally, ANG units can be operated up to a practical limit of about 5 MPa, which is only one-fifth to one-sixth of the pressure of CNG at 25 MPa and involves the use of only inexpensive two-stage compressors. As a general rule and also for practical implications, to make ANG equivalent to CNG, the same or even larger amounts of natural gas should be delivered at one-fifth or less of the pressure of CNG.

In terms of energy density, the value of 180 v/v corresponds to the energy density of compressed natural gas stored at a very high pressure of 16.3 MPa. This value can be considered as a yardstick for the time being, because this target value was set considering consumer acceptance, safety issues, cost, and so on. In terms of driving distance, the storage value of 180 v/v corresponds to one-fifth of the driving range of the equivalent volume of gasoline tanks; thus storage capacities higher than this value would be desirable for longer driving distances. The U.S. Department of Energy recently announced a new program called "Methane Opportunities for Vehicular Energy (MOVE)" that sets new and aggressive targets for ANG vehicles.[22] CNG compression at 25 MPa requires five-stage compression, which is energy-consuming and requires high installation costs. The MOVE program demands adsorbent materials to meet energy densities equivalent to that of compressed methane at 25 MPa, but strictly at lower pressures, typically ≤3.5 MPa, to reduce the burden on home refueling. More specifically, to make the energy density of ANG equivalent to that of CNG at 25 MPa, the sorbent-level volumetric capacity must exceed 0.188 g/cm^3 or 11.72 mmol/cm^3 (which is the density of compressed natural gas at 25 MPa and 298 K). At standard temperature and pressure (STP) conditions of 273.15 K and 0.1 MPa, 1 g of methane occupies a volume of 1.4123 L. This volumetric capacity of 0.188 g/cm^3 at 25 MPa and 298 K occupies a volume equivalent to 266 v/v (based on adsorbent volume). The gravimetric adsorption capacity of the adsorbent must be as high as 0.5 g/g. If a 25% packing loss (in the actual storage tank) is taken into account, the required volumetric capacity becomes ridiculously high, 355 v/v and 50 wt %, which is considerably higher than the previous target of 180 v/v. It is worth mentioning here that the value of 266 v/v is obtained based on STP conditions according to IUPAC. Traditionally, researchers try to obtain this value by multiplying the amount adsorbed at 298 K by a factor of 1.5 L/g, which is slightly higher than the density of methane at 273.15 K and 1 bar (1.4123 L). For the case of conformed materials, if the monolith adsorbent volume fits the entire tank, then the value of 266 v/v can be taken as a milestone for research motivation. In addition, secondary targets of the DOE MOVE program demand ideas for the integration of sorbent materials into gas tanks to improve packing density, conformability factor, tank-filling and delivery rates, and so on. Table 1 reports the volumetric storage capacity and energy density of CNG at different pressures; for comparison/reference, the energy density values of liquefied natural gas (LNG), gasoline, and diesel are included in Table 1 as well. Although not practically possible to attain, Table 1 also gives the required levels of methane density in a CNG tank to make it equivalent to gasoline and diesel.

Table 1. Energy Densities of Methane and Conventional Fluids[a]

pressure (MPa)	volumetric storage capacity (v/v) at STP	energy density[b] (MJ/L)
CNG (15 MPa)	168	5.80
CNG (20 MPa)	222	7.68
CNG (21 MPa)	232	8.01
CNG (22 MPa)	241	8.33
CNG (25 MPa)	266	9.2
LNG (110 K and 0.1 MPa)	600	22.2
gasoline	c	34.2
diesel	d	37.3

[a]Density of methane taken from National Institute of Standards and Technology (NIST) database. [b]1 L of CH_4 = 0.0345 MJ) [c]Required density of methane in a CNG tank to make it equivalent to gasoline: 0.9889 g/cm^3 [d]Required density of methane in a CNG tank to make it equivalent to diesel: 1.0785 g/cm^3

Although there are no suggestions about the targets on delivery, the DOE MOVE program mentions that the engine inlet pressure must be greater than 0.48 MPa, and proposals for novel ideas on how to mitigate the inaccessible methane stored below this pressure were encouraged. At this stage, even though none of the above targets demanded by DOE break any law of nature, they appear daunting from a practical point of view, given that, to date, there is no convincing evidence available in the literature allowing even the old target of 180 v/v at 3.5 MPa and 298 K to be reached in terms of storage or delivery with any conformed porous material. To the best of our knowledge, no research has been reported in the literature that allow one to on reaching these new DOE targets (0.188 g/cm^3 or 266 v/v and 50 wt %, both at 298 K and 1 bar at 298 K). The rest of this review focuses on the work that has been carried out with the goal of developing novel porous materials that approach the 2000 landmark methane storage value of 180 v/v.

Aiming to reach the objective of 180 v/v, several research groups worldwide have tried to develop different classes of porous materials over the past two decades. These materials include Amberlite, dow resins, zeolites, silica-based compounds, xerogels, aerogels, MCM41, and carbon-based materials such as superactivated carbons, single-walled carbon nanotubes (SWCNTs), activated carbon fibers, and carbon nanohorns.[13,18,23−41] Conventional zeolites typically exhibit very low storage capacities not exceeding 100 v/v, which are far from the DOE targets.[14,20] Attempts to increase their low storage capacities have been hindered by their structural limitations such as the presence of cylindrical mesopores and difficulties in practically reaching surface areas greater than 1000 m^2/g.[26,27] The grand canonical Monte Carlo (GCMC)

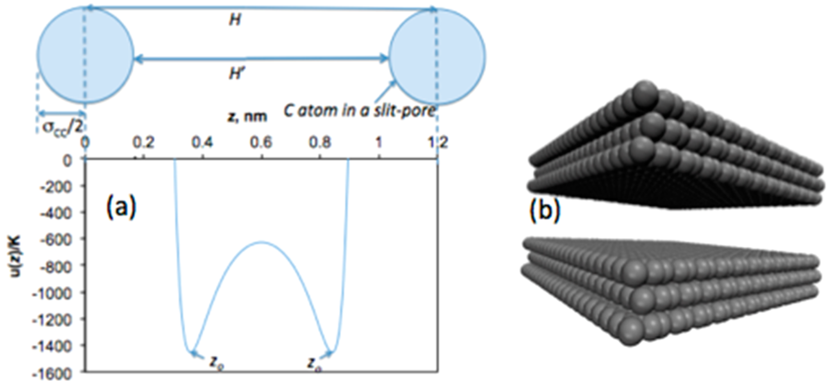

Figure 1. (a) Potential energy, $u(z)$, for a spherical methane Lennard-Jones (LJ) site interacting with the walls of a slit pore of width $H = 1.2$ nm. The LJ parameters for C and CH_4 were taken directly from the literature,[49] and z is a measure of the distance between the center of a carbon atom on the pore walls and the center of a methane molecule. (b) Carbon prototype of a slit-shaped pore that can be taken as a reasonable model representing the porosity of activated carbon.[29]

simulation results of Cracknell et al.[19] confirmed that, for the adsorptive storage of natural gas, a microporous carbon that has an optimal pore size is better than an optimal zeolite. They found that, at 3.4 MPa and 274 K, a prototype carbon with slit-shaped micropores yields a theoretical storage capacity of 166 g/L compared to 53.1 g/L for a zeolite with cylindrical pores of the same dimensions. If one could ignore the adsorption forces, then it could be accepted that the packing density of a spherical molecule in micropores with widths about twice the molecular dimensions of the probe molecule is about 65% for cylindrical pores, but over 90% for slit-shaped pores.[42]

In general, carbon-based materials represent the best adsorbent materials because of the much higher packing density of methane molecules in slit-shaped pores; thus, other classes of materials exhibit lower storage capacities when compared to carbon materials with similar surface areas.[26,43] Typically, as discussed in the next section, porous carbons exhibit storage capacities ranging from 50 to 160 v/v, and only one scientific publication has included a carbon material exhibiting a storage capacity higher than 180 v/v;[44] however, the fuel deliverable capacity of the latter was accepted to be less than 165 v/v. Because of the practical difficulties associated with most high-surface-area carbons reaching the DOE targets, storing natural gas as hydrates in wetted carbon structures has been considered as a complement to the ANG technique in recent years, as described in section 6. Additionally, metal−organic frameworks (MOFs), with periodic porous structures, have also received considerable attention from the research community, as they seem to exhibit storage capacities comparable to or even superior to those of carbon-based materials.[45−47] Although some MOF compounds have been claimed to exceed the landmark value of 180 v/v for methane storage capacity by a significant amount,[47,48] these values should be considered with care, as discussed in detail in section 5.

The aim of this work is to summarize recent advances and other technological issues, as well as advantages and drawbacks involved in storing natural gas in two of the most promising adsorbents, namely, carbon-based materials and MOFs. The rest of this review is divided into several sections as follows: Sections 4 and 5 describe the methane storage properties of some novel carbon-based materials and some of the most promising MOF structures, respectively. Section 6 highlights the advantages and limitations of storing natural gas as hydrates within the wet carbon nanopores, and sections 7 and 8 discuss design factors and technical issues that should be considered for the implementation of ANG technology in vehicles. Finally, section 9 presents visions for the future use of ANG technology in the transportation sector. At every stage of this review, a structure−property relationship between the different porous materials and the storage capacity for methane is described, which allows us to emphasize specific points/approaches to be considered in the design of adsorbents for the storage of natural gas.

4. CARBON MATERIALS

The extensive pore structure, chemical stability, variety of structural forms, and ability to modify or tune the porosity using a wide range of preparation methods from a large set of precursors make carbon materials a primary class of adsorbents for the storage of methane for vehicular applications. The adsorption of methane on the carbon surface is essentially due to van der Waals forces, as methane has no permanent dipole or quadrupole moment. Thus, the performance of the adsorbent depends on the attractive forces between the carbon atoms at the surface and the methane molecules, which depends on the distance z between the center of a methane molecule and the center of a carbon atom on the pore wall. Figure 1a shows a plot of the Lennard-Jonnes interaction for a spherical methane molecule with a surface carbon atom in a model slit pore (Figure 1b) of width $H = 1.2$ nm, as measured between the centers of two carbon atoms on opposite walls of the pore. ($H' = 0.86$ nm is the distance between the surfaces of two carbon atoms on opposite walls of the pore.) It can be observed that methane experiences a strong attractive force and finds a more stable position (z_0) at 0.36 nm, which is about one molecular diameter of methane; at the center of the pore, methane experiences attractive forces that are too weak to expect any formation of a second layer. Thus, during adsorption, after the completion of a first layer, the gas fills the remaining space and might form a low-density methane layer or just fill the remaining pore volume with a gaslike density. The interactions between methane and the pore wall gradually decrease with increasing pore width.

Methane, the main constituent of natural gas (NG), has a critical temperature of 191 K and, consequently, cannot be liquefied at room temperature alone. At room temperature, after the completion of a monolayer by adsorption, the bulk

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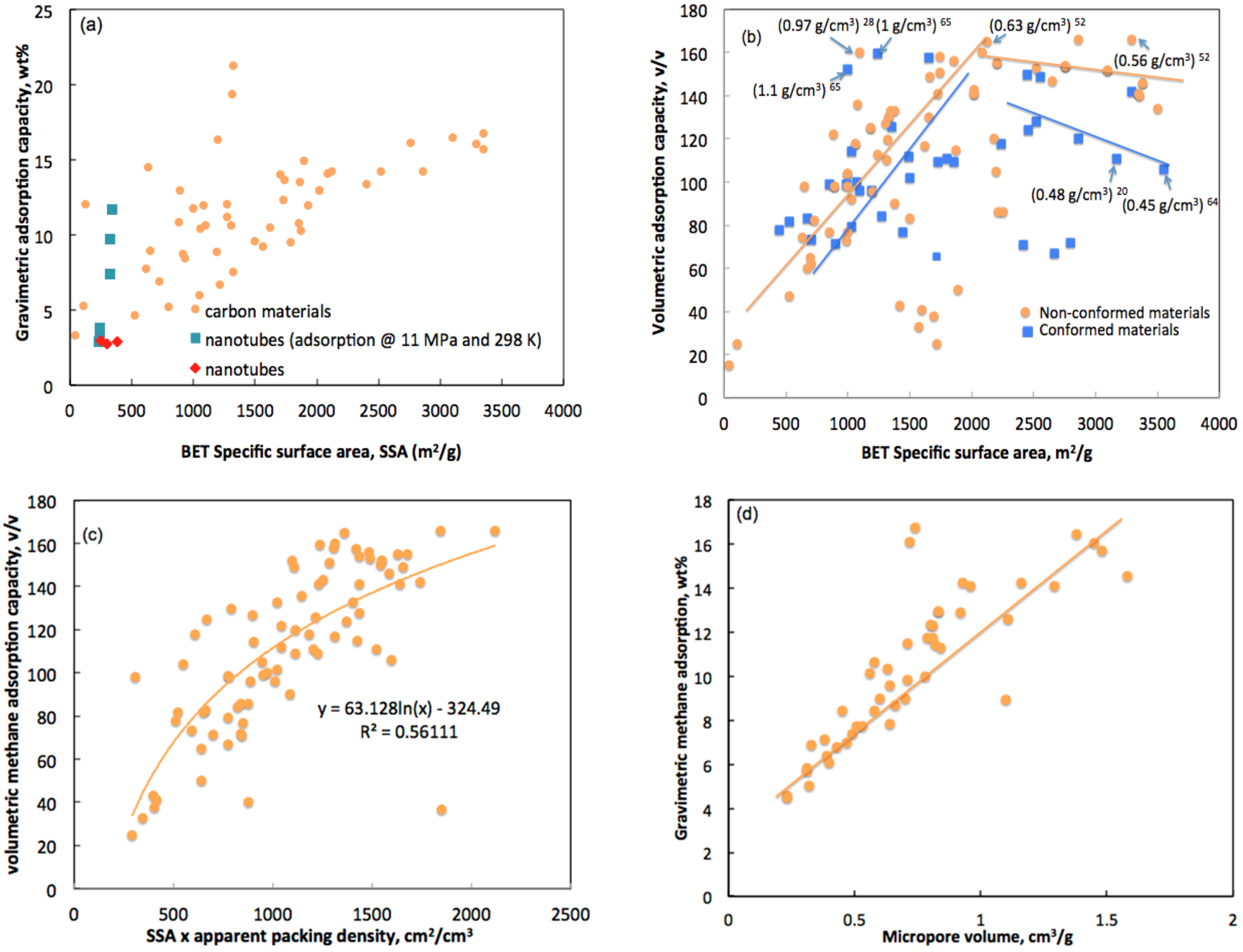

Figure 2. (a) Gravimetric adsorption capacity of methane (in weight percentage) versus the BET specific surface area of carbon structures. (Orange circles represent carbon materials corresponding to materials with slit-shaped pores, including activated carbons and carbon fibers.) (b) Volumetric adsorption capacity (v/v) versus the product of the BET specific surface area (SSA) and packing density. (For the case of conformed materials such as monoliths, the packing density corresponds to the piece density.) (c) Volumetric adsorption capacity (v/v) of carbon structures versus the BET specific surface area. (d) Gravimetric adsorption capacity of methane (in weight percentage) versus the micropore volume of carbon structures. (Unless specified otherwise, all of the adsorption capacities correspond to excess adsorption, and all of the adsorption capacities shown correspond to the amount adsorbed at 3.5 MPa and ambient temperature. All BET surface areas and micropore volumes taken from literature were assumed to be measured following IUPAC standards.[21,23,24,37,38,50−65])

methane molecules interact mainly with the adsorbed methane molecules, as the interactions with the surface carbon atoms are almost negligible. Thus, after completion of the monolayer in larger pores, the methane molecules eventually move around the available pore space, filling the available volume with a gas density (compressed gas) depending on the pressure, forming a gaslike density at the center of the pores. For practical purposes, and also to meet the DOE requirements, the pore size should be optimized to store methane with a density equivalent to CNG at 20−25 MPa but at lower pressures, typically approximately one-fifth to one-sixth that of CNG.

