

Open carbon frameworks - a search for optimal geometry for hydrogen storage

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Abstract Properties of a new class of hypothetical high-surface-area porous carbons (open carbon frameworks) have been discussed. The limits of hydrogen adsorption in these carbon porous structures have been analyzed in terms of competition between increasing surface accessible for adsorption and the lowering energy of adsorption. From an analysis of an analytical model and simulations of adsorption the physical limits of hydrogen adsorption have been defined: (i) higher storage capacities in slit-shaped pores can be obtained by fragmentation/truncation of graphene sheets into nano-metric elements which creates surface areas in excess of 2600 m²/g, the surface area for infinite graphene sheets; (ii) the positive influence of increasing surface area is compensated by the decreasing energy of adsorption in the carbon scaffolds of nano-metric sizes; (iii) for open carbon frameworks (OCF) built from coronene and benzene molecules with surface areas 6500 m² g⁻¹, we find an impressive excess adsorption of 75–110 gH₂/kg C at 77 K, and high storage capacity of 110–150 gH₂/kg C at 77 K and 100 bar; (iv) the new OCF, if synthesized and optimized, could lead to required hydrogen storage capacity for mobile applications.

Keywords Hydrogen adsorption · Monte Carlo simulations · Porous carbons

Introduction

Hydrogen contains the highest energy density (142 MJkg⁻¹) compared to other fuel sources, burns producing only water, so it will be an important future energy carrier. Although it is the most abundant element on Earth, only less than 1 % is present as molecular hydrogen gas H₂. Therefore, it needs to be produced from other chemical compounds (from water or hydrocarbons) at the energy expense that is higher than the gain when it burns. Ideally, hydrogen could be produced using a renewable energy source and then stored reversibly. The most technologically demanding is storage for mobile (vehicular) applications where ultimate tank should have gravimetric and volumetric densities at least equal 75 g kg⁻¹ and 70 g L⁻¹, respectively. These numbers, defined by US Department of Energy (DOE) to allow future H₂-powered vehicles at least 300 miles autonomy [1], are most frequently used as a reference when discussing the mechanism of hydrogen storage. In this paper we discuss extensively storage mechanism by adsorption in porous (activated) carbons with detailed analysis of physisorption.

There are three important factors which determine the adsorption uptake: total surface accessible for adsorption, energy of adsorption and the number of adsorbed layers. The number of layers is defined mostly by the intermolecular interactions between hydrogen molecules which are relatively weak. However, mechanism of adsorption depends also on details of adsorbent structural characteristics which can be divided into two categories: the heterogeneity of its three-dimensional (3D) structure and the

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heterogeneity of adsorbing wall. The different combinations of those factors lead to different mechanisms and all of them should be taken into account when determining physical limits of adsorption. Adsorbed hydrogen forms one (contact) layer of molecular hydrogen when physisorbed or one layer of atomic hydrogen when chemisorbed. Multilayer adsorption of molecular hydrogen is theoretically possible, but only at low temperatures, approximately below 100 K. For example, the partial second molecular layer is observed at 77 K. The density of the second layer may be increased by introducing stronger interaction with surfaces but at 77 K its density is always lower than this of contact layers [2]. At temperatures above 77 K the intermolecular interactions are not strong enough and the thermal energy destabilizes the second layer. In chemisorption the unique adsorbed atomic layer is naturally determined by the chemical bonds formed between the surface and the adsorbed atoms which cannot be formed beyond the contact layer.

Having the multilayer adsorption excluded, one needs to optimize the energy of adsorption and the total surface accessible to adsorption. Obviously, only light materials can be taken into account if the DOE goal of 75 g (H₂)/kg (adsorbent) should be achieved with a single layer adsorption. First of all, these are carbon based systems as carbon is relatively light atom, easily accessible and non toxic. This defines the references for the adsorption energy and the accessible surface and storage capacity. The adsorption energy of hydrogen on graphite substrate is below 5 kJ mol⁻¹ [3]. The total surface of ideal graphene layer is 2600 m² g⁻¹. The maximal excess adsorption is limited to 70 g kg⁻¹ if the adsorbed layer is very dense (low temperature) and it does not exceed 20 g kg⁻¹ at room temperature (Fig. 1). This numbers show that even the best activated carbons currently existing (with surface up to 3000 m² g⁻¹ [4]) cannot be directly used in mobile applications [5]. It shows why the final goal is not easy to achieve [6–12]. We need new materials with larger surface and higher energy of adsorption [13].

Currently, metal organic frameworks (MOF) constitute a large group of materials which have specific surface greater than 3000 m² g⁻¹ [8, 14]. Starting from the landmark MOF-177 [15] with a surface area of 4750 m² g⁻¹, several high surface area structures have been successively proposed (MIL-101 with surface area of 5900 m² g⁻¹ [16], NOTT with surface area of 4000 m² g⁻¹ [17] and porous coordinate polymers with surface area over 5000 m² g⁻¹ [18]. The record surfaces within MOF structures belongs to MOF-210 [19] (6240 m² g⁻¹), NU-100 [20] (6140 m² g⁻¹) and a polymer network with diamond structure PPN-4 [21] (6460 m² g⁻¹).

The covalent organic frameworks (COF) have similar structures to MOFs but their surface areas are below 4500 m² g⁻¹ [22, 23]. Another promising group of materials

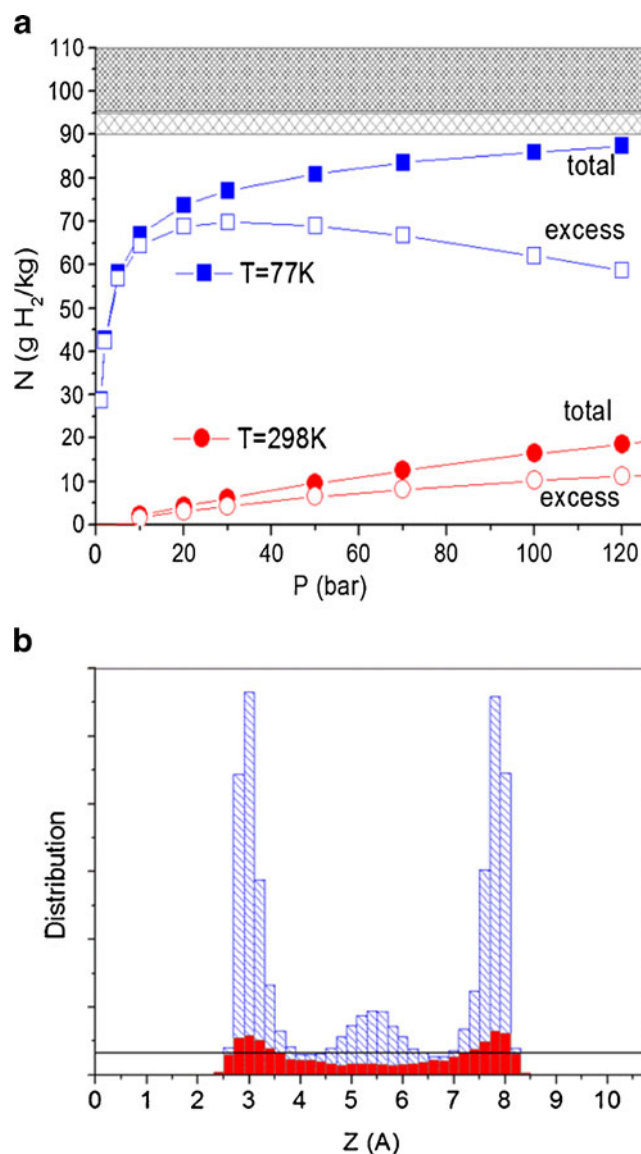


Fig. 1 Hydrogen adsorption in 1.1 nm pore calculated from grand canonical Monte Carlo simulations. The shaded area on the isotherm figure indicates physical limits due to the density of the adsorbed layer. The distribution gives the total density of the hydrogen at 100 bar as a function of the distance between the pore walls at 77 K (shaded, blue) and at 298 K (full, red). The solid horizontal line gives the density of the gas at 77 K; it contributes for 25 % to the total density in the pore

for gas storage are porous aromatic frameworks (PAFs), showing, the experimental surfaces above 5000 m² g⁻¹ [24, 25].