For graphite intercalated with two layers of adsorbed methane, with the interlayer distance increased by twice the molecular dimension of methane, assuming that the molecules are closely packed in a two-dimensional hexagonal lattice, given the specific surface area of graphite (2620 m^2/g), the saturation capacity for methane, a_s, can be analytically estimated.[16] Assuming that the energy of interaction between methane and carbon could be optimized, Matranga et al.[16] analytically obtained an adsorption isotherm for the perfect binding affinity, C, of a Langmuir isotherm ($n = a_sCp/1{+}Cp$) to deliver the maximum amount of methane, a_s (0.552 g/g), over a cycle operating between a storage pressure of p_1 and a delivery pressure of p_2. For a system operating under isothermal conditions (300 K) between p_1 = 3.45 MPa and p_2 = 0.136 MPa, to deliver the maximum amount of methane, they found that the optimal binding affinity should be C = 1.461 MPa. They compared the optimum isotherm with some of the experimental isotherms obtained with activated carbons with different BET (Brunauer−Emmett−Teller) specific surface areas (1000−3000 m^2/g) and theoretically obtained isotherms using molecular simulations. They found that the affinity of the carbon materials in practice was much lower than the optimum affinity and, thus, that the actual storage would be <55 wt % at 298 K, regardless of the energy of interaction. Adsorption capacities closer to 55 wt % have never been reported, especially at 3.5 MPa. A mesoporous carbon [mesocarbon microbeads (MCMBs)] with a surface area of 3180 m^2/g and an average pore size of 2.47 nm was found to store up to 34.2 and 45.5 wt % (markedly higher but estimated value) of methane at 3.5 and 7 MPa, respectively, with a deliverable capacity of 29.97 wt % (volumetric storage capacity was not provided) at 298 K.[50] This is still far from the value obtained by Matranga et al.[16] using the analytical method.

What is the relation between the physical properties of the carbon materials and the methane adsorption capacity? If the amount adsorbed is expressed in terms of gravimetric adsorption capacity and plotted against the BET specific surface area for several carbon-based materials (both powdered and conformed materials) of different morphologies obtained by different activation methods from different precursors, a fairly linear relationship between these two parameters can be found (Figure 2a). The scattering observed in the relationship between the surface area and storage capacity can be attributed to the uncertainty associated with the experimental method used to determine the surface areas of the carbon materials from the adsorption of N_2 at 77 K. Another explanation for the scattering of the data in Figure 2a might be the properties of the material itself. For instance, high-surface-area carbons obtained by chemical oxidation or physical activation usually contain larger pores (mesopores), and the high surface areas in these materials are created at the expense of material loss due to etching, that is, a decrease in carbon framework density. The framework density plays a very minor role in the uptake of N_2 at 77 K, whereas it can play a crucial role in the uptake of methane, which is a supercritical fluid at 298 K.

In a recent study, Srinivas et al.[59] showed that carbons derived from graphene oxide seem to deviate from the relationship between structural properties and gravimetric storage capacity that usually exists for carbon materials. They observed that a graphene oxide derived carbon (GODC4-800) with a lower surface area, 1276 m^2/g, adsorbed more methane than carbon Norit R1, which has a surface area of 1450 m^2/g. They also reported that another graphene oxide derived carbon (GODCsol-900) with a surface area of 1894 m^2/g adsorbed more methane (on a weight basis) than the commercial carbon Maxsorb, which has a surface area of 3250 m^2/g. In any case, when the results for carbon materials are plotted as a function of surface area (Figure 2a) on a global scale, the same linear trend is found (see the trend line in Figure 2a).

To determine the extent to which the surface area of the activated carbon plays a role in the volumetric storage capacity, we also plotted the volumetric adsorption capacity of methane as a function of the surface area (Figure 2b). It can be clearly seen that the volumetric storage capacity globally increases with surface area up to 2000 m^2/g, after which an apparent drop in volumetric storage capacity occurs. This behavior can be explained through the concept of the packing density of carbon materials. By definition, the term volumetric storage capacity is not a material property, as it involves an additional parameter, for example, the packing density in the case of powdered materials and the geometric density in the case of solid monoliths. The packing density of a material is strongly influenced by the activation process itself: The higher the degree of activation, the higher the surface area and porosity and, thus, the lower the packing density and vice versa. Because the volumetric storage capacity is a function of the product of the gravimetric storage capacity and the carbon packing density and also because these two parameters vary in opposite ways because of the limitations of the available synthesis and activation strategies, an optimum value for the volumetric storage capacity at which there is an appropriate balance between the mass storage capacity and the packing density exists. This is evidenced in Figure 2b by the fact that several materials (both powdered and conformed materials) with a wide range of surface areas exhibit the same remarkable methane adsorption capacity of ≥160 v/v at 3.5 MPa and 298 K under STP conditions. For instance, a carbon pellet made from single-walled nanohorns (SWNHs) with a low surface area of 1097 m^2/g and a high packing density of 0.98 g/cm^3 was found to exhibit a volumetric storage capacity of 160 v/v.[28] On the other hand, a high-surface-area carbon (3290 m^2/g) with a low packing density of 0.53 g/cm^3 was reported to have a lower volumetric adsorption capacity of 142 v/v.[64] In Figure 2b, we show the packing densities of some low-surface-area carbons and some high-surface-area carbons that have methane adsorption capacities of >150 v/v. As can be easily realized from this figure, no simple correlation exists between the adsorbent design parameters and the volumetric storage capacity. In an attempt to find such a correlation, we plotted the volumetric adsorption capacities of the same carbon materials versus the product of their BET specific surface areas (SSAs) and their apparent packing densities (PDs) (i.e., SSA × PD) (Figure 2c). The product of the specific surface area and the packing density gives a measure of the amount of surface area per unit volume of adsorbent. Figure 2c shows that the volumetric storage capacity increases logarithmically with increasing value of SSA × PD. If the logarithmic expression included in Figure 2c holds true, then to achieve the DOE targets of 180 and 263 v/v, materials are needed that have surface areas per unit volume of adsorbent of 2955 and 11543 m^2/cm^3, respectively. As a word of caution, these numbers are approximate values obtained using the empirical expression shown in Figure 2c. In addition, the logarithmic relationship presented in Figure 2c ignores a crucial adsorbent design parameter, namely, the pore volume and its distribution, as well as the loss of material properties that would occur during the transformation of powdered materials into conformed products (such as monoliths). Thus, the values extrapolated from the expression provided in Figure 2c can provide only a global picture on what type of material property is required to achieve the DOE targets. For instance, to achieve the new DOE MOVE target of 266 v/v, even a material with very high packing density of 1.5 g/cm^3 should have a surface area of 7695 m^2/g. Materials with such combination of properties are practically hard to obtain at least with the available techniques. On the positive side, based on the papers reviewed in this work and according to the expression shown in Figure 2c, there is a hope to reach the DOE target of 180 v/v with a conformed material that has a packing/apparent density of about 1.2 g/cm^3 and 2463 m^2/g. Such properties are achievable and are possible to obtain with proper design of experimental synthesis.

Other parameters that are considered to be of great importance in designing carbon materials are pore volume and pore width. As emphasized earlier in Figure 1, a pore size greater than twice the diameter of a methane molecule is not useful for the storage of methane at room temperature and 3.5 MPa (although such pores are useful for increasing the adsorption kinetics), and in fact, plenty of research points to the fact that the storage capacity is linearly proportional to the total micropore volume.[29,51,66] In some articles, the fact that the storage capacity is a strong function of the volume of narrow micropores (<0.7−0.8 nm) and the micropore size distribution rather than just the total micropore volume has been reported.[18,29,52]

To obtain a clear picture of the role of microporosity in the adsorption of methane, we plotted the amount of methane adsorbed versus the microporous volume (Figure 2d). It can be seen from Figure 2d that the methane adsorption increases linearly with increasing micropore volume up to 1.3 cm^3/g, after which a decrease in the methane uptake occurs. This trend can be explained by considering the micropore size distributions of carbon structures. Materials with huge micropore volumes usually contain larger micropores (0.8–2.0 nm), and methane is expected to fill such pores with a higher density at pressures of >3.5 MPa. On the other hand, a carbon structure that contains a large volume of narrow micropores (<0.8 nm) can confine methane with a relatively higher density within the pore volume, and thus, such a material can exhibit a higher methane uptake. Rodríguez-Reinoso et al.[18] and Molina-Sabio and Rodríguez-Reinoso[35] performed experimental studies that exclusively considered the above-mentioned issues. Their studies emphasized the influence of the micropore size distribution on the ultimate methane storage capacity. Their experimental results revealed the need for a certain level of pore size heterogeneity to improve the storage capacity of an adsorbent tank operating at pressures greater than 2.5 MPa. Specifically, they found that, at 298 K, the adsorption in narrow micropores (0.7–0.8 nm) reached a saturation limit due to pore volume restrictions at about 2.5 MPa and, above this working pressure, larger micropores were essential to increase the excess adsorption by a significant amount. Their experimental results confirmed that, although narrow micropores do favor methane adsorption at 298 K, wider micropores (0.7–2 nm) are needed to improve the storage capacity of adsorption systems operating at pressures higher than 2.5 MPa. Their experimental results showed a linear trend in the relationship between the volume of narrow micropores and the methane density. Their calculations, which relied on a graphical method, indicated that a methane density of up to 0.21–0.23 g/cm^3 could be reached within narrow micropores at 3.0 MPa and a methane density of up to 0.09 g/cm^3 could be reached in wider micropores (0.7–2.0 nm), roughly 3 times lower than in narrow micropores. These results seem to be in agreement with the results obtained using in situ small-angle neutron scattering.[52] For comparison, the bulk density of compressed methane at this pressure (3.0 MPa) is 0.02 g/cm^3, which is 4.5 and 11.5 times lower than the densities of methane achieved in wider and narrow micropores, respectively. Despite the low density of methane achieved in larger micropores, larger micropores still seem to play a crucial and exclusive role in the uptake of excess methane at higher pressures (p > 2.5 MPa).

All of these experimental works clearly highlight the following concept: For low-pressure storage of methane, only narrow micropores are needed, but for storage by adsorption at intermediate pressures, typically >3.5 MPa, the presence of larger micropores might be essential. For this reason, increasing the surface area typically above 2000 m^2/g produces a loss of the volumetric storage capacity at the typical pressure of 3.5 MPa, as attempts to increase the surface area are always accompanied by the penalty of a loss in narrow porosity. When the pore dimensions exceed the size of two methane molecules, the interaction at the center of the pore is very weak (as emphasized earlier based on Figure 1a), and the excess adsorption is not sufficient to form any additional high-density methane layers in the pore centers or within the available pore volume, especially at lower pressures (~3.5 MPa). The above experimentally observed results were found to be in excellent agreement with the results obtained from molecular simulations. Using GCMC simulations, Matranga et al.[16] determined that a slit-shaped pore with a size of H = 1.14 nm (H' = 0.8 nm; see Figure 1a for the definitions of H and H'), which is able to hold exactly two layers of methane, is the optimum pore for obtaining a relatively higher usable methane storage capacity at 3.5 MPa. Assuming that three graphitic planes bound each pore wall (as in a typical graphite crystal structure; see Figure 1b), we performed GCMC simulations using the MUSIC code[67] in an atomistically represented slit pore with a similar pore width. (See the Supporting Information for the simulation details and details of the carbon prototype used.) These simulations showed that storage capacities of up to 129 v/v (4.129 MJ/L) and 133 v/v (4.32 MJ/L) (both corresponding to excess adsorption, a quantity that can be measured experimentally) can be achieved in this type of pore at 298 K and pressures of 3.5 and 5 MPa, respectively. These values can be taken as realistic limits for this type of carbon pore for the storage of methane at 298 K. Although not practically correct, one can consider an extreme scenario in which the two-dimensional carbon pore is bounded by only single graphitic planes (see eq 2 in the Supporting Information), in which case these values correspond to 282 and 290 v/v, respectively. (These values can be taken as theoretical upper limits for this particular carbon prototype.) Further, we noticed that, in this pore (a slit pore with H = 1.14 nm), the excess adsorption reached a maximum at 6.0 MPa, which means that it is theoretically possible to reach a volumetric adsorption capacity greater tha 290 v/v in carbon materials at 298 K. These values can at least provide some motivation and serve as milestones and target goals for experimental work. The theoretical values obtained for a slit-shaped narrow micropore (H = 1.14 nm) bounded by a single layer of graphene, which can typically hold up to two layers of methane, appear promising and provide some hope for reaching beyond the landmark value of 180 v/v and even attaining the DOE MOVE target of 266 v/v.

Despite the huge effort put forward by several research groups throughout the world, such values have not been obtained experimentally with any carbon material so far. This outcome also points to the concept that the new DOE MOVE target can be achieved only in a very low-density carbon framework, which is typically a carbon pore with the optimum pore size (H = 1.14 nm) bounded by single layer of graphene sheets. Although experimental results have confirmed that the already-high-surface-area carbon materials (materials with surface areas of >2600 m^2/g) cannot be pushed to the theoretical limit exceeding 200 v/v, some of the experimental values did surpass the estimated (theoretically obtained) realistic limits of 129 v/v at 3.5 MPa and 133 v/v at 5 MPa. To our knowledge, only one article published in a scientific journal (by Celzard and Fierro[68]) has reported a value of storage capacity near the 2000 DOE target, 195 v/v (with a deliverable capacity of ~165 v/v), at 3.5 MPa and 293 K. Additional reports have been published elsewhere (194 v/v at 4 MPa and 298 K by Chaffee et al.[69] and 180 v/v at 3.5 MPa and 298 K by the group of Pfeifer[44]). However, these values have not been independently verified or reproduced elsewhere. In any case, in some of these works,[68,69] the analytical method used to obtain the volumetric storage capacity remains vague or at least not clearly reported, which obviously make these values

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debatable. Apart from a few works reporting very high storage capacities of carbon materials, as a general case, irrespective of the method of preparation, activation precursors, and pore topology, carbon materials generally exhibit maximum storage capacities ranging from 150 to 160 v/v at room temperature and 3.5 MPa, and in all of these cases, the gravimetric storage capacity correlates linearly with the surface area or micropore volume of the material (Figure 2a,d).

The trend of methane storage capacity increasing with surface area and micropore volume clearly indicates that one possible route for increasing the storage capacity of carbon materials is to synthesize them with both of these properties improved, but also with a higher packing density. However, both of these aspects remain standing problems because of (i) the difficulty of generating higher surface areas from carbons with already-high surface areas (>2600 m^2/g) and (ii) the complexity associated with increasing the surface area without enlarging the micropore dimensions of the carbon materials. An additional practical problem is that, in many cases, the activated carbons with very high adsorption capacities for methane are in the form of fine powders and the volumetric capacity is calculated by measuring the density after compaction of the powders under pressure. Thus, the calculated volumetric capacity at the laboratory scale could then be considered as the practical limit for that particular carbon, but not the real one for practical onboard application. It should be highlighted that the actual carbon disks reported by Alcañiz-Monge et al.,[55] Molina-Sabio et al.,[34] and Marco-Lozar et al.[70] are the conformed carbon materials with the highest methane adsorption capacities published to date, at over 160 v/v, although their actual deliveries were lower than 150 v/v.

Functionalization of the carbon surface is considered to be a promising design strategy for altering the adsorption capacity for a specific target molecule. In essence, the presence of surface functional groups alters the solid−fluid interactions, which ultimately either increases or decreases the binding energy of the target molecule with the carbon pore surface. Such efforts were carried out at the laboratory scale in the early 1990s. Cook et al.[21] and Barton et al.[71] determined the adsorption isotherms of a series of activated carbons that had had their surfaces oxidized to various degrees using a nitric acid treatment. No relationship between the degree of oxidization and the methane uptake could be determined. As a general case, they found that the presence of an oxidized surface decreased the overall binding energy between methane and the carbon atoms on the pore surface, thus lowering the methane uptake. Their results thus confirmed that the treatment of a carbon surface with nitric acid does not favor methane uptake. More recently, the adsorption of methane on graphene covered by titanium was studied using density functional theory (DFT) and molecular dynamics by Carrillo et al.[72] They reported that the attractive forces between the Ti atoms and the H atoms in methane were large; however, it was not clear that the presence of Ti ions would enhance the natural gas storage capacity of a carbon structure at room temperature. Recently, Wood et al.[73] used ab initio DFT calculations to study methane adsorption on edge-functionalized model carbon structures. Their results showed that carbon edges functionalized with polar groups such as COOH, NH_2, NO_2, and H_2PO_3 would help increase the methane uptake. These controversial results can be explained if one considers the storage pressure and the pressure at which these functionalities take up guest molecules such as methane or any other gas molecule with similar fluid properties. The functionalities introduced onto the carbon framework or surface often play a crucial role in increasing the binding energy at lower pressures, depending on the concentration and type of functionalities (and also the pore properties such as surface area and pore volume and even the pore structure). At higher pressures, the adsorption is instead dictated by the available pore volume, the pore structure, and the packing effects of the methane molecules within the available pore volume. For instance, DFT calculations are often performed with limited numbers of atoms, and thus, they can provide a reliable picture of the adsorption of guest molecules or the forces involved only at lower pressures. This explains the experimental observation of the negligible influence of functionalities on methane uptake under storage conditions (at $p > 2$ MPa). The discrepancies are also influenced by other effects such as a decrease in the available pore volume due to functionalization or a change in the surface curvature due to the inclusion of functionalized groups on the carbon surface. For instance, in an ultramicropore, introducing functionalities will significantly reduce the pore volume accessible for methane, whereas in a mesopore, introducing functionalities can improve the fluid-confining properties and thus the excess adsorption. Clearly, this issue can be resolved only by studying in detail a wide range of carbon materials with different pore structures and pore size distributions with different surface chemistries. A theoretical study performed on another class of porous materials by Düren et al.[74] using grand canonical Monte Carlo (GCMC) simulations showed that functionalization can improve the isosteric heat at lower loadings as well as the methane uptake at 3.5 MPa. At this stage, it is likely that high-surface-area carbons, which are known to have high edge-to-graphitic plane ratios, if synthesized to favor the presence of these functional groups, would probably increase their methane uptake values at 3.5 MPa. Additional experimental and theoretical studies are still needed to explore how this strategy can be useful in reaching the DOE target of 180 v/v at $p \geq 3.5$ MPa and 298 K.