The surface areas of the best disordered carbons reported in the literature are between 2600 m² g⁻¹ and 3800 m² g⁻¹. The former value is the surface of a single graphene layer the latter one represents two recently produced materials: nitrogen-doped carbon [26] and Spanish anthracite [27]. The theoretical limits of accessible surface area in porous disordered structure have been recently discussed by Sarkisov

[28]. It has been suggested there that it is not impossible to prepare disordered carbon materials with surface area exceeding $6000 \text{ m}^2 \text{ g}^{-1}$. In this paper we discuss properties of new hypothetical carbon porous structures that can have the surface areas comparable with the best MOF structures. We call them open carbon frameworks (OCF)[29].

The best performing carbons versus theoretical predictions

The main purpose of this chapter is to test the interaction model and the simulation methodology versus available experimental results, before applying them in the following chapters to characterize new hypothetical open carbon frameworks.

Let us start with a presentation of the best performing activated carbons and an analysis of their properties using grand canonical Monte Carlo (GCMC) simulations. Figure 1 presents the theoretical adsorption in 1.1 nm infinite slit pore with the walls built of single graphene layers. Slit pore size is defined as the distance between the positions of carbon atoms in the pore walls.

It is worth emphasizing that at 77 K the second partial layer is observed (see Fig. 1, molecular density at 77 K) but its density is much lower than this of the contact layers. There is no second layer at 289 K. The $\text{H}_2\text{-H}_2$ interaction energy is too small to form the second layer at high temperatures. From the point of view of the gravimetric and volumetric capacity the optimal pores width [2] is between 0.9 and 1.3 nm. These pores allow adsorption of two contact layers and, if the pore is larger than 1.0 nm, the additional one appears in the middle of the pore (at low temperatures). However, even the best existing activated carbons do not have the pore structure corresponding to this optimal distribution [4, 10]. To the best of our knowledge, there are two activated carbons with very high specific surfaces and exhibiting high capacity for hydrogen adsorption.

Historically, the first was the MSC-30 sample [10, 30] that is now commercially available; the second is corncob derived activated carbon prepared at the University of Columbia: we call it 3 K activated carbon [4, 31]. Figure 2 presents isotherms of hydrogen adsorption in both samples (at 80 K). The description of experimental setup and methodology have been presented in previous papers [4, 31]. The main structural difference between both carbons is smaller fraction of larger pores (above 1.5 nm) in the 3 K sample which gives higher excess adsorption. This observation confirms experimentally the importance of pores with 0.9–1.3 nm sizes for the hydrogen uptake.

Numerical analysis brings more insight into the mechanism of adsorption and possible way to improve it. The experimental data can be easily modeled and reproduced

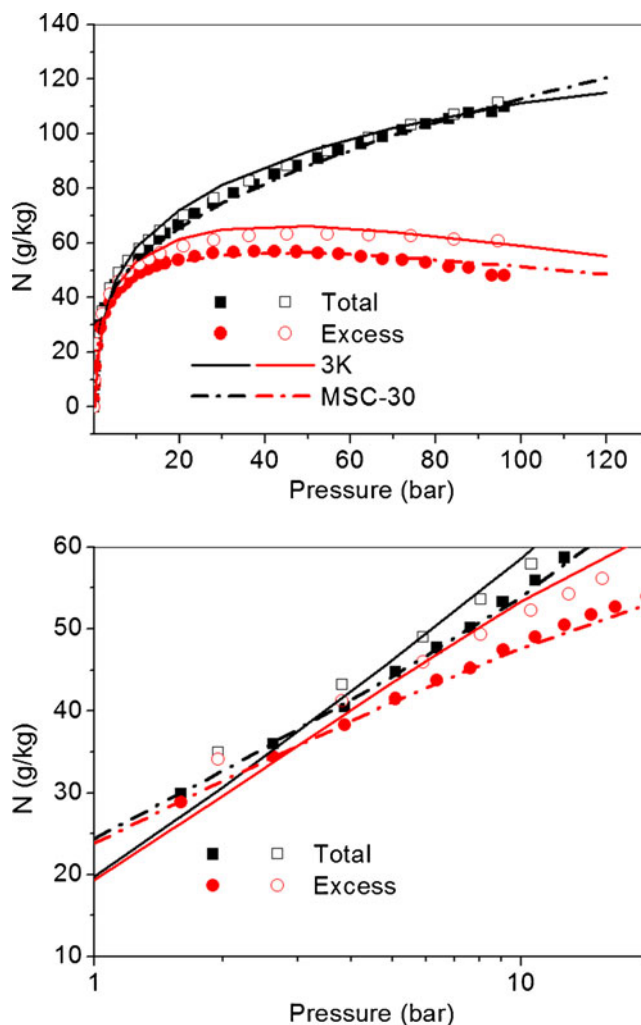


Fig. 2 Experimental isotherms of hydrogen adsorption ($T=80 \text{ K}$) measured for the Missouri sample (3 K - open symbols) and for the commercial (MSC-30 - closed symbols) samples. The lines represent fits calculated from grand canonical Monte Carlo simulations data. The low pressure (1–10 bar) data have also been shown on semi-log scale to emphasize the high quality of the fit

by simulations of H_2 adsorption (see Fig. 2). The final model isotherms have been calculated as linear combinations of isotherms simulated for the slit pores [29]. The final calculated isotherms reproduce the experimental ones with great accuracy (see Fig. 2), in the whole range of pressures. This suggests that the analyzed carbon systems have a slit-like local structure with homogenous distribution of the energy of adsorption. The details of the numerical approach (based on grand canonical Monte Carlo (MC) simulations) and the interaction parameters have been published before [2, 32]. These parameters model the potential energy of H_2 -graphene type systems with high accuracy as it has been observed in the previous papers [2, 32] and confirmed by the excellent agreement between experimental and calculated isotherms presented above. However, we have not

verified if the model is transferable to other carbon based systems.

Open carbon framework - adsorption

It has been recently discussed [13, 33] that the fragmentation of the graphene sheet creates additional surface accessible for adsorption because of the fragment edges. Therefore one can imagine hypothetical porous structures as composed from nano-metric graphene fragments [34] of different sizes: we call them the open carbon frameworks (OCF) [29].

There are three large groups of materials that naturally fit in the same category [3, 28]: covalent organic framework (COF) [23], metal organic frameworks (MOF) [8, 14] and polycyclic aromatic frameworks (PAF) [25]; however, they do not achieve the level of adsorption necessary to fulfil the goal required for mobile applications. It is easy to justify that these geometries are not optimized for hydrogen adsorption. Although their structures (basically built of phenyl rings) can attain extremely high specific surface areas (even more than $7000 \text{ m}^2 \text{ g}^{-1}$), their adsorption energy is substantially lower than that of graphene layer. This is a direct effect of the use of very small carbon structural units; the energy of adsorption on benzene-like fragment is much lower than on graphene, especially close to and on the edges of the fragments (see Fig. 3). One can see from Fig. 3 that the situation is much better even for coronene molecule which has the linear dimension about two times larger than benzene molecule and the absolute value of adsorption energy is already bigger (although on average still considerably lower than for graphene layer). This observation defines the main idea discussed in this paper; we would need to optimize sizes of fragments to have the energy of adsorption at least comparable to the graphene values. Following this observation we proposed a new strategy to extend the limits of hydrogen adsorption in porous carbons by optimizing the open carbon frameworks in a way which will take advantage of high specific surface and the energy of adsorption comparable with graphene [29].

The logical question is: what is the optimal size of the structural blocks? They must be large enough to ensure in-plane adsorption energy comparable to the graphite one but small enough to have important contribution from the pore edges to the total adsorption surface. Therefore, the optimal parameters are defined by a competition between increasing edge surface (roughly proportional to $S^{-1/2}$ where S is the fragment surface) and the decreasing adsorption energy due to the edge influence. First, we estimate the effect of this competition using a simple analytical model. In this model we assume that the carbon building blocks are fragments having circular shape (that is the shape with minimal edge