Another interesting question is whether there might be any advantage in using curved graphenic surfaces for methane adsorption? In a confined pore with a curved graphene surface, as in the case of carbon nanotubes, with pore widths no greater than a few molecular diameters of methane, all of the carbon atoms in the perimeter of the tube will add to the interactions; thus, the attractive forces acting on the methane molecules are greater than on a flat graphitic surface as in a slit-shaped pore.[42] In the case of slit-shaped pores, such effects can be noticed for methane only in narrow micropores, where the contributions from both pore walls add to the interactions; however, their open pore structure offers a relatively high accessible pore volume when compared to nanotubes where the pore structure is confined. Studies on the adsorption of methane in nanotubes are influenced by several design factors such as the tube geometry, chirality, structural defects, and spacing between tubes, which often explain the conflicting results that regularly appear in the literature. Due to the practical difficulties in controlling the pore geometry with experiments, molecular simulations are typically used by researchers to explain the influence of these design parameters on methane adsorption and the storage limits of carbon nanotubes.

Tanaka et al.[75] performed theoretical studies by nonlocal density functional theory (NLDFT) on the adsorption of methane at 303 K on a range of isolated single-walled carbon nanotubes (SWCNTs) that differed in pore size and compared their performance with idealized carbon slit-shaped pores of similar dimensions. They found that, on a weight basis, the total excess adsorption on the internal and external surfaces of an isolated SWCNT exceeded that for an idealized slit-shaped pore with the same dimensions, although the adsorption capacity in the interior of the SWCNT was lower than that for the slit pore geometry. Their results suggest that up to 20 wt % of methane (adsorption excess) can be stored in a nanotube with a pore size that can hold two layers of methane (a layer on the internal periphery plus a column of methane in the tube center). This work also emphasized, for the first time, a new physical insight that the fluid−fluid interactions between the molecules adsorbed on the internal and external surfaces of a tube to contribute significantly (by 2.7 wt % in a tube that can hold two layers of methane) to the overall adsorption capacity. The interesting results of Tanaka et al. were obtained with isolated nanotubes and might not represent a realistic value in the practical case of SWCNTs appearing in bundles. The work of Tanaka et al.[75] assumed the walls of the tubes and slit-shaped pores to be smooth rather than atomistic, which might also influence the ultimate storage capacity. It will be shown later in this review that the results obtained from molecular simulations performed in atomistically represented tubular arrays and slit-shaped pores produce some results in clear conflict with Tanaka et al.'s description.

Cao et al.[76] used GCMC simulations to optimize an array of armchair SWCNTs arranged in a triangular shape for the storage of methane at room temperature. They found that the adsorption (excess) of methane in interstices plays a major role in the total volumetric and gravimetric capacities of nanotube arrays. Their studies further confirmed that this interstitial adsorption is highly dependent on the van der Waals (vdW) gap between the tubular arrays. An array of (15,15) SWCNTs separated by a vdW distance of 0.8 nm was found to be an ideal structure with volumetric and gravimetric storage densities of 216 v/v and 21.5 wt %, respectively, at 4.1 MPa and 298 K. They found that, in this ideal structure, the exohedral adsorption alone contributes 60% of the total methane adsorption. Their results suggest that, if synthesis strategies permit the precise tuning of the vdW distance between the tubes, then nanotubes could become a promising candidate for the storage of natural gas. In a theoretical study, Mahidzadeh et al.[77] showed that the interstitial adsorption process is tricky and varies with the tube size in addition to the distance between the tubes in a triangular array. They found that a volumetric storage capacity (excess adsorption) of up to 173 v/v (96% of the landmark value 180 v/v, if taken as the storage capacity instead of the delivery capacity) can be reached at 3.5 MPa and 298 K with an array of (14,14) nanotubes with a diameter of 1.9 nm separated by a vdW distance of 0.34 nm. Zhang and Wang[78] used GCMC simulations and DFT to study the adsorption of methane in an array of nanotubes with diameters of 2.04 and 4.077 nm arranged in a square lattice, with the tubes separated by a van der Waals distance of 0.334 nm (as in a typical graphitic pore). They found that, on a weight basis, the absolute adsorption (adsorption excess values were not reported) in the nanotubes, which are essentially mesoporous, was relatively higher than the adsorption in slit-shaped carbon pores, which are essentially microporous. An array of nanotubes with diameters of 4.077 nm was found to store up to 22 mmol/g (35 wt %) at 300 K and 6 MPa, whereas a slit pore with a pore width of 1.91 nm could store only up to 17 mmol/g (27 wt %) under similar temperature and pressure conditions.

All of these values obtained from theoretical studies seem encouraging for methane storage in SWCNTs, but so far, attempts to achieve or even approach such values using this class of materials have failed, and none of the carbon nanotubes synthesized in the laboratory have exhibited such high ideal adsorption capacities. The conflicts between theory and experiments are most probably due to the fact that the nanotubes used in experiments are far from ideal theoretical structures, as they are often distorted, contain mixtures of opened and unopened and single-walled and multiwalled nanotubes of various diameters and helicities. In a recent work, Delavar et al.[54] claimed that, at the expense of temperature (283.15 K), gravimetric storage capacities as high as 52 wt % (33 mmol/g) (volumetric storage capacity and packing density were not reported) could be achieved with MWCNTs at 5.0 MPa. The group of Kaneko[28] reported a volumetric storage capacity of 160 v/v (delivery capacity not provided) for compressed single-walled carbon nanohorns at 3.5 MPa and 298 K, and this value still remains the highest value ever achieved experimentally with a conformed carbon material that has curved surfaces at the atomic level.

In addition to nanotubes, several hypothetical carbon structures with curved surfaces have been proposed in the literature, and their storage capacity have been evaluated using molecular simulations. All of these studies mostly aimed to propose or search for an ideal structure with curved surfaces that might exhibit some remarkable adsorption properties or safety aspects when compared to regular nanotubes. Most of these structures were computer-generated based on "theoretical thoughts" and thus deviated from experimentally realized structures such as SWCNTs or MWCNTs. Kowalczyk et al.[79] reported a carbon pore with a wormlike structure that could store methane energy up to 5.4 MJ per liter of carbon at low to moderate pressures ranging from 1 to 7 MPa at 293 K. Vakshrushev and Suyetin[80] came up with a hypothetical bottlelike nanocapsule where the pore surface itself virtually acts as a high-pressure vessel that allows the safe storage of a large methane mass content at a relatively high pressure. The nanocapsule consists of two or more nanotubes combined together to form a bottlelike structure. The atomistically represented nanobottle was capped with an endohedral complex that was operated by an electric field. Molecular dynamic simulations showed that the nanobottle could retain approximately 17.5 wt % of methane at an internal pressure of 10 MPa and a temperature of 300 K.

Despite the several conflicting theoretical results claiming that nanotubes perform better than slit-shaped pores and vice versa and despite the frequently appearing concepts that claim the superiority of nanotubes for methane storage,[19,76,78] there are no conclusive reports that nanotubes, which are expensive, are better than other carbon-based materials such as activated carbons,[34,55,70] which are cheaper and easier to synthesize, especially at a large scale. In addition, the unique one-dimensional pore structure and low framework densities of nanotubes (when compared to a slit pore bounded by three graphene planes) do not seem to provide any additional advantages such as improved accessible volume, gravimetric storage capacity, or porosity when compared to activated carbons.

Does the effect of pore geometry play a role in methane storage capacity? It was already mentioned that the storage capacity in a porous material with slit-shaped porosity (as is the case for activated carbons) is larger than that in a solid with cylindrical pores of identical dimensions (for instance, a zeolite). Although many theoretical and experimental studies focusing on the search for the best storage material are available in the literature, only very few have reported on the effects of pore structural characteristics or textural properties on the storage density of methane.[33,37,81] Menon and Komarneni[26] showed that, regardless of the pore structure and morphology of the adsorbent, the storage capacity of methane correlates exclusively with the surface area and micropore volume. However, in a recent study, Delavar et al.[54,82] noticed a strong influence of the pore morphology on the ultimate performance of carbonaceous materials in the case of methane storage. Their experimental adsorption isotherms for the three different temperatures of 283.15, 298.15, and 318.15 K demonstrated that a multiwalled carbon nanotube adsorbed more methane than a granular activated carbon (GAC) with a large surface area. The MWCNT (with an average value of $H' > 4$ nm) with a surface area 294 m^2/g and pore volume of 0.623 cm^3/g stored up to 33 mmol/g (52 wt %) at 5 MPa and 283 K, whereas the GAC with a surface area of 822 m^2/g and a pore volume of 0.66 cm^3/g could store only up to 6.5 mmol/g under the same experimental conditions. The authors further claimed that the MWCNTs at room temperature and 3.5 MPa reached a gravimetric storage capacity as high as ∼21.5 mmol/g (34.4 wt %), whereas the GAC could store only 5 mmol/g (8 wt %) under similar operating conditions.[54,82] Such high storage capacity values for MWCNTs over activated carbons seem surprising, especially considering the restricted pore sizes of MWCNTs, the supercritical temperature of the fluid, and the accessible surface area/framework density ratio and lower accessible pore volume. Furthermore, no satisfactory arguments were put forward by the authors about why the MWCNTs adsorb better than activated carbons, although the authors mentioned that the superiority of MWCNTs is due to their smaller effective pore size and higher pore volume. Contesting the results of Delavar et al., a few other works pointed out that, even at the expense of high pressures of 7 and 10.5 MPa, MWCNTs that are essentially microporous can store only up to 4.48 wt % (2.8 mmol/g) and 11 wt %, respectively.[38,62] Obviously, all of these works confirm the results that can detail the effects of pore structure on the adsorption capacity of natural gas are inconclusive and, in some cases, even controversial. The adsorption capacity of methane in curved structures estimated through simulations or experiments are influenced by multiple parameters, such as the number of walls that bound the porosity, surface irregularities, local C-atom vacancies, the size distribution of tubes, the presence of open-/closed-end tubes, the diameter of the tubes, the distance between the neighboring tubes, the helicity, and the array geometry. All of these parameters demonstrate the difficulty of performing systematic experimental studies and make the results less tractable and comparable to results obtained from simulations.[28,83] Surface curvature can improve the isosteric heat or pressure at which a fluid tends to fill the entire pore volume, as a methane molecule can experience interactions with a relatively greater number of carbon atoms than for a planar surface (as in graphene). Despite the fact that a higher isosteric heat can favor the uptake of methane at lower pressures (Henry region), it is the volume of methane that is adsorbed at storage pressures (≥3.5 MPa) that dictates the properties of the adsorbent for the onboard storage of natural gas. The curved surfaces in nanotubes, especially in micropores, affect the accessible pore volume of the carbon framework and, thus, the amount of fluid confined within the pore volume (as a methane molecule adsorbed on one side of the pore surface will disturb the surface adsorption of a methane molecule on the opposite adsorption site). This also explains why there is no convincing evidence from either experiments or theoretical simulations to confirm that carbon frameworks with curved surfaces surpass activated carbons for the storage of methane at room temperature. Based on the works considered in this review, we observed (see Figure 2, where we show the adsorption of methane in carbon nanotubes as a function of their surface area[38,62]) that nanotubes exhibit a low methane uptake when compared to other activated carbons with high surface areas. If one compares their performance with those of activated carbons of similar surface area, it can be understood that the curved surface and confined pore volume do not offer any interesting properties toward methane uptake. In some cases, even at the expense of pressure (11 MPa), nanotubes exhibit a very low methane adsorption capacity.[38] This is not a disheartening result, as the production of nanotubes often relies on expensive techniques such as arc discharge or chemical vapor deposition methods, whereas activated carbons are relatively easy to synthesize and economically cheaper than nanotubes.

As discussed in the next section, hopes of obtaining viable adsorbents for methane storage have recently focused on metal−organic frameworks (MOFs),[47,84,85] as some recent studies apparently showed that MOFs could exceed the storage capacity of carbon-based materials. MOF structures combine very open scaffolding with unique high-energy sites; however, they suffer from several handicaps, including chemical and thermal instability, low packing density, and cost. For this reason, nanoporous carbon materials continue to be truly effective adsorbents if the appropriate structure, packing density, and pore size can be found. The results from GCMC simulations that we performed for this work showed that a slit pore with a pore width of $H' = 0.8$ nm (bound by one layer of graphene) can theoretically store (adsorption excess) up to 282 and 290 v/v at 3.5 and 5 MPa, respectively. These values are higher than the theoretical volumetric capacities of most of the MOFs synthesized to date. This can be explained if one considers the nature of the pore volume in an ideal slit pore and an MOF. MOFs are highly porous materials (∼90% porosity), and this high porosity can benefit several applications in industrial processes; organic linkers that connect the metal node and built the entire framework are associated with several edge sites. Even though these edge sites can provide a remarkable surface area, the energy of interaction of guest molecules, such as methane, with the edge sites is lower than that of guest molecules on more planar surfaces such as graphene (as the number of carbon atoms associated with the interaction energy is higher). This effect will be even more pronounced in a microporous carbon structure, as the carbon atoms from both sides of the wall will add to the interactions, which ultimately increases the methane adsorption capacity.

To summarize, based on the works considered in this review, it is clear that even carbons with surface areas exceeding the surface area of ideal graphene with high levels of microporosity can hold only about 160 v/v, which is still below the 2000 DOE target and far below the DOE MOVE targets. This obviously shows the need for a proper adsorbent design strategy to achieve these targets. The correlations between the surface area and micropore volume of nanoporous carbons and the adsorption capacity of methane (Figure 2) clearly show that techniques such as improving the surface area do not offer any significant improvement in the methane uptake. Additionally, the idea of improving already-high surface areas does not seem to be a feasible option. One strategy that can improve the methane storage capacity is to synthesize carbon materials with pores that are bounded by exactly one layer of carbon atoms. Creating such a sophisticated carbon material in large quantities with a very high packing density and extremely low framework density is a very challenging task, especially with the available synthesis techniques. Another strategy is to improve the surface area and packing density simultaneously (in Figure 2c, we showed that such strategy can achieve the 2000 DOE target of 180 v/v), which is difficult to accomplish by chemical activation or physical activation techniques.

Finally, it is worth mentioning that targeting the sorbent level adsorbent capacity of the DOE MOVE goals (12.5 MJ/L at ≤3.5 MPa and 298 K) in carbon-based materials would be a very difficult task, as it can only be achieved in a carbon structure that has a very low framework density, a material that contains pores bounded by only one layer of graphene sheet, and a high packing density. The feasibility of obtaining such a material with a desirable combination of these properties is still questionable. Thus, our suggestion for researchers, mainly experimentalists, is to reconsider the targets or relax the operating conditions (storage pressure can be pushed to a much higher pressure instead of 3.5 MPa) before making any further investments in material design.