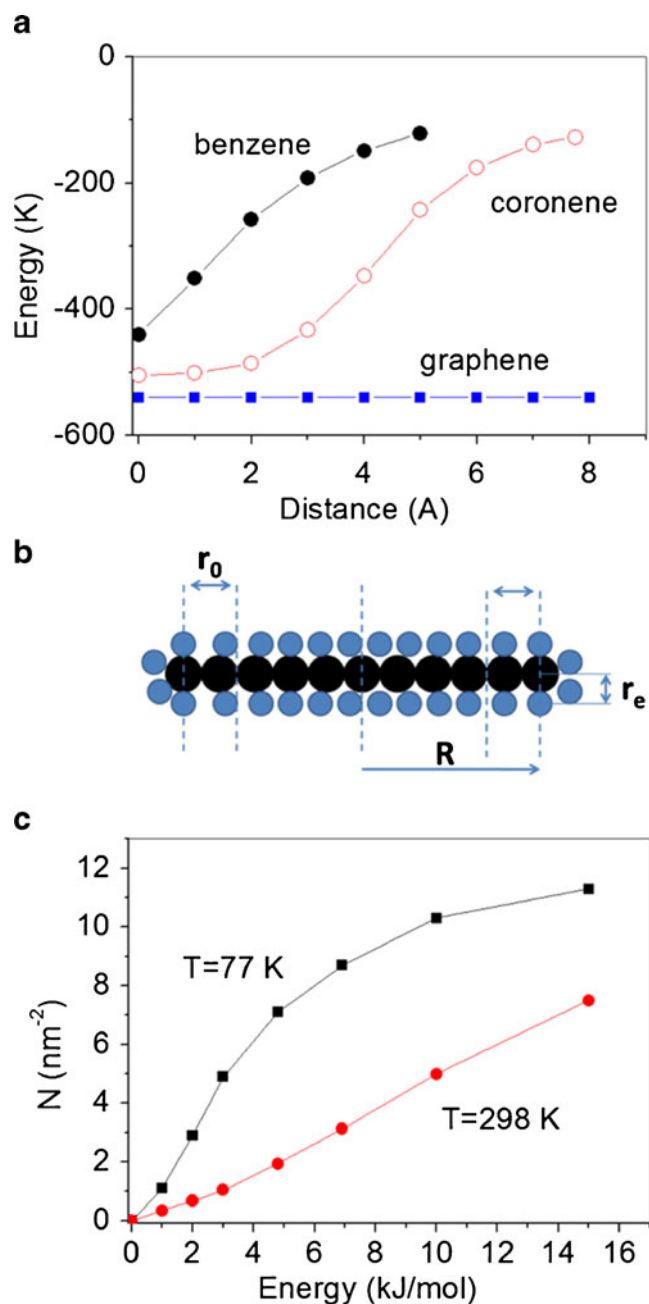


Fig. 3 **a** Adsorption energy of hydrogen on individual benzene and coronene molecules. The distance R is calculated with respect to the geometrical center of the molecules. The energies calculated for molecules are extended beyond the molecular edge to have the energy of adsorption on edges. The graphene energy is averaged over the atomic corrugation, **b** graphic definition of the parameters R , r_0 and r_e . Black atoms represent carbon wall, blue atoms adsorbed hydrogen, **c** maximal density of the adsorbed hydrogen layer (excess adsorption) in pores with width $H=0.9 \text{ nm}$ as a function of the adsorption energy (calculated in ideal slit pore with graphene walls)

length among all possible forms having the same surface) which adsorption properties are defined by $C(\text{graphene})\text{-H}_2$ interaction model [2, 32]. For the sake of our model calculations we divide the fragment surface (of radius R) into

three parts (see Fig. 3b): the middle surface defined by a parameter r_0 (where the distance r from the fragment center is $r < R - r_0$), the external surface ($R - r_0 > r > R$) and the edge surface ($r > R$). We assume that the density of the adsorbed layer is constant in the first part. It is decreasing linearly in the second one and is constant on the third, edge surface.

The model is defined by six system-dependent parameters which can be calculated from numerical simulation results. Three of them define the density of the adsorbed hydrogen layer. N_0 is the adsorbed layer density at the middle part of the patch ($r < R - r_0$, where the energy of adsorption is practically constant, example: for $r < 2$ Å for coronene, see Fig. 3a). The density is decreasing from N_0 to N_1 for distances $R - r_0 < r < R$ (example: for $2 < r < 5.5$ Å for coronene, see Fig. 3a) and N_2 is the density characterized for the edge surface $r > R$ (example: for $r > 5.5$ Å for coronene, see Fig. 3a). Three additional geometrical parameters are: r_0 , r_e and R_s . In the model we assume that the density is changing linearly between N_0 and N_1 when approaching pore edge ($R - r_0 < r < R$). Parameter r_e characterizes the edge surface accessible for adsorption. We assume that it can be calculated as a surface of a semi-cylinder of radius r_e , where r_e is the distance between the positions of the first (contact) adsorbed hydrogen layer (calculated numerically) and the carbon atoms (see Fig. 3b). The third geometrical parameter R_s is the radius of smallest pore wall for which N_0 is independent of the pore wall radius R . For very small patches N_0 is decreasing to have $N_0 = 0$ at the $R = 0$ limit. This limit defines the adsorption properties in pores with walls built from very small fragments ($R < R_s$), for which the energy of adsorption is weak (see the case of benzene, Fig. 3, where energy of adsorption is substantially lower than in the graphene layer or even coronene molecule).

In the model, the surface of a circular slit pore wall having radius R can be calculated as

$$S = 2\pi R^2 + 2\pi^2 R r_e.$$

The first and the second contributions are from the inside-pore and edge surfaces, respectively. In an ‘ideal’ case, if the adsorption energy was constant the uptake would be proportional to the surface S , so, the relative ideal uptake *Ideal_Ads* (that is, calculated with respect to the adsorption in infinite pore built from graphene walls where the edge contribution is zero) would be:

$$\text{Ideal_Ads} = 1 + \pi r_e / R$$

where the second term gives directly the ratio of the ‘edge surface’ to ‘in-pore surface’ in our model. In this case the excess adsorption would increase always when the size of the wall decreases (see Fig. 4, ‘ideal adsorption’ curve). However, the real situation must take into account the variation of the adsorption energy at the edges which always

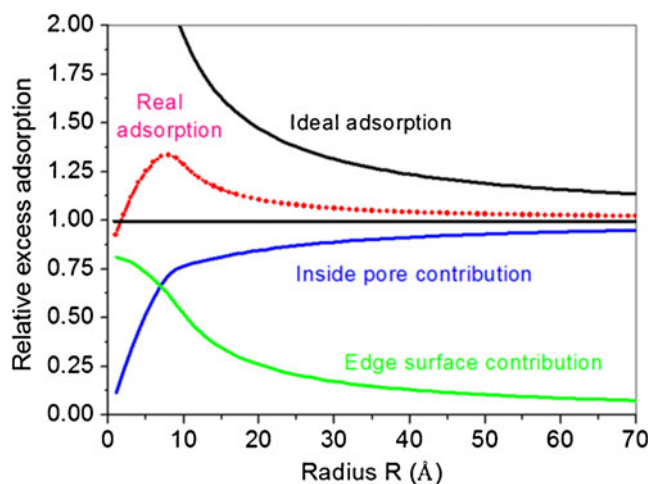


Fig. 4 Relative maximal excess adsorption in a model adsorbent build of slit pores with finite size circular walls of the radius R . The reference adsorption (equal 1 - black line) corresponds to the same adsorbent with energy of adsorption of graphene and no adsorption on the edges, that is, only inside surface contribution. The model upper limit gives a theoretical adsorption if also the edge surface adsorbs with energy of graphene. The model adsorbent (total adsorption - red dotted line) has the inside adsorption reduced due to the distribution of the adsorption energy on the inside surface close to the edge (inside surface - blue line) and the edge contribution (edge surface - green line)

reduces the adsorbed amount of gas with respect to the ideal case. It can additionally be reduced due to the bonding between the fragments.

Let us take numerical parameters estimated for hydrogen adsorption: $N_1 = 0.5 N_0$, $N_2 = 0.45 N_0$, $r_0 = 4$ Å, $R_s = 10$ Å. The parameters N_1 and N_2 reflect the fact that the energy of adsorption becomes weaker closer to the fragment edge (see Fig. 3). As a result, the average density of the adsorbed layer on the edge surface is about 0.45 of the density in the middle of the wall. With these parameters the optimal size of carbon fragment radius is between 0.5 and 1.5 nm (the curve ‘real adsorption’, Fig. 4). The exact position of the maximum can be slightly shifted if different shape of the edge is considered. However, the general feature will not change: there is an optimal size in nano-metric range and adsorption decreases toward the limit of very small fragments.