5. METAL–ORGANIC FRAMEWORKS

Metal–organic frameworks (MOFs) are among the most fascinating recent developments in the class of nanoporous materials, with exceptional pore properties offering great promise for many applications, including natural gas storage. In essence, MOFs are porous (almost 90% porosity), crystalline sponges made up of metal or metal oxide "nodes" connected by organic "linker" compounds.[86] O'Keeffe[87] used the term "MOF" to include only materials with frameworks built by linking polyaromatic clusters (secondary building units) entirely by strong covalent bonds, and this does not include coordination polymers, which generally have some weaker bonds and lower stability. The vast numbers of metal clusters and organic linkers available for the synthesis of new MOF structures make it possible to build an unlimited number of solids with desired pore sizes and shapes plus functionalities to provide optimal host–guest interactions.[88] Kondo et al.[89] were the first to report the adsorption of methane in an MOF structure $[Co_2(4,4'\text{-}2,2'\text{-bipyridine})_3(NO_3)_4.4H_2O]_n$, although this compound exhibited a very low gravimetric storage capacity for methane of 3.68 wt % at 3 MPa. The same research group later reported a new and novel three-dimensional coordination polymer, $\{[CuSiF_6(4,4'\text{-bpy})_2]\cdot 8H_2O\}_n$, which had a higher methane uptake of 10.42 wt % at 3.6 MPa (volumetric storage capacity and crystallographic density not reported).[90] In 1999, Li et al.[85] published the MOF structure $[Zn_4O(BDC)_3]$, also known as MOF-5, which exhibited an ultrahigh porosity (80%) and a remarkable surface area of 2900 m^2/g. The properties of MOF-5 in this work and the need for a porous material with a high surface area, plus the difficulties associated with increasing the already-high surface areas of carbon materials, sparked a flurry of both experimental and theoretical research over the past decade, most of the which focused on finding a material with excellent fuel (hydrogen and methane) storage properties.

From the experimental point of view, several thousand MOFs have been synthesized to date by several research groups worldwide. Some of them do not support permanent porosity and collapse in the absence of guest molecules such as solvents. The reported materials could be seen as only a tiny fraction of imaginable materials, considering the large variety of possible linkers and corner units and the possibility of postfunctionalizing the resulting MOFs.[88] The storage capacity of MOFs for methane has been reviewed several times in recent years by several researchers,[45,46,91−94] and consequently, the scope of this review is restricted to considering only a short comprehensive review emphasizing the adsorption properties of some of the benchmark or milestone MOF compounds that showed promising natural gas storage values at room temperature. New concepts that need to be considered in the design of MOF adsorbents for the storage of natural gas are also included. Works that report on the MOFs with excellent storage capacities but at much lower temperatures (<280 K) are not considered here. However, a detailed literature analysis of the storage capacities of different MOFs can be found later in this section to emphasize the influence of the pore structure/properties of MOFs on the ultimate storage capacity of methane at 298 K and 3.5 MPa. Additionally, some of the reported results from theoretical studies that support the findings derived from the experiments will be highlighted. To avoid confusion, experimentally reported MOF structures with excellent storage capacities are discussed first, followed by a special focus on theoretical results to support the reported experimental work and to emphasize the importance of the relationship between MOF structural properties and storage capacity.

Seki[84] was the first to demonstrate the apparently remarkable storage capacities of coordination polymers for methane at 298 K. This researcher synthesized novel three-dimensional metal complexes by a heterogeneous reaction between porous copper dicarboxylates and triethylenediamine (TED), $[Cu(O_2CRCO_2)\cdot{}^1/_2TED\}_n]$ [R = 4,4′-$C_6H_4C_6H_4$ (**1**) or *trans*-$C_6H_4CH{=}CH$ (**2**)], the latter (**2**) being recorded as the first ever to achieve a volumetric storage capacity for natural gas (with MOF structures) of up to 225 v/v. In terms of gravimetric storage capacity, this corresponds to 213 cm^3 (STP)/g at 3.5 MPa and 298 K. However, such a high volumetric storage capacity is due to the high apparent density (**2**, ~0.983 g/cm^3) of the complex, which was obtained by mercury porosimetry. In addition, these materials (**1** and **2**) showed a combination of pore properties dictating their performance toward methane storage: (i) high surface areas (3265 and 3129 m^2/g); (ii) large pore volumes (1.18 and 1.07 cm^3/g), with effective pore sizes of 1.08 and 0.95 nm for **1** and **2** (microporous, with no mesoporosity), respectively; and (iii) bimodal pore size distributions with two types of adsorption sites having different adsorption potentials. In recent years, these estimated values were placed under debate and criticized, as the estimated apparent density was higher than even the calculated crystallographic density. Ma and Zhou[45] recalculated the volumetric capacity value for **2** considering its crystallographic density (0.80 g/cm^3), and they found that it could store up to 175 v/v at 3.5 MPa and 298 K. Nevertheless, the remarkable storage capacity reported by Seki in 2001 must have inspired many researchers to work with coordination frameworks in an attempt to obtain the best candidate material for fuel (H_2 or CH_4) storage. All of these storage capacity values were obtained directly from adsorption experiments and, thus, correspond to excess adsorption. In a frequently cited work of Eddaoudi et al.,[95] a series of isoreticular MOF (IRMOF) compounds that had cubic porous structures but were functionalized with different groups were tested for their structural and gas adsorption properties. IRMOF-6 (crystallographic density = 0.65 g/cm^3), with an exceptionally high surface area and pore volume, exhibited a remarkable gravimetric storage capacity of 240 cm^3(STP)/g (155 v/v) at 3.6 MPa and room temperature, the highest (gravimetric) value achieved with this class of materials at that point (2002). IRMOF-1 (also widely known as MOF-5) and IRMOF-3 exhibited volumetric storage capacities of 135 and 120 v/v, respectively, at 3.6 MPa; these values are impressive when compared to the storage capacities of other classes of crystalline materials such as zeolites (87 v/v)[26] and similar to values reported for many carbon adsorbents. The hydrophobic nature of the C_2H_4 units in IRMOF-6 favors methane adsorption, thus explaining its superior performance when compared to those of IRMOF-1 and IRMOF-3. To our knowledge, the work of Eddaoudi et al.,[95] which was published in 2002, seems to have been the first to report or define the volumetric storage capacity of methane based on the crystallographic density of MOF structures. In recent years, although several researchers have employed this definition, it is often criticized because it ignores the void spaces between the particles when MOFs are packed in an adsorbent storage tank, where the packing density is more realistic.

Inspired by an in silico-generated MOF structure, IRMOF-993,[96] Ma et al.[97] synthesized a microporous metal−organic framework based on the anthracene derivative 9,10-anthracenedicarboxylate, which led to the ultramicroporous MOF PCN-13, which had a very limited methane storage capacity. In a follow-up study, they increased the pore size by employing the new ligand 5,5′-(9,10-anthracenediyl)di-isopthalate (adip) under solvothermal reaction conditions to obtain the new MOF PCN-14.[47] This material recorded the highest-ever-achieved excess methane volumetric storage capacity of 220 v/v and a gravimetric storage capacity of 252 cm^3/g at 290 K and 3.5 MPa, although the first value should be taken with care as, the crystallographic density was used to calculate the volumetric storage capacity, which is almost always larger than the more realistic packing density. Since the year 2008, PCN-14 has been considered and accepted by several researchers as a benchmark material to compare the performance of any MOF adsorbent for methane storage. Although the deliverable capacity of PCN-14 was not reported, the recorded excess adsorption was apparently 22% higher than the DOE's landmark value of 180 v/v at room temperature (because of the use of the crystallographic density for the estimation of the volumetric storage capacity). The highest storage capacity in this structure was associated with an isosteric heat, Q_{st}, of 30 kJ/mol. Although this value is lower than the Q_{st} values for some carbon-based materials,[51] this seems to be the highest value recorded for this class (MOFs) of porous materials. A DFT study[98] showed that the binding energy at the open Cu sites is roughly 25 kJ/mol and that the bottom site of the small cage in PCN-14 has the highest binding energy of 32 kJ/mol, which probably explains the high isosteric heat achieved. Apart from the performance of this material in terms of its volumetric storage capacity, this work also focuses on the importance and role of the ligands in the methane storage capacity of MOFs.

Inspired by the high storage capacity of PCN-14, Wu et al.[99] carried out some preliminary studies in 2009 and reported that the apparently impressive storage capacity of this material is due to the presence of coordinated unsaturated Cu ions. This conclusion was based on the fact that, if all open Cu sites were saturated with at least one CH_4 molecule, then it would give an adsorption capacity of 59, which is roughly one-quarter of the total adsorption capacity (at 290 K and 3.5 MPa). Motivated by this concept, they performed methane adsorption isotherm experiments on a series of isoreticular MOF compounds with metal ions of the form M_2(dhtp) (open metal M = Mg, Mn, Co, Ni, Zn; dhtp =2,5-dihydroxyterepthalate). All of these MOFs had significantly higher densities of open metal sites in their crystal structures (4.5 sites/nm^3) than PCN-14 (~1.6 sites/nm^3). Thus, conceptually, these MOFs should perform better than or equal to PCN-14, or they should at least approach the DOE target. The adsorption isotherm results showed that the volumetric storage capacities (obtained using the crystallographic densities) of the M_2(dhtp) MOFs at 298 K and 3.5 MPa ranged from 149 to 190 v/v. The highest storage capacity of 190 v/v was recorded for one of the MOFs that contained Ni ions, and it was claimed to be the second best material (in the year 2009) for methane storage, next to PCN-14. Through neutron diffraction experiments, the authors confirmed that the metal sites were fully responsible for the high storage capacities of these M2(dhtp) MOFs, which is now considered to be the right strategy for the design of MOFs for methane storage.

In the same year (2009), Dietzel et al.[100] reported similar results based on the adsorption isotherms obtained for the series of MOFs $M_2(dhtp)(H_2O)_2{\cdot}8H_2O$ (CPO-27-M, M = Ni, Mg), which were selected because of their honeycomb structures, large micropores (1.1−1.2 nm), and the presence of open metal sites. These authors confirmed the results of Wu et al.[99] and reported that the metal sites play a major role in the adsorption of methane. Their estimations revealed that up to 1.73 CH_4 molecules are adsorbed on every Ni atom at 179 K and 1 MPa for the case of Ni_2(dhtp), whereas for the case of Mg_2(dhtp), at 179 K and 4 MPa, every Mg atom could take up to 1.68 molecules. Because adsorption is exothermic, these values are prone to decrease at room temperature (not reported). As in the results of Wu et al.,[99] the MOF containing Ni exhibited the best performance toward methane storage at 298 K. At 3.5 MPa, Ni_2(dthp) exhibited a volumetric storage capacity of up to 198 v/v when using the crystallographic density of the MOF framework compound (which was slightly higher than the values of Wu et al.). The same material was found to meet the 180 v/v goal at a much lower pressures of 2.0 MPa, whereas Mg_2(dhtp) comes close to this landmark value (169 v/v). Although the estimated delivery was not reported, the authors claimed that Ni_2(dhtp) already exceeded the DOE target by a significant amount; however, the problem of using the crystallographic density for their calculations should be realized.

In another closely related and more recent work, Guo et al.[48] used two strategies simultaneously to increase the storage capacity of MOF structures: (i) the immobilization of high-density open metal sites and (ii) the construction of suitable pore spaces within the MOF framework. The authors demonstrated this strategic concept with the MOF compound UTSA-20, which was synthesized by the solvothermal reaction of H_6BHB and $Cu(NO_3)_2{\cdot}2.5H_2O$ in *N*,*N*-dimethylformamide (DMF, 1.5 mL) with the addition of two drops of HBF_4 at 65 °C for 48 h to yield small green block-shaped crystals. The developed structure, which was formulated as [Cu_3(BHB)-

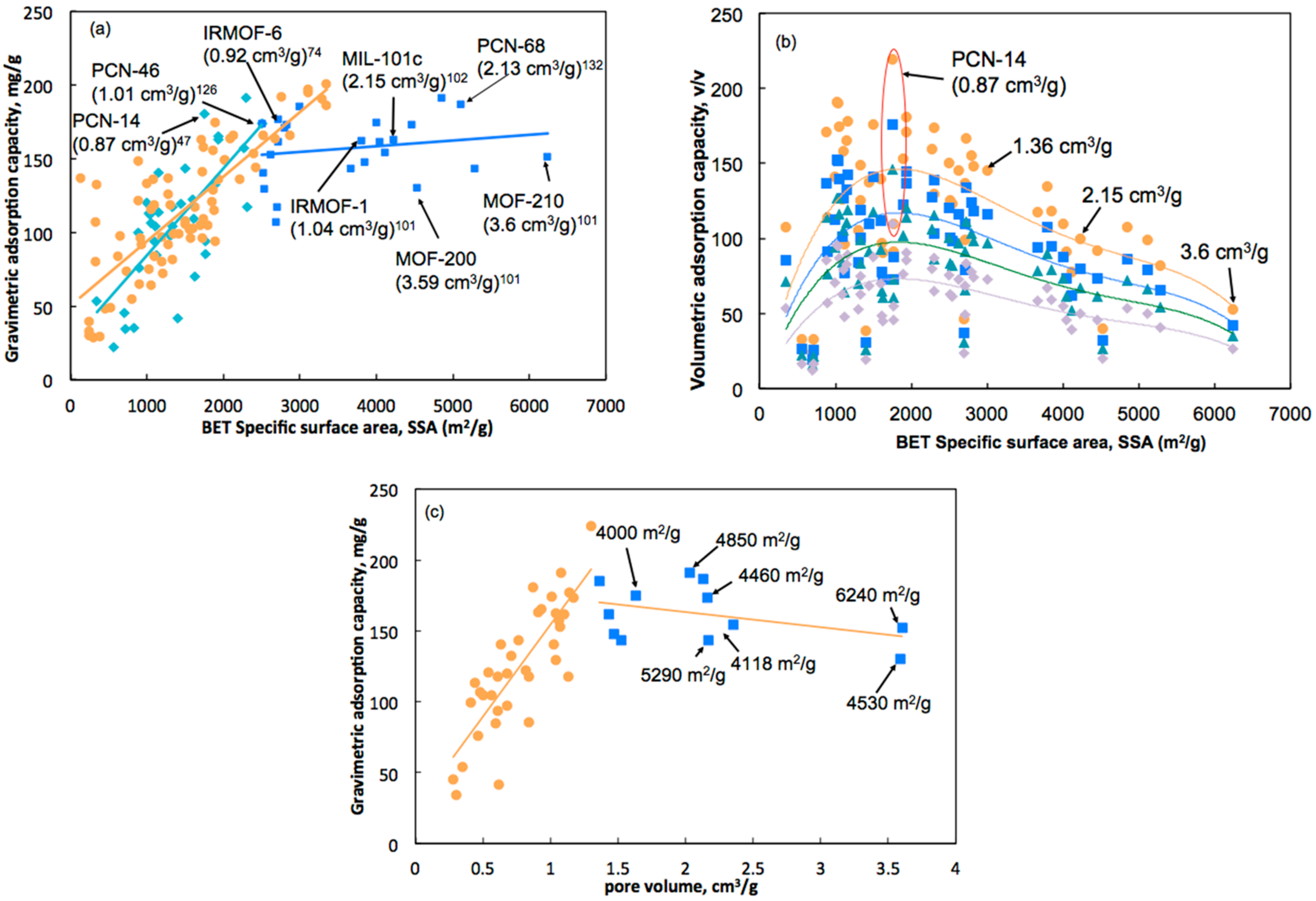

Figure 3. (a) Gravimetric methane adsorption capacity at 3.5 MPa and 298 K versus BET surface area (teal diamonds, MOF structures with specific surface areas of ≤2500 m^2/g; blue squares, MOF structures with specific surface areas of ≥2500 m^2/g; orange circles, carbon-based materials). (b) Volumetric methane adsorption capacity at 3.5 MPa and 298 K versus BET surface area for different assumed values of packing efficiency, where X_d represents the packing density/crystal density (orange circles, $X_d = 1$; blue squares, $X_d = 1.25$; teal triangles, $X_d = 1.5$; lilac diamonds, $X_d = 2$). (c) Volumetric methane storage capacity at 3.5 MPa and 298 K versus pore volume (orange circles, MOFs with pore volumes of ≤0.92 cm^3/g; blue squares, MOFs with pore volumes of ≥0.92 cm^3/g).[47,48,84,87,90,95,97−137] All of the adsorption values correspond to adsorption excess. All of the adsorption values correspond to adsorption excess (except PCN-14, all the adsorption values correspond to the experiments performed at 298 K; adsorption value in PCN-14 was performed at 290 K).

$(H_2O)]\cdot(DMF)_6(H_2O)_{2.5}$, had a three-dimensional pore structure of **zyg** topology, with open Cu sites and optimal pore spaces that were formed by the self-assembly of the hexacarboxylate organic linker H_6BHB (H_6BHB = 3,3′,3″,5,5′,5″-benzene-1,3,5-triylhexabenzoic acid) with the paddle-wheel Cu_2-$(COO)_4$SBU (SBU = secondary building unit). They compared the performance of this structure with the performances of some of the benchmark MOFs (PCN-14, PCN-11, IRMOF-6) and found that, although UTSA-20 had a moderate surface area and pore volume (1156 m^2/g and 0.63 cm^3/g), the high density of the open Cu sites and the optimum pore size contributed to the high absolute volumetric methane storage capacity of 195 v/v at 3.5 MPa and 300 K. In terms of excess volumetric storage capacity, this equals 178 v/v at 300 K and 3.5 MPa, which is closer to the landmark value of 180 v/v, although they also used the crystallographic density instead of the packing density for their calculations. Although this value falls below the storage capacities of the best-performing MOFs, PCN-14 and Ni_2(dhtp),[47,48,99] it apparently surpasses those of most of the best-performing materials in the MOF category[92,95,101,102] and other classes of materials[26,52,81] with similar surface areas and pore volumes. Computational investigations revealed that the high adsorption capacity was favored by the open Cu sites and "linker channel sites", with channel-like pores present in this MOF framework. Simulations further revealed that the Cu sites contributed almost half (89 v/v) of the total storage capacity of UTSA-20 at 3.5 MPa and 298 K. The results of Dietzel et al.[100] and Guo et al.[48] clearly emphasize the importance of the presence of open metal sites and the optimum pore structure (a novel trinodal net of **zyg** topology) and pore size to reach the DOE target in this class of high-surface-area porous materials.

Another work that frequently appears in the literature of recent years is that of Furukawa et al.,[101] in which they claimed that an MOF with a very high BET surface area can perform better at pressures higher than 3.5 MPa. Three MOF compounds with ultrahigh surface areas, namely, MOF-200 (4530 m^2/g), MOF-205 (4460 m^2/g), and MOF-210 (6240 m^2/g), exhibited storage capacities of 446, 394, and 476 mg/g, respectively, at 298 K and 8 MPa; all of these materials exceeded the storage capacity of PCN-14, but at the expense of higher pressure. The authors claimed that the methane adsorption isotherms of these MOFs were almost linear up to 8 MPa, and using some simple extrapolation, they concluded that these MOFs would favor a higher gravimetric adsorption capacity at higher pressures and could possibly perform better at CNG pressure (20 MPa). In any case, despite the impressive gravimetric storage capacities obtained at higher pressure (8 MPa), the volumetric storage capacities seemed to be too low even considering the assumption that the crystallographic density is equal to the packing density. For instance, the best-performing MOF, MOF-210 with a surface area >6000 m^2/g, could only store up to 99 v/v at 8 MPa and 298 K, which is only 11% higher than the amount of methane stored in CNG at the same pressure (89 v/v). Despite the ultrahigh surface areas and the striking gravimetric adsorption capacities of these MOFs, their significantly lower volumetric storage capacities lead us to an important conclusion: Working toward a high surface area might not be the appropriate approach for reaching the DOE goal. Rather, focusing on finding the right balance among the pore volume, surface area, and packing density is a more promising strategy.

In an attempt to determine where and how methane is stored in some of the MOFs that apparently have outstanding methane storage properties, Wu et al.[98] carried out a systematic study of the high-storage-capacity MOF compounds HKUST-1, PCN-11, and PCN-14 using a combination of different techniques: (i) neutron diffraction measurements, (ii) grand canonical Monte Carlo simulations, and (iii) density functional theory calculations. Although HKUST-1 does not exhibit very inspiring methane adsorption properties, it is one of the most studied MOF compounds for the adsorption of other gases such as N_2, H_2, and CO_2.[102] These three MOF compounds were selected by Wu et al. because, structurally, they contain the same dinuclear $Cu_2(CO_2)_4$ "paddle-wheel" cluster but different organic linkers with cagelike pore structures, different sizes, and different geometries. This strategy allowed them to study the roles of pore structure and linker functionality in methane adsorption. They found that the high adsorption capacities of these materials are due to two types of strong adsorption sites: (i) the open metal (Cu) coordination sites, which enhance the Coulombic attraction toward methane, and (ii) the van der Waals potential pocket sites, in which the total dispersive interactions are enhanced due to the molecule being in contact with multiple "surfaces". According to that work, the rational development of new materials for the storage of methane should focus on (i) enriching the open metal sites, (ii) increasing the percentage volume of accessible cages and channels, and (iii) minimizing the fraction of large pores.

Is there any simple relation that correlates the physical pore properties of the MOF structure with the storage capacity under the conditions specified by DOE (3.5 MPa and 298 K)? Most of the studies highlighted above propose various strategies to improve the storage capacity of MOFs by designing the pore topology, tuning the pore volume and surface area, and increasing the isosteric heat, among other strategies. Despite these factors, as a general rule, most results reported in the literature rely on the approach of improving the surface area as the key factor in enhancing the storage capacity. Apart from the conclusion derived from the adsorption isotherms in the discussed works, some of the theoretical reults showing snapshots obtained during the adsorption of methane in different MOF structures clearly indicate that structures with pores of a size that can hold one or two layers of methane exhibit the highest adsorption capacities, which is analogous to the pore size of carbon-based materials recommended for methane storage a few years earlier.[16] This implies that no (highly dense) multilayer adsorption can be expected to occur in MOF structures at room temperature, at least when the pressure is p = 3.5 MPa. Thus, a linear correlation between the surface areas of MOF materials and their gravimetric storage capacities should likely exist. We tried to verify this concept in this review by plotting the storage capacities of different MOFs as a function of the pore properties. Such plots should help to trace or identify the practical limit for the storage capacity as a function of the pore properties, such as surface area and pore volume, in addition to the relationship that might exist between these parameters and the storage capacity. Figure 3a includes plots of the amount adsorbed (mg/g) at 3.5 MPa as a function of surface area for different MOF structures with a wide range of pore properties, as reported by several research groups in the past 10 years. Because volumetric storage capacity is not a property of the material, given that it depends on the packing density and the efficiency of packing, only the gravimetric methane storage capacity as a function of surface area is considered.

Figure 3a clearly shows that, despite the different pore properties, such as the presence of open or coordinated metal sites, pore width, and pore size, the storage capacity fairly increases with increasing surface area. Figure 3a also shows that increasing the surface area above 2500 m^2/g does not increase the amount adsorbed by a significant amount at 3.5 MPa, although some of these high-surface-area materials (for example, the MOFs in the work of Furukawa et al.[101]) are prone to hold more methane, but at the expense of higher pressures (p > 5 MPa). Typically, these high-surface-area MOFs (>2500 m^2/g) have larger pore sizes and pore volumes (in Figure 3a, the pore volumes of some of these high-surface-area MOFs are provided), where methane molecules typically experience weak interactions with surface atoms and can experience a stable position only at much higher pressures, typically >3.5 MPa. Although, the presence of open metal ions increases the adsorption capacity at lower pressures, they do not seem to result in any significant improvement in the adsorption capacity at 3.5 MPa, because at this pressure, the excess adsorption is just proportional to the surface area, irrespective of other factors. Increasing the specific surface area beyond 2500 m^2/g does not seem to provide enough scope for improving the storage capacity, as above this value, we observed only a very slight increase in storage capacity (almost linear with a slope equal to 0.0039; see the trend of the blue line in Figure 3a). For comparison, the excess adsorption of carbon-based materials as a function of their BET surface areas is also plotted in Figure 3a. It is interesting to note that the gravimetric adsorption capacity as a function of surface area was found to be almost independent of the class of materials considered in this review. In the case of carbon-based materials, there is a lack of synthesis strategy that allows the improvement of the surface area (>4000 m^2/g) of carbons equivalent to some of the high-surface-area MOFs, as the available high-surface-area carbon materials are already equal to or beyond the limit of the surface area of an ideal graphene sheet (2630 m^2/g). This creates a practical difficulty when comparing the performances of high-surface-area MOFs with those of carbon-based materials. Despite these known facts, the projection in Figure 3a helps to safely conclude that there exists a limit (~2500 m^2/g) up to which the surface area dictates the methane storage capacity at 3.5 MPa, irrespective of the class of porous materials considered here (MOFs or carbon-based materials). It should be noted that the adsorption capacity of PCN-14 (at 290 K), which holds the record for the highest volumetric storage capacity, is highlighted in Figure 3a; although if the adsorption is expressed on a weight basis (Figure 3a), its performance appears to be quite ordinary and comparable to those of other MOF structures. This means that the density of the storage material is the clue to the apparently high storage, and this value cannot always be clearly defined or measured, because almost all authors use the crystallographic density of MOFs instead of the packing density, as would be used in a practical application. For the convenience of readers, Figure 3a also highlights some of the benchmark MOF compounds and their pore volumes.

Plotting the excess volumetric storage capacity versus the pore volume or surface area (Figure 3b,c) leads to the same conclusion as above. Figure 3b,c indicates that the excess amount adsorbed is proportional to the MOF surface area and/or pore volume until it reaches an "optimum value", after which, irrespective of the high surface area of the MOF structures, there is no significant increase in the excess adsorption at 3.5 MPa and 298 K. According to Figure 3b,c, this optimum surface area and pore volume value lie roughly within the ranges of 1750−2000 m^2/g and 0.8−0.95 cm^3/g, respectively. Increasing the pore volume above this range (irrespective of the surface area of the solid frameworks) decreases the excess adsorption, as methane molecules tend to fill the pore volume with a gaslike density after surface adsorption. In larger pores, as analogues to the experimental results reported for the case of carbon materials, the interactions between methane and the metal sites or linker molecules on the MOF structures are too weak to expect any multilayer adsorption or fluid condensation of methane at 3.5 MPa and 298 K. While this article was in preparation, Simon et al.[138] reported a similar conclusion based on the large-scale screening of 650000 materials including MOFs, zeolites, porous polymer networks, and zeolitic imidazolate frameworks for the adsorptive storage and delivery of methane. They screened the MOFs based on their deliverable capability, which is simply the amount of methane stored at 65 bar minus the adsorption of methane stored at 5.8 bar at 298 K. They found that there exists a maximum for surface area and pore volume for the optimal delivery of methane at 298 K. They also declared that it might be practically impossible to reach the targets identified by the DOE MOVE program. It is worth mentioning here the very recent work of Mason et al.,[139] who observed pressure- and temperature-induced framework flexibility during the adsorption of methane in two different MOFs, namely, Co(bdp) and Fe(bdp). Such materials can obviously deviate from the relationship between the amount adsorbed and the material properties (shown in Figure 3). Pressure-induced framework flexibility is usually associated with adsorption hysteresis. In any case, none of the materials considered in this review exhibited such framework flexibility at 3.5 MPa and 298 K or adsorption hysteresis.

The presence of open metal sites in MOFs is considered to be one of the design strategies for increasing the adsorption performance of these structures; however, Figure 3a−c clearly indicates that, to meet the U.S. DOE target, the ideal material for storing methane should be one that has the right balance among surface area, pore volume, and packing density, irrespective of other design strategies. It can be clearly deduced that the high volumetric storage capacities published for many MOFs are only due to the use of the crystallographic density in the calculations. Thus, the design strategies for MOFs should focus on tuning the surface areas and pore volumes of the materials to obtain the optimum values simultaneously, without compensating any of these parameters to improve the storage capacity for methane. This conclusion is in agreement with those obtained from the GCMC simulations carried out by Wang,[103] who studied the adsorption properties of 10 different MOF structures with the aim of establishing the most desired properties of an optimal adsorbent for methane storage. He found that, although a high isosteric heat of adsorption, low framework density, high specific surface area, and high free volume are desirable for a better storage capacity, there exists a complex interplay among these parameters that influences the ultimate adsorption capacity. Despite these facts, the accessible surface area and free volume seem to play decisive roles in the storage capacity at 3.5 MPa and 298 K. It is worth emphasizing the value of the presence of open metal sites in improving the isosteric heat of adsorption, thus significantly increasing the amount of methane adsorbed at lower pressures. The study of Wang also highlighted this trend through a linear relationship between the amount adsorbed at lower loadings and the isosteric heat of adsorption.[103] In fact, a DFT study revealed that methane molecules adsorb first on the open metal sites.[99] The isosteric heat of PCN-14 at a lower loading (0.1 mmol/g) was near 30 kJ/mol, because of the strong binding energy of methane to the open metal sites, but it decreased to 25 kJ/mol at intermediate loadings (0.5−1 mmol/g).[99] In a theoretical study performed with a new force field for CH_4/PCN-14 systems (adjusted to improve the fitting between the experimental and simulated isotherms), it was shown that the open metal sites increased the overall binding energy of PCN-14 by a significant amount only at 150 K, but not at higher temperatures (290 K),[104] supporting the arguments stated above.

How far can these novel MOFs be pushed to reach the 2000 DOE target (adsorption or deliverable capacity of 180 v/v at 3.5 MPa and 298 K)? Most MOF structures described in the literature exhibit storage capacities ranging from 50 to 160 v/v.[101,102] As an extraordinary case, PCN-14 has a very high volumetric capacity of 220 v/v, apparently beating every other porous material.[47] As already mentioned, although MOFs exhibit high volumetric storage capacities, almost all reported values have been obtained by converting the gravimetric capacity to a volumetric capacity by using the crystallographic density rather than packing density, and most of these works further claimed that MOFs outperform other classes of materials, for instance, activated carbons. As noted throughout this section, such estimations are not realistic and assume that the MOF materials will fill the fuel tank to form a single bulk crystal, ignoring the fact that the effective packing density is much lower because of the existence of voids between particles. Senkovska and Kaskel[140] recently reported that the crystallographic density can vary from the packing density for some MOFs by at least a factor of ∼2. This is the first work and most probably the only one appearing in the literature in recent years claiming the superiority of an MOF material, $Cu_3(btc)_2$, based on the volumetric storage capacity obtained using the packing density. The authors found that $Cu_3(btc)_2$ could store up to 228 v/v but only at the expense of higher pressures (15.0 MPa). It is worth mentioning that, at such high pressures, storage capacities of up to 178 v/v can be reached by CNG, without the expense of any adsorbent. In any case, the work of Senkovska and Kaskel clearly emphasizes that the practical limit of MOF materials are far from the volumetric storage capacity values estimated using the crystallographic density. A study by

Peng et al.[141] also highlighted this particular issue. In particular, Peng et al. measured the methane adsorption isotherms in a series of packed polycrystalline HKUST-1 materials with different packing densities. They found that decreasing the packing density of HKUST by a factor of 2 with respect to its ideal crystalline density also decreased the excess volumetric uptake by a factor of 2 with respect to the ideal performance of HKUST.

If one assumes that the findings reported in the works of Peng et al. and Senkovska and Kaskel hold true for every other MOFs, then the volumetric capacities of the MOFs (including PCN-14) estimated using the crystallographic density can be taken only as the upper limits for the apparent volumetric storage capacities that can be attained in these materials. A word of caution should be introduced here: If the crystallographic density were used for porous carbons (up to 2.26 g/cm^3), then the corresponding volumetric storage capacity would be 3−4 times larger than if the packing density (well over 500 v/v for the best carbons described in the previous section) were used. A strategic study of this particular issue was performed by Sun et al.,[142] who stressed the fact that the crystallographic and packing densities should not be confused. The volumetric storage capacities of MOF structures reported by several research groups are plotted in Figure 3b as a function of surface area. The surface area in the plot is taken only as a reference to represent the MOF structures, and it should be remembered that volumetric storage capacity is not a property of the material. Figure 3b shows the volumetric storage capacities of different MOF structures for different assumed values of packing density. The packing density, d_{packing}, was assumed to be lower than the actual crystallographic density, d_{crystal}, by roughly a factor X_d, where X_d ranges from 1.25 to 2 ($d_{\text{packing}} = d_{\text{crystal}}X_d$). The trend lines are shown to illustrate (as a guide to the eye) the difference in the magnitudes of the results obtained for different values of X_d. The projected estimations show some interesting facts. Even if an effective packing density of up to 80% is reached ($X_d = 1.25$), the performance of most of the MOFs falls into the range of 80−130 v/v, which is lower than the values obtained for some of the promising conformed high-surface-area activated carbons.[18,36,55,70] Again, these estimated values assume that packing/compression of an MOF does not affect the porosity of the material. These estimated values could probably be taken as the practical limit of these materials for methane storage at 3.5 MPa, yet this needs to be experimentally verified. Even PCN-14, which has a fascinating pore structure and properties with van der Waals potential pockets, and other MOFs with open metal sites cannot outperform other classes of porous materials such as carbon, and none of them seems to be able to meet the milestone of 180 v/v.

On the theoretical side, molecular simulations have been used to characterize MOFs, to predict their methane adsorption properties and to gain insights into the adsorption process at a molecular level under the desired experimental conditions. Düren et al.[96] performed GCMC simulations to investigate the characteristic adsorption of methane in several computer-generated IRMOFs, molecular squares, zeolites, MCM-41, and carbon nanotubes. Their results suggested that the surface area favors the methane storage capacity, in addition to pore volume, framework density, and adsorbent/methane interactions. They also proposed new (and not synthesized at that time) IRMOF structures having 1,4-tetrabromobenzenedicarboxylate and 9,10-anthracenedicarboxylate as linker molecules. Simulations showed that these structures should exhibit very high methane storage capacities when compared to that of IRMOF-6,[95] one of the promising materials for methane storage existing at that time. Specifically, using 9,10-anthracenedicarboxylate as the linker molecule resulted in a material, IRMOF-993, with a crystallographic density of 0.81 g/cm^3 that exhibited a theoretical storage capacity of 181 v/v, with an isosteric heat adsorption of 15.48 kJ/mol. This work set the inspiration and showed the synthesis path leading to the development of two other MOF compounds, PCN-13 and PCN-14, whose adsorption properties were discussed earlier in this section.[47,97] The initial study of Düren et al. demonstrated the power of computational tools to provide an idea of how to synthesize a material that would provide better performance for a desired application.

Inspired by the computational studies of Düren et al., Thornton et al.[143] proposed a hypothetical MOF structure (Mg-C60@MOF) in which a magnesium-decorated fullerene is incorporated into an MOF structure. The hypothetical material was generated relying on the concept of placing a fullerene doped with metal ions that has a low surface area but high heat of adsorption for methane into intimate contact with an MOF of high surface area and moderate binding energy for methane. This, in turn, would increase the overall binding energy or solid potential of the resulting structure for enhanced methane adsorption. Despite the void spaces taken by the fullerene, its impregnation in IRMOF-8, to give Mg-C60@IRMOF-8 (crystallographic density not reported), provided a remarkable methane uptake value of 265 v/v, the highest reported value achieved with a hypothetical material at that time. This value surpassed the 180 v/v landmark by a significant amount (47%). Despite this remarkable storage capacity value, the path to realize such materials experimentally is not clear and has yet to be explored.

In recent years (following the work of Düren et al.[96]), computational studies have advanced sufficiently to generate several "thought" structures of metal−organic frameworks from a given chemical library of building blocks and metal clusters in silico. In principle, these structures are assembled automatically using computers to generate unlimited numbers of MOFs, although a significant amount of human intuition and investment is required to synthesize these materials experimentally. Most of these efforts are aimed at generating structures with high surface areas and appropriate pore properties that would exhibit high storage capacities for methane. Wilmer et al.[144] generated 137953 hypothetical MOF structures from a library of 102 building blocks. They further calculated the pore size distributions and surface areas and performed a large-scale computational screening of these materials by testing the methane storage capacities (at 3.5 MPa) of all of these structures. They identified over 300 MOFs with potential storage capacities exceeding the performances of the best-performing or well-established MOF compounds. The most promising hypothetical MOF was predicted to store ∼267 v/v at 3.5 MPa and 298 K, which is slightly higher than the value reported for Mg-C60@MOF by Thornton et al.[143] Apart from these inspiring results, the authors also estimated a structure−property relationship, which clearly indicated that (i) increasing the surface area beyond the optimal point, 2500−3000 m^2/g, only worsens the methane storage capability and (ii) pore volumes larger than the optimal value again decreases the methane storage capacity. These results seem to be in reasonable agreement with the interpretations made earlier based on the experimentally obtained data reported in the literature (see Figure 3a) and also with the results reported more recently by Simon et al.[145] based on a large-scale computational study of methane uptake in different classes of porous materials.

To our knowledge, although MOFs are known for their high porosities , no MOF has been claimed to have an ultrahigh surface area compatible with a pore size distribution that is essentially narrow and microporous, with a pore size typically equivalent to twice the diameter of the methane molecule. The results of Wilmer et al.'s study[144] indicate the need for a synthesis protocol that incorporates chemical intuition and synthesis experience and, in turn, creates many possibilities for researchers to develop new MOF structures with better pore structures and adsorption properties in the years to come.

Before we summarize this section, it is important to emphasize that, although the DOE target (delivery of 180 v/v at 298 K and 3.5 MPa) could sometimes be considered as only a yardstick, it is useful to compare the performance of any porous material for the storage of methane typically at 3.5−5 MPa versus CNG at 20−25 MPa, even if the values published are expressed in terms of excess adsorption. Thus, to make comparisons among different materials easier, in the future, adsorption results obtained for new MOF structures should be reported in terms of both the gravimetric and volumetric storage capacities at 298 K and 3.5 MPa (or at higher pressures) and always using the packing density of the adsorbent. To verify the potential of a developed material for practical usage, researchers should report the volumetric storage capacity obtained using the true packing density rather than using the crystallographic density. Furthermore, the micropore volume should be correlated with the volume of the vessel and not simply with the unit mass of the solid framework, making the packing density more relevant than the crystallographic density. The packing density is as important as the micropore volume and surface area, and thus, this parameter cannot be simply ignored in the design and evaluation of the performance of any adsorbent for the storage of natural gas. It must also be mentioned here that ANG is not yet commercialized to the same level as CNG and reporting the volumetric storage capacity obtained using the crystallographic density does not answer how much a material would fill an onboard fuel storage tank for the aforementioned reasons. Instead, it merely introduces a difficulty in comparing reported results for other classes of materials. Despite the huge investment in research and the extensive literature available on natural gas storage in MOFs, it is still not clear how well MOFs really perform when compared with other classes of materials such as activated carbons, for which the storage capacities are commonly obtained using the packing density. Research reported about the volumetric adsorption capacities of MOFs based on the packing density leads to a disheartening conclusion.[140] At 303 K, even at the cost of a high pressure, the high-BET-surface-area MOFs $Cu_3(btc)_2$ (1502 m^2/g), $Zn_2(bdc)_2(dabco)$ (1448 m^2/g), and MIL-101 (2693 m^2/g) reached maximum excess volumetric storage capacities of only up to 59 v/v (at 7.5 MPa), 104 v/v (at 7.5 MPa), and 122 v/v (at 12.5 MPa), respectively. Their deliverable capacities were even lower, and the storage performances at 3.5 MPa for methane could hardly reach the storage capacity values of any other class of crystalline materials, for instance, zeolites.[21] PCN-14 undoubtedly holds the record for the highest methane storage capacity at 3.5 MPa (using crystallographic density), but this reported uptake was measured at 290 K, and thus, its storage capacity at 298 K should be even lower, making the comparison of its performance with those of other materials at 298 K difficult. Earlier, Sun et al.[142] made the effort to predict the storage capacity of PCN-14 at 3.5 MPa and 298 K by extrapolating the reported results of Ma et al.[47] at different temperatures and found that PCN-14 could store up to 180 v/v at 298 K. In terms of gravimetric storage capacity, this value corresponds to 207 cm^3/g. Assuming that an effective packing density of up to 80% could be reached and assuming that compression of the material does not affect the adsorption properties or fluid permeability, a rough estimate indicates that PCN-14 can store up to 144 v/v, a value comparable to those of most other MOFs and carbon-based materials. On the other hand, PCN-14 is being considered as a benchmark material for comparing the performances of MOFs or other classes of materials for methane storage. Thus, the storage properties of this material for methane should be verified individually, and the true packing density should be measured. In a simulation study[144] performed on a pseudo-MOF structure, NOTT-107, which has a structure similar to that of PCN-14, it was shown that the predicted storage capacity of this material at 290 K is much lower than the experimentally obtained results. Thus, these aspects should be analyzed in detail in the future to clarify the adsorption properties of this or other MOF structures or other classes of porous materials in general for practical applications. Apart from searching for the best material for methane storage, research is also needed to define a probable relationship between the structure and properties, emphasizing the effects of ligands, functionality, open metal sites, framework density, surface area, and pore volume on the adsorption properties (for methane or for other gas molecules).

Because of the ultrahigh surface areas of some MOF structures; the available theoretical knowledge at the molecular level; the flexibility to design and tune the pore topology, pore size, and isosteric heat of adsorption (although very challenging); the available room for exploration; and the immense amount of research being carried out in several stages at a skyrocketing pace from pioneering researchers worldwide, it is most likely to expect a conformed MOF material in the near future that exceeds the 2000 DOE target and can be considered as a potential onboard natural gas carrier. In any case, the possibility of obtaining an MOF structure (conformed material, such as a monolith) that can surpass the DOE MOVE target might be questionable. Considering the similarity in trends between the physical properties of carbons and MOFs and their storage capacities, if an MOF with a unique pore geometry is developed that comes close to the DOE target, the properties of such materials might also dictate the pore properties required for the high storage of natural gas that can be used as a design strategy for the synthesis of other classes of porous materials (for instance, carbon) and vice versa. To emphasize this point again, to date, a considerable amount of research has been reported on the adsorption capacity of methane. Despite the large number of MOFs synthesized and the fascinating properties being realized, at this stage, it is only possible to speculate on their practical usefulness as onboard natural gas carriers, as most works report the volumetric adsorption capacity using the crystallographic density, ignoring the most important parameter, namely, the "packing density". Thus, at least in the nearest future, we expect and recommend that researchers report adsorption capacities based on both crystallographic and packing densities to assert their practical usefulness as onboard natural gas carriers.

6. STORING METHANE AS CLATHRATES IN MOISTENED CARBON

Gas hydrates or clathrates are solid, nonstoichiometric compounds of small gas molecules trapped inside cages of hydrogen-bonded water molecules.[146] Clathrate hydrates are formed when a small guest molecule such as methane (which is the topic of interest in this work) contacts water, typically at temperatures less than ambient temperature (near 0 °C) and moderate pressures (>6.0 MPa). Among other important scientific and industrial contexts, such hydrates that can enclathrate guest molecules seem impressive when considered as fuel storage and transport media. For comparison, the concentration of a nonpolar gas such as methane in the solid hydrate lattice is about 2 orders of magnitude higher than the solubility of the same gas in liquid water.[147] The three main crystal structures of clathrates are called structure I (sI), structure II (sII), and hexagonal structure (sH), and they contain cages of different sizes dictating the sizes of the trapped guest molecules. Methane is believed to be the primary guest component of gas hydrates of types sI and sII, as the water cages are large enough to hold methane molecules, but other structures do occur at higher pressures, typically above 5.0 MPa.[148] In the case of methane, sI hydrates can store one molecule for every six molecules of water, an extremely high value when compared to its solubility in water (one molecule of methane in 4000 water molecules).[146] Both the sI and sII structures have cages made of 12 planar pentagonal faces; sI contains both smaller cages (denoted 5^{12}) and larger cages (denoted $5^{12}6^{2}$), whereas the sII structure contains larger cages (denoted $5^{12}6^{4}$). These two hydrate structures have average cavity radii in the ranges of 0.395−0.473 and 0.391−0.473 nm, respectively, which is sufficient for holding methane molecules. The energy densities of hydrates are approximately the same as that of compressed gas, but lower than the energy density of LNG. If 100% of the cavities are filled with methane, then 1 m^3 of methane hydrate contains up to ∼180 m^3 of methane gas at STP, which is comparable to the energy density of methane gas compressed at 298 K and 15.2 MPa (STP). This energy content per unit cell remains the same for all three hydrate structures as, when filled, all three of these structures contain 85% water molecules and 15% methane molecules.[147] The ability to liberate such a substantial amount of energy makes hydrates ideal candidates for the storage of natural gas. It was already confirmed in recent years that storing methane as frozen hydrate is a practical and promising approach for the large-scale transport of methane fuel gas over long distances.[149] The tempting energy content (per unit cell) of hydrates, the possibility of exploiting the propertyies of hydrates to use them as fuel storage container, together with the practical difficulties in reaching the DOE storage capacity target, even with ultrahigh-surface-area adsorbents, all together forced researchers to find an alternative concept for storing methane gas as hydrates within moist carbon porosity. This concept relies on a reasonable strategy focused on improving the properties of a carbon structure that already has a large storage capacity by creating additional porosity through an external medium (force) during the process of adsorption, where methane molecules can adsorb in excess to the amount already adsorbed by physisorption alone. The natural tendency of water to form cages in the presence of methane at low temperatures acts as an additional medium or in other words like virtual porosity where methane molecules are trapped, which could ultimately increase the adsorption capacity. The equilibrium pressure of methane in water given in Table 2 indicates that there exists an inverse relation between temperature and the genuine hydrate-formation pressure. Methane hydrates within the wetted carbon pore structures can be expected to occur above the equilibrium pressure (allowing sufficient induction time), and their enormous energy contents will ultimately increase the excess adsorption of methane in carbon (host) structures.

Table 2. Equilibrium Pressures of Methane Hydrates at Different Temperatures[154]

T (K)	p_{eq} (MPa)	$p_f{}^{a}$ (MPa)	$p_{\text{inflection point}}$ (MPa)
275	3.2	4.6	>4
277	3.9	5.3	>5
279	4.8	6.2	>6
281	5.9	7.3	∼7
283	7.4	8.8	>7.5

[a] Obtained assuming a pore diameter of ∼1.9 nm.

Okui et al.,[150] in a U.S. patent, were the first to attempt to confirm this concept experimentally. They performed methane adsorption isotherm experiments at 30 °C on activated carbon with already-adsorbed water (0.259 g of water/g of carbon); the carbon had a surface area of 1765 m^2/g, with an average pore diameter of 1.13 nm and a pore volume of 0.971 cm^3/g. They found that 1 cm^3 of wetted activated carbon at STP could store up to 191, 203, 271, 290, and 326 cm^3 of methane at pressures of 0.07, 0.15, 0.5, 1.0, and 2.0 MPa, respectively. The storage capacity of 191 v/v at subatmospheric pressure would be remarkable because such a very high storage capacity has never been achieved with any moderate- or ultrahigh-surface-area porous materials even at much higher pressures. Such a huge storage capacity for methane in water-adsorbed carbon micropores at subatmospheric pressures and 30 °C was also later reported in a scientific article by Miyawaki et al.[151] The results of Miyawaki et al. showed that a microporous carbon with preadsorbed water (P20) can store more than 100 mg of methane/g of carbon even at pressures of less than 0.1 MPa and, furthermore, that this storage capacity changed with the fraction of pore volume filled by preadsorbed water molecules, ϕ_w. For ϕ_w = 0.28 and 0.40, P20 adsorbed more than 100 and 180 mg of methane/g, respectively, at 0.1 MPa. The same carbon, when not preadsorbed with water, stored only 125 mg of methane/g of carbon, even at the cost of higher pressure (10 MPa). The amount stored was found to increase linearly with increasing ϕ_w until ϕ_w = 0.4, suggesting the formation of a stable water−methane compound in the ratio (stoichiometry) of CH_4/H_2O = 1:2. Based on this unusual CH_4/H_2O stoichiometry, the authors suggested the formation of stable nanohydrates with a new structure. Despite the striking results, the authors did not document or provide any further evidence for this system (P20) or other similar systems. In another study, Perrin et al.[152] noticed the same unusual CH_4/H_2O stoichiometry. However, they inferred that such nanohydrates could occur in micropores, as methane is preferentially adsorbed on the pore walls of micropores as a result of the strong potential experienced from the opposing walls. In this case, water molecules might be confined near the CH_4 molecules within the available carbon (micro)pore space, trying to build incomplete hydrate cages, resulting in nanohydrates with extreme stoichiometries such as $CH_4{\cdot}2H_2O$. Nevertheless, these works clearly led to the striking conclusion that hydrates can significantly improve the storage capacity of a porous carbon material and that the water in porous carbons acts somewhat similarly to a catalyst, probably promoting the formation of hydrates even at subatmospheric pressures and room temperature, far from classical conditions.

Aiming to understand and reproduce the striking results reported in the works of Okui et al.[150] and Miyawaki et al.,[151] Zhou et al.[153] performed adsorption isotherm experiments at 273 and 298 K and pressures up to 10 MPa on a coconut-shell-based activated carbon with a surface area and pore volume of 1800 m^2/g and 1.5 mL/g, respectively. They carried out adsorption isotherm experiments on both dry and moistened carbons with different levels of moisture content, ranging from 0.096 to 26.06 mmol of H_2O/g of dry carbon. Their results challenged the above-reported works in the following respects: (i) There was no formation of hydrates at room temperature and 3.5 MPa, and the methane adsorption globally decreased with increasing moisture content, although there was a minor increase in adsorption in a carbon sample with a lower moisture content (0.096−1.023 mmol of H_2O/g of dry carbon). (ii) The presence of water decreased the amount of methane adsorbed at 273 K even at the high pressure of 10.0 MPa. Although hydrates can be expected to occur at higher pressures and lower temperatures, the temperature of 273 K does not seem adequate for the formation of hydrates. Later, the same research group performed another set of methane adsorption isotherm experiments with coconut-shell-based (moistened and dry) activated carbons over a wide range of temperatures, 275−283 K, at pressures up to 11.0 MPa.[154] They also carried out a detailed study to explain the influence of the water content in the wetted carbon on the methane adsorption at 275 K. This time, they observed the formation of hydrates under classical conditions by (i) a stepwise adsorption isotherm, which showed a negligible amount of adsorption and no hydrate formation until the pressure reached an inflection-point pressure or hydrate-formation pressure, p_f, which was experimentally observed at about 4.0 MPa. (ii) After this pressure (i.e., for $p > 4.0$ MPa), a sharp increase was observed in the isotherm, and at 6.0 MPa, the amount adsorbed in wetted pores surpassed the amount adsorbed in the (same) dry carbon. Increasing the weight-based water content R_w (defined as the weight of water per unit weight of dry carbon) from 0.7 to 1.4 increased the storage capacity from 24.78 wt % at 9.52 MPa to 31.74 wt % at 9.26 MPa; however, the increase in moisture content did not change the hydrate-formation pressure. The net gain with respect to dry carbon were 27.5% and 63.3% for $R_w = 0.7$ and $R_w = 1.4$, respectively. Increasing R_w beyond 1.4 had a negative effect and decreased the storage capacity by a significant amount. These results led to the conclusion that the water could act as a catalyst inside the pore space only if it was in the right amount to provide sufficient access for methane molecules to penetrate the available pores or water cages. Zhou et al.[154] suggested that the reduction in storage capacity for higher moisture contents, such as $R_w = 3$, was due to the fact that the content of water was more than enough to fill all of the pore volume available so that the methane could only touch the surface of the water and did not experience any potential from the carbon pore surface. They also realized that, irrespective of the moisture content, the hydrate-formation pressure within the moistened carbon pore was always higher than the genuine hydrate-formation pressure (p_{eq} in Table 2), because the driving force for the formation of hydrates in the former case was controlled by pore resistance to the diffusion of methane and percolation effects within the pore structure. Alternatively, Perrin et al.[152] pointed out that the adsorbed water inside the pores is not free, but rather is trapped inside the pores, so that it is prone to capillary effects. They suggested that the hydrate-formation pressure p_f can be related to the genuine hydrate-formation pressure by the expression $p_f = p_{eq} + \Delta p$. The term Δp is the pressure difference across the fluid interface and is related to the pore diameter d through the Young−Laplace equation $\Delta p = (4\sigma_{lh} \cos \theta)/d$. For comparison, Table 2 lists the equilibrium data for methane hydrates at different temperatures, the theoretical formation pressure (p_f), and the formation pressure in moistened carbon pores observed experimentally by Zhou et al.[154] Table 2 clearly shows that the inflection point nearly matched the mathematically determined p_f value, thus clearly indicating the importance of pore width in the methane adsorption process. The authors also noticed a similar trend in the adsorption isotherms at higher temperatures, with the inflection point occurring at different pressures depending on the temperature. In any case, working at higher temperatures does not seems to be an attractive option, as the gain in storage capacity obtained with wetted carbons, when compared to the dry material, was found to decrease progressively with increasing temperature.[154]

In a follow-up work, Zhou et al.[155] experimentally verified these concepts and showed that the pore size distribution also plays a crucial role in the increase in storage capacity due to the effect of wetting. They measured methane adsorption isotherms on three different dry and moistened activated carbons, denoted as AX-21 (BET surface area = 2745 m^2/g), JX-406 (2585 m^2/g), and BY-1 (1056 m^2/g), that differed in their pore properties such as surface area and pore size distribution. In the case of the dry samples, they found that the storage capacity was proportional to the surface area. However, in the case of the moistened samples, the relationship between surface area and storage capacity was not linear; rather, the storage capacity seemed to be influenced by a combination of several other complex factors including the pore size distribution, total micropore volume, and moisture content. They found that the storage capacity of a moist carbon is more likely to be a material property, that is, unique rather than global, as it changed from one carbon to another depending on the pore volume and pore size distribution. The results of Zhou et al.[155] at least confirmed that, depending on the pore properties of the individual carbon sample, an optimum moisture content that ultimately increases the storage capacity (at higher pressure) might exist or no such optimum moisture content exists at all. A moist activated carbon containing pores with sizes of >2 nm favors the storage capacity for methane at high pressures when compared to activated carbons containing pores with sizes of <2 nm. Zhou et al.[155] put forward a reasonable argument to explain this behavior by considering the side length of type I clathrates (1.2 nm) and the collision diameter of methane molecules (0.381 nm), which clearly indicates that a pore width of 1.6−2.8 nm would allow the formation of one or two layers of clathrate where methane molecules could move in and out.

Following some of the above-mentioned research, Perrin et al.[152] performed methane adsorption experiments with dry and water-moistened micro- and mesoporous activated carbons at 275 K. They found that the classical carbon adsorbents with high micropore volumes seemed not to be useful for forming methane hydrates, as hydrates preferentially formed in larger pores, essentially mesopores. The mesoporous carbon Picazine was found to store methane up to 227 v/v at 8 MPa and 275 K, whereas the dry microporous carbon could store only <150 v/v under similar experimental conditions. Similarly to Zhou et al.,[153,155] they noticed a stepwise isotherm with a very low but constant methane uptake with increasing pressure until the pressure reached p_f, after which the methane uptake rose sharply and became higher than when measured in dry carbon. The authors found that the CH_4/H_2O stoichiometry within the moistened pores could be improved by manipulating the carbon pore width and the water content inside the carbon pores. In fact, their experimental results confirmed that hydrate structures with different stoichiometries do occur within partially moistened (unsaturated) carbon pores depending on the pore size. They experimentally obtained nanohydrates (or clathrates) with stoichiometries of $8.9CH_4{\cdot}46H_2O$, $11.4CH_4{\cdot}46H_2O$, and $18.6CH_4{\cdot}46H_2O$ in the mesopores, whereas in the micropores, they obtained a nanohydrate with a stoichiometry of $5.8CH_4{\cdot}46H_2O$. All of these stoichiometric ratios comprise more methane than the expected value for an sI hydrate. The authors argued convincingly that these unusual stoichiometries do not represent a new hydrate structure as claimed in other works,[150,151] but rather are due to the effects of partial saturation of the carbon pores by moisture, which leaves free pore volume where methane molecules are either adsorbed or compressed depending on the pore width. Although the research of Perrin et al.[152] confirmed that the formation of hydrates increases the ultimate storage capacity by a significant amount in both micro- and mesoporous carbons, their results seem complicated, as the increase in the storage capacities of all of the carbon structures reported might only be due to an increase in packing density because of the wetting process rather than an actual increase in excess adsorption. The sole factor increasing the storage capacity was not clearly reported, and the ambiguity in the volumetric storage capacity probably arises from many factors involved in the derivation of the volumetric storage capacity values of any moistened adsorbent: (i) the gravimetric storage capacity (mass of CH_4/mass of dry carbon) expressed in terms of the weight of dry carbon, (ii) the gravimetric storage capacity expressed in terms of the weight of wetted carbon (mass of CH_4/mass of wet carbon), (iii) the packing density of dry carbon, and (iv) the packing density of wetted carbon. Typically, all of these factors play a crucial role in the discrepancies found among reported values and conclusions derived in the literature on the storage of methane in moistened carbon structures. For instance, if water is treated as a coadsorbate rather than as a compound in the adsorbent framework, then a dry Picazine carbon reported in the work of Perrin et al.,[152] which adsorbed 40 mmol of CH_4/g of dry carbon at 8 MPa and 2 °C, exceeded the wetted material, which stored only up to 35.7 mmol/g under similar experimental conditions. If these values are converted into volumetric storage capacities using the packing densities of the dry (0.16 g/cm^3) and wet (0.54 g/cm^3) Picazine, then storage capacities of 157 and 474 v/v could be reached with the dry and wet Picazine, respectively, at 275 K and 8 MPa. In contrast, if water is treated as a compound in the adsorbent framework, that is, if the gravimetric storage capacity is expressed in terms of grams of CH_4 per gram of wet carbon, then after some manipulation, the storage capacity of wet Picazine appears to be only 231 v/v at 8 MPa and 275 K.

Despite these complicating factors, the results of Zhou et al.[154] and Perrin et al.[152] reveal that there is no unique way to relate the pore size to the clathrate structure or the ultimate storage capacity of the moistened carbons, although the formation of hydrates usually increases the storage capacity by a greater amount for a mesoporous carbon than for a dry microporous carbon.

In a more recent work, Liu et al.[156] performed a systematic study with activated carbons that confirmed the results of Perrin et al.[152] They performed methane adsorption isotherm experiments in a wet corncob-based carbon with an optimum high surface area of 3452 m^2/g, with 58.6% of its pores tuned to match the dimensions of methane hydrates (1.6–2.8 nm). As in the earlier research, the storage capacity was found to be a function of the moisture content inside the carbon pores, with an optimum moisture content value. The gravimetric density reached a maximum of 63 wt % at 9.0 MPa when the water content R_w (weight ratio of water to carbon) reached a maximum of 3.35 (whereas dry carbon stored only 23.6 wt %), and the volumetric storage capacity reached a maximum of 204 v/v at 9.0 MPa for an R_w value of 2. A further increase in the moisture content only decreased the methane adsorption, as the excess water molecules occupied the pores, restricting the access for methane molecules.

All of the above-mentioned publications point to the fact that hydrates can be formed within micropores/mesopores of carbon materials under classical conditions (Table 2), and in some extreme cases, hydrates seem to form even under unrealistic conditions (room temperature and subatmospheric pressure), although the latter results have yet to be confirmed. Even though most of the moistened carbon materials exhibited promising storage capacities close to 200 v/v, these results showed that such high adsorption capacity values can be obtained only at the expense of high pressures (up to 10 MPa) and temperatures near 273 K. Irrespective of the carbon pore properties, mesoporous or microporous, the adsorption in dry pores is always small when compared to that in moist pores. Apart from these issues, adsorption on wet carbons also has some other serious drawbacks, one of which is the slow kinetics of hydrate formation, ranging from about 24 h to 1 week per individual experimental point and, in extreme scenarios, up to one month.[152,157] This makes the application of this approach in vehicles extremely impractical. Some studies also showed that, although the moisture content increased the storage capacity, it decreased the hydrate-formation kinetics by a significant amount, making the tank-filling process a significant issue. Some attempts have been made to increase the hydrate-formation kinetics by adding surfactant;[157] however, they only decreased the hydrate-formation pressure and improved neither the storage capacity nor the hydrate-formation kinetics. In addition, experimental investigations on the desorption kinetics revealed that, although the discharge of methane stored as hydrates is rapid, a great deal of water evolves during desorption and is, therefore, irreversibly lost.[152,157] This would require the vehicle user to readjust the water content back to the initially optimized value of R_w before subsequent refilling of the tank. Another serious concern is that the volumetric storage capacities of wetted carbon structures look impressive only at pressures ranging from 8.0 to 10.0 MPa. Such high-pressure storage cannot be carried out in flat storage tanks designed for ANG systems and would demand tanks with design strategies comparable to those required for CNG storage tanks, probably with a cylindrical shape that would occupy most of the trunk space of the vehicle. Some experimental research suggested that increasing the water content inside the pores could reduce the hydrate-formation pressure from ∼5 to ∼3.2 MPa; however, this did not have any influence on the storage capacity as a high pressure was still needed to reach the storage capacity.[152] Furthermore, the added water would significantly increase the weight of the storage tank, and experimental results confirmed that the gravimetric storage capacity of wetted carbons is significantly lower than that of dry carbons.[152] Another issue that needs to be considered is the possibility of storing methane as ANG at 275 K and at higher pressures. In section 4, we discussed several conformed carbon materials that can store methane up to 160 v/v at 3.5 MPa and 298 K. Thus, it is likely that methane can be stored as an adsorbed gas in carbon pores at capacities of >180 v/v at 275 K and at higher pressures. In a recent experimental study, it was shown that a corrugated porous graphene can store up to 236 v/v at 9.0 MPa and 274 K.[158] If the storage capacity is the only objective, irrespective of the use of a working/storage temperature that requires an onboard refrigeration unit for the storage of fuel, then at 274 K, at the expense of high pressure (9 MPa), a properly tuned dry carbon-based material itself is sufficient to surpass the landmark number of 180 v/v by a significant amount. The experimental results of Ning et al.[158] clearly show that, if such high storage capacity values can be achieved with ANG at 274−275 K, then storing methane as hydrates that suffer from slow kinetics does not seem to be an interesting option in the search for an optimal method for natural gas storage.

7. ISOSTERIC HEAT OF ADSORPTION

Increasing the isosteric heat of adsorption is being considered as a design strategy for improving the storage capacities of adsorbents. By definition, the isosteric heat, Q_{st}, of adsorption is always positive and is simply the absolute value of the differential enthalpy of adsorption, $-\Delta H$. Q_{st} is a state function and is a function of surface coverage, and it can be obtained experimentally by differentiating the series of adsorption isotherms at a constant loading for a pure perfect gas.[159] The isosteric heat gives a fundamental measure of the solid−fluid and fluid−fluid interactions depending on the pressure and temperature, and its value at zero coverage gives a fundamental measure of the fluid−solid (in the present case, CH_4−carbon atoms in the solid) interactions with negligible contribution from the fluid−fluid (CH_4−CH_4) interactions. The higher the adsorption isosteric heat of an adsorbent, the higher its capacity to host the guest molecules of interest. According to recent reviews published by Konstas et al.[92] and He et al.,[111] in the case of MOF structures, the isosteric heat of adsorption at low or zero coverage (i.e., adsorption at infinite dilution) typically ranges from 9 to 20 kJ/mol. As exceptional cases, the two MOFs PCN-14 and SNU-50 were found to exhibit very high Q_{st} values of 26 and 30 kJ/mol, respectively, outperforming any other MOFs to date.[47,124] For the case of carbon-based materials, the Q_{st} values typically lie in the range of 16−30 kJ/mol.[54,160−169] The activated carbon MHz-RC was found to exhibit a remarkable Q_{st} value of 40 kJ/mol at low loadings,[51] which is much higher than the Q_{st} values of PCN-14 and other classes of materials, although its storage capacity was only about 130 v/v at 3.5 MPa and 298 K.

Computational studies[170−172] have confirmed that the storage properties of adsorbents that already have reasonable adsorption capacities could be further improved by increasing their isosteric heats of adsorption. The thermodynamic calculations of Bhatia and Myers[173] suggested an optimal Q_{st} value of ∼18 kJ/mol for an adsorption cycle operating at 298 K between 0.15 and 3.0 MPa. Although the isosteric heats of adsorption of most MOF and carbon materials exceed this value, experimental values reported in different works, which have already been reviewed, and also our own estimations (see Figure 3b) reveal that none of the conformed materials seem to guarantee a storage or delivery value of 180 v/v. The few conformed materials that seem to be promising for reaching a storage value of 180 v/v either have not been independently verified or have not been checked for repeatability, in addition to other problems such as the use of vague experimental and calculation procedures.[44,68] Thus, to reach such high storage or delivery values, the isosteric heat for methane adsorption should probably be improved beyond 18 kJ/mol. At this stage, it should be mentioned that most MOFs and carbon structures, irrespective of their ultimate storage capacities, already exhibit high isosteric heats greater than 16 kJ/mol, which is higher than the heat of vaporization of methane (8.17 kJ/mol at 112 K) and sufficient to create thermal fluctuations inside the adsorbent bed. Thus, it should be considered that materials with high isosteric heats and any attempts to increase Q_{st} values might also demand adapted systems to maintain isothermal conditions during adsorption/desorption cycles.

It is also important to take into account the technical issues that are associated with the design strategy of increasing the storage capacity by increasing isosteric heat, which is always related to a significant increase in adsorption at lower pressures and a strong binding energy, both of which make desorption a more difficult process, thus decreasing the amount of methane that can be delivered.

8. TECHNICAL CHALLENGES WITH ANG

Natural gas is technically a generic name for a combination of gases in which methane is the primary component, along with other compounds such as heavier hydrocarbons (C_{2+}), nitrogen, water, CO_2, sulfur, and some traces of rare gases; such gas mixtures are usually termed wet natural gas. Although methane hydrates lying under the deep sea can be dissociated to yield dry (pure) methane, at the current level of understanding, this extraction of methane is still in a preliminary stage. The methane available in casinghead gas, gas-well gas, and coal-seam/coal-bed gas and the gas obtained from fossil fuels or other carbon-containing materials by gasification are all mixtures (wet natural gas). Most of the studies on ANG systems described in the literature have focused mainly on the development of novel porous materials that could ultimately exhibit very high storage capacities for pure methane. On the other hand, some of these works (all of them focused on carbon-based materials), discussing the adsorption of both dry and wet natural gas, illustrate the fact that the adsorption mechanisms for the two cases are different in terms of the fuel energy storage capacity, deliverable capacity, and adsorbent efficiency for cyclic usage. Among other operational problems, one of the main issues that hinders the success of ANG technology is the deterioration of the ultimate storage capacity of adsorbents for methane upon extended operation as a result of the complex nature of the actual natural gas composition.[174]

In real systems, natural gas will be stored as a fuel onboard and will contain other high-molecular-weight compounds that are likely to be adsorbed more strongly than methane, especially in the low-pressure region.[158,174,175] This would reduce the deliverable capacities and storage capacities of the adsorbent during cyclic operation. Li and Chen[176] investigated the adsorption capacities of all of the components of natural gas at 25 °C for the first time and found that the adsorption capacities of the various components of natural gas at 3.5 MPa follow the trend $C_3H_8 > H_2S > CO_2 > C_2H_6 > CH_4 > N_2$. Ridha et al.[177] showed that non-methane hydrocarbon gases reduced the deliverable capacity of an activated carbon, denoted as AC-L in their study, by a factor of 19.4% for a natural gas containing 14.98 and 14.54 vol % of ethane and propane, respectively, discharged from the tank at a rate of 1 L/min. They found that the reduction in storage/deliverable capacity was due to the gradual filling of the adsorbent micropores by higher-molecular-weight hydrocarbons, thus reducing the active sites available for methane and thereby decreasing the storage capacity, especially during cyclic adsorbent usage. These high-molecular-weight compounds remained adsorbed at the discharge pressure, thereby reducing the deliverable capacity. The adsorption of these high-molecular-weight compounds is usually associated with higher isosteric heats,[177−179] and such compounds can be removed only by special means such as heating or application of a vacuum. In a more recent study using molecular simulations,[180] it was shown that the presence of even a very low amount of nitrogen (5%) greatly influences the amount of methane adsorbed in the available pore volume, as the nitrogen molecules tend to adsorb on the surface and coadsorb between the methane molecules. Li and Chen[176] tested the adsorption capacity of a carbon for 10 charge/discharge cycles and found that mixed gas significantly reduced the adsorption reversibility, as heavy or polar components such as C_3H_8 and H_2S tended to continuously accumulate within the micropores and remain in the adsorbed state even at lower pressures. Pupier et al.[181] performed large-scale adsorption experiments with natural gas containing 95% methane along with other components, by charging and discharging a fuel tank with activated carbon for 700 cycles, which corresponds to approximately 250000 km for a vehicle with a fuel tank allowing for a driving range of 400 km. They found that, because of the accumulation of heavier components, the efficiency of the activated carbon decreased by almost 50% after 700 cycles. This scenario did not change even when the methane was stored as hydrates within wetted micropores.[174]

Storage capacity is the main factor limiting the commercialization of ANG at the level of CNG. To commercialize ANG, the natural gas must be purified to eliminate heavy hydrocarbons and polar components before the gas is supplied to the ANG fuel tanks, as the presence of such compounds hinders the storage capacity of the process. Alternatively, a properly designed carbon-based filter or guard bed could be used to prevent the contamination of the storage tank. The latter option still requires a great deal of research, and its practical applicability has not yet been studied for onboard (mobile) applications. However, there are recent studies[182,183] on new carbon molecular sieves showing that their selectivity in the adsorption of contaminants of methane can be high, thus facilitating their use as guard beds.

Another technical problem associated with ANG technology arises from the nature of the adsorption process itself. Because of the fact that adsorption is exothermic, the rate of adsorption is associated with a rise in temperature of the bed that will directly influence the rate of adsorption and the ultimate storage capacity. For example, Ridha et al.[177,178] reported that a temperature rise of up to 99 °C was noticed in an ANG bed that was charged at a flow rate of 1 L/min, especially in the center region of the adsorbent bed, because of its poor thermal conductivity. They found that this thermal fluctuation became worse and the temperature of the bed reached 116 °C when the tank was filled at a much higher rate of 5 L/min. Their work further confirmed that the presence of ethane and propane could cause more thermal fluctuations because these gases have higher isosteric heats than methane. These facts clearly indicate that, irrespective of the class of porous material and despite their storage capacities under ideal isothermal conditions, thermal fluctuations could reduce their ultimate storage capacities under practical conditions. Ridha et al. claimed that the heating process reduced the storage capacity of a carbon material by 26.9% compared to the storage capacity of the same carbon material charged with methane under isothermal conditions.[171,172] Yang et al.[184] showed that thermal fluctuations also affect the rate of desorption of methane from an adsorbent tank filled with activated carbon. They found that, during discharge, which is an endothermic process, the temperature of the bed dropped instantaneously by a significant amount, which, in turn, severely affected the amount of methane released at the discharge pressure and thus dramatically reduced the rate of discharge at intermediate pressures. During a desorption process operated between 0.3 and 4.5 MPa, the temperature instantaneously (in 145 s) dropped by more than 40 °C, which, in turn, decreased the desorption rate from 0.52 to 0.11 L/s. They found that 92% of the total dischargeable amount was delivered in 900 s, and after this time, the flow rate dropped to 0.01 L/s and stayed almost constant throughout the remaining desorption process that ran up to 8000 s. Because the desorption process is endothermic, the complete discharge of the ANG will be a longer process unless an external heat is supplied to compensate for the endothermic heat and the heat transfer driven by the temperature difference between the adsorbent bed and the surroundings. These drawbacks require further research, which should focus on possible ways to increase the heat-transfer properties of the bed to mitigate some of the problems encountered during the operation of ANG tanks, especially for onboard applications. At this stage, several accessories such as external fins, vessels with several tubes compacted with adsorbent, gas distribution pipes, perforated tubes in the tank centers, and external cooling jackets have been proposed during ANG tank design to resolve this particular issue.[185−187] Increasing the thermal conductivity of the carbon adsorbent would be an optimal approach, as it could help to dissipate the heat evolved/supplied during the adsorption/desorption process. All of the works mentioned above were carried out for the case of a storage tank filled with carbon materials. For the case of MOFs or other classes of porous materials, little work has focused on this area detailing the problems of thermal conductivity and thermal fluctuations of the adsorbent bed during charge/discharge cycles. Most of the promising MOFs are characterized by their constant isosteric heats of adsorption for methane over wide ranges of surface coverage values, which, in turn, would be sufficient to impose some heat-/mass-transfer effects throughout the entire desorption process. Thus, the efficiency of ANG systems with some of the new classes of porous materials with high methane storage capacities, for example, MOFs, should be engineered, checked, and optimized for their heat- and mass-transfer kinetics for several charge/discharge cycles.

9. VISIONS FOR THE FUTURE

Oil depletion due to the continuous increase in the use of oil, motor traffic, and the quality of the environment are all intrinsically related. Every year, more than 3 million cars are added to the car fleet in Europe. In terms of energy consumption, this corresponds to an increase of roughly 4% each year. Oil demand and the quality of the environment can be jointly addressed by selecting an appropriate alternative fuel that burns cleanly. Although hydrogen is the cleanest fuel available on Earth, current technologies to produce, store, and transport hydrogen are not sufficient to be economically feasible at present. Thus, in view of the increasing energy consumption of transportation and the lack of adequate/economical solutions for the production and storage of hydrogen for fuel cells or combustion engines, natural gas seems to be the primary fuel for this century. Natural gas vehicles are currently receiving considerable attention from all sectors, including governmental and environmental agencies, researchers, and automobile manufacturers. Although CNG vehicles have already picked up a top rank in developed countries such as the United States and the countries of the European Union, there is hope to see ANG vehicles on the market in the near future, operating at room temperature and at much lower pressures. ANG vehicles can be more pleasing for the vehicle user than CNG vehicles, because they operate at lower/safer pressures and have easy delivery processes and space aesthetics, because of their compatibility with flat fuel tanks. Recent combustion technologies allow passenger cars to be run for up to 100 km with carbon emissions of just 79 g/km and use of only 2.9 kg of CNG.[188] If the right storage material with a high storage capacity is developed, ANG will help to increase the driving range of modern vehicles.

This review has emphasized some ideal facts/parameters that a perfect storage material should exhibit, such as high surface area, pore volume, optimum pore width, low framework density, and high packing density. In recent years, most of the research has been targeted on developing materials with ultrahigh surface areas for gas storage applications. However, this review illustrated that the targeting of ultrahigh surface areas might not be the sole crucial factor for attaining optimum gas storage at ambient temperature conditions. Irrespective of the class of material (MOFs or carbons), a practical limit for the surface area exists above which further increases do not provide any specific advantage for natural gas storage (at 3.5 MPa). In this review, it has been shown that the ideal material should have a high packing density with a surface area of ~2500 m^2/g and should contain pores of optimum size, roughly twice the size of a methane molecule. Most of the research has followed the path of obtaining high-surface-area materials to reach the goal of 180 v/v or more. Theoreticians continuously try to propose new structures that might be difficult to obtain experimentally, so we suggest a stronger collaboration between experimentalists and theoreticians in the future. Improving the surface area/packing density and isosteric heat while strictly maintaining the pore size at the optimum value seems to be the most promising way to improve the methane storage capacities of porous materials.

Upon developing and adapting an adequate design strategy, there is a great deal of scope to reach a porous material, either a carbon-based or MOF structure, that could possibly provide some solution to the problems associated with driving distance and fuel storage in natural gas vehicles.

Although storage in hydrate form might receive attention for the transport of fuels at larger scales, it would be excessively optimistic to expect them onboard standard passenger cars soon. CNG, as an already-established technology, operates at extreme pressures (>20 MPa) but has a reasonable driving distance, and thus, adsorbents for ANG, operating at 3.5 MPa, should be able to compete with CNG in several aspects related to operating conditions, compatibility with a flat storage tank, and driving distance.

In recent years, a great deal of research has appeared, especially in the area of MOFs, claiming the achievement of high volumetric storage capacities that meet or even exceed the DOE target by significant amounts. Most of these values, however, were obtained by calculating the volumetric storage capacity from the experimental excess isotherms using the crystallographic density, ignoring the fact that approximately 25−30% of the volume corresponds to intraparticle space that is not occupied by the adsorbent. In a practical case, for methane storage, the problem is related with the volume of fuel stored in the vessel, which, for ANG systems, is the sum of the amount of methane adsorbed, the density of the solid framework, and the amount of methane stored as a gas phase in the void and macropore volume. The MOF design strategy should take into account the additional parameter of the packing density, which is as important as the nanoscale properties of the adsorbent such as the pore volume/size/topology or surface area. Thus, as stressed in earlier sections of this review, attention should be paid to this important parameter when drawing conclusions based on the volumetric storage capacities of materials.

Another area that requires further research is the practical possibility of reaching the new DOE targets with porous materials. This review emphasized the fact that it already seems difficult in practice to reach the older demanding target of 180 v/v in terms of either delivery or storage capacity with any of the actual conformed materials available. The new DOE MOVE goals for both gravimetric (0.5 g/g) and volumetric (266 v/v) storage capacities at $p \leq 3.5$ MPa seem to be set too high and, thus, should probably be revised. A powdered porous material with a gravimetric storage capacity of 0.5 g/g could meet the volumetric storage capacity of 266 v/v only if the packing density reached 376 g/L. A careful screening of the existing literature, including some reports from DOE laboratories, clearly indicates that, even to reach a storage capacity of 180 v/v, a packing density much higher than 500 mg/L would be needed. At this stage, it is also important to emphasize that it is time to revise the conditions and few specific demands set by state agencies such as that the storage pressure should be ≤3.5 MPa, as set by state agencies. Most MOFs and activated cabons with hierarchical pore structures can reach adsorption saturation at much higher pressures, and thus, such materials (especially those that contain larger micropores) can exhibit higher gravimetric adsorption capacities at pressures of >3.5 MPa. This property should be properly exploited. Even though the ANG storage pressure of 3.5 MPa can provide a uniform and unique design parameter and standards for engineers for the design of pressure sensors or valves or pipelines that connect ANG tanks with the engines, it is absolutely necessary to bring new opportunity by introducing a new system (at least to encourage materials scientists) for classifying the performance of the natural gas storage materials. Thus, it would be meaningful to introduce a grading system for adsorbent materials, for example, grade 1, materials that can store 266 v/v (or even more) at 3.5–4 MPa; grade 2, materials that can store 266 v/v at 4–5 MPa; and grade 3, materials that can store 266 v/v at $p > 5$ MPa. Such a grading system based purely on volumetric storage capacity will force researchers to explore the storage properties of adsorbents to the full extent. Suggestions from both experimentalists and theoreticians about the possibility of reaching a daunting target of 266 v/v and some design strategies and perspectives for reaching such high values are needed to find appropriate porous materials. A full-scale theoretical study on the feasibility of reaching the new DOE targets with all of the available classes of porous materials, before any further significant investments or efforts are made, should also be considered. State agencies of both developed and developing countries are already announcing more incentives for natural gas vehicles and are in the process of bringing awareness to the public. Transportation is among the most energy-consuming sectors, which is why adopting methane fuel vehicles will be a key factor, for at least the next two decades, in achieving the concept of energy diversity and improving the economy without sacrificing our environment.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemrev.6b00505.

> Simulation details, force field used, details of the carbon prototype, and methods used to obtain the theoretical methane adsorption capacity (PDF)

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The authors declare no competing financial interest.

Biographies

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Ms. Kathrin Preuss obtained her M.Sc. degree in Industrial Biotechnology at the Technical University of Munich (München, Germany). She is currently a Ph.D. student under the supervision of Prof. Magdalena Titirici at Queen Mary, University of London. Her research focuses on the development of sustainable platinum-free electrocatalysts for the oxygen-reduction reaction in proton-exchange-membrane fuel cells. Her research interests include sustainable energy materials and gas storage.

Prof. Magdalena Titirici graduated from University of Bucharest in 2000 with a B.Sc. in Chemistry. She obtained her Ph.D. at the University of Dortmund (Dortmund, Germany) in 2005. Between 2006 and 20012, she led the group “Sustainable Carbom Material” at the Max Planck Institute of Colloids and Interfaces (Potsdam, Germany), where she also did her hablitation. In 2013, Prof. Titirici became an Associate Professor in Materials Science at Queen Mary, University of London. She was promoted to a full profesorshop in Sustainable Materials Chemistry in 2014. Since 2015, she has been the Director of Research for the Functional Materials center. Prof. Titirici is the author of approximately 120 publications highly cited in the field of sustainable materials for various renewable energies, several book chapters, and one edited book. She is on the editorial boards of *ChemSusChem* (Wiley) and *ChemPlusChem* (Wiley) and is an associate editor for *J. Mater. Chem. A* (RSC). Prof. Titirici was awarded the 2016 Rosenhain Medal and Prize from the Institute of Materials and Mines in London in recognition of distinguished achievement in materials science for researchers under the age of 40.

Prof. Francisco Rodríguez-Reinoso is a world-recognized leader in the field of carbon, with expertise in activated carbon and carbon molecular sieve preparation, characterization and utilization; carbons for the storage of natural gas and hydrogen; carbon-supported catalysts; mesoporous carbons and carbon foams; isotropic graphite and its use in structural applications; and carbon–ceramic and carbon–metal composites. He has published over 350 articles in refereed journals (h-index = 62) and has supervised the theses of 50 Ph.D. students. He was responsible for a total of >120 research projects and industrial contracts in the period 1982–2009 at the University of Alicante (San Vicente del Raspeig, Spain). He was the founding president of the Spanish Carbon Group in 1991, and he is the recipient of several prestigious awards, including the Japan Carbon Award for Lifetime Achievement (2008), the SGL Carbon Award from the American Carbon Society (2010), and a Ubbelohde Lecturer from the British Carbon Group (2013). He was the editor of the journal *Carbon* from 1991 to 2012 and a NATO consultant for the Science for Peace Programme (2000–2006).

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