Following the above conclusion we have analyzed two different hypothetical structures which have been defined using polycyclic aromatic hydrocarbons (PAH): coronene ($R \approx 0.55$ nm), benzene ($R \approx 0.25$ nm). The molecules have been arranged to form adsorbing open layers (Fig. 5) which are used to construct ‘open’ slit pores. The molecules forming the layers are bonded using molecules being in orthogonal orientation. We compare adsorbing properties of two structures: (i) PAH-type (Fig. 5a) built from coronene molecules bonded using coronene as a linker and (ii) PAH-type (Fig. 5b) built from coronene molecules bonded using benzene as a linker. The proposed structures represent intermediate topologies between slit pores built from graphene

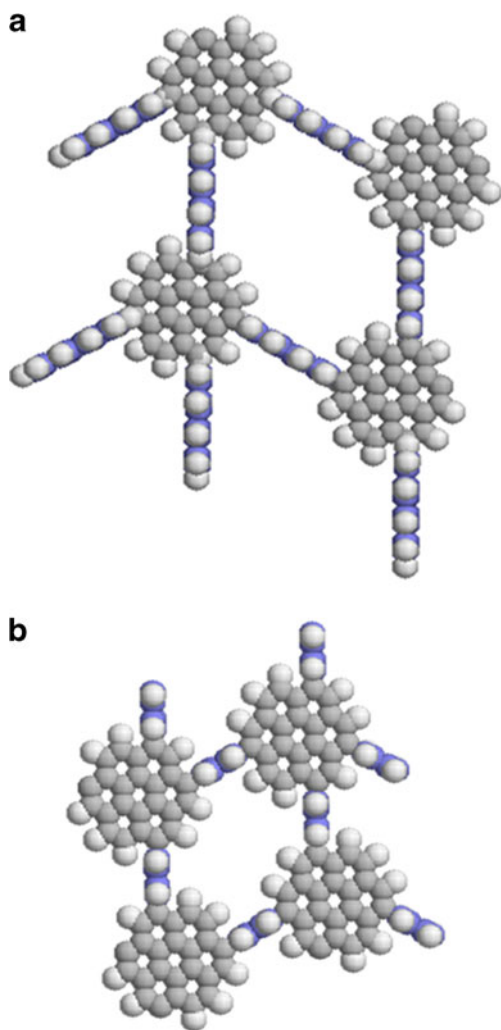


Fig. 5 The hypothetical open carbon framework pore wall structures. **a** Cor_Cor OCF : basic unit of the pore wall structure built from coronene molecules bonded by coronene linker, **b** Cor_Benz OCF: basic unit of the pore wall structure built from coronene molecules bonded by benzene linker. Two different colors have been used to make better contrast between carbons in in-layer molecules (gray) and linkers (blue). Light gray indicates H atoms

infinite walls and the open structures like COF, MOF or PAF. The most important property of our structures is their open architecture which introduces substantial surface contribution due to the fragment edges. The two types of OCF presented in Fig. 5 have different structural characteristics. The specific surface of the structure built from coronene molecules equals $5500 \text{ m}^2 \text{ g}^{-1}$ whereas that of PAH-with benzene reaches $6500 \text{ m}^2 \text{ g}^{-1}$. The difference in the specific surfaces is a consequence of the building block sizes. Table 1 gives the basic parameters characterizing the discussed OCF structures. The surfaces of the OCF structures have been estimated geometrically as the surfaces defined by the centers of adsorbed H_2 molecules (modeled as spherical superatoms) forming one layer at the distance $r_c=3\text{Å}$ from the centers of atoms in the OCF structures.

The calculated H_2 adsorption isotherms are presented in Fig. 6. We compare the conventional slit pore model where the walls are built from infinite graphene layers with slit pores built from the PAH-type walls from Fig. 5. Two options have been studied for each type of structure. One represents porous structure built from coronene/benzene molecules, second is the same topologically structure but with hydrogens substituted by hypothetical atoms interacting stronger with adsorbed hydrogen molecules (see Fig. 6 caption for detailed definition). We call them ‘decorated’ structures. Both total (gravimetric and volumetric) and excess adsorptions are presented. Although it is the total adsorption that gives us the storage capacity of the systems (Fig. 6a), it is the excess adsorption which better characterizes the adsorption properties of the pores (Fig. 6b). All OCF structures show increased adsorption uptake with respect to the graphene wall pores.

Open structures from Fig. 5 show important increase of the excess adsorption with respect to the graphene-wall slits, up to 50 % for their decorated forms. As expected, the Cor-Benz structures adsorb more than the Cor-Cor structure. It is because the former one is built from on average smaller fragments and it has larger specific surface. At the same time, the difference is not so big as could be expected from

Table 1 Properties of the modeled OCF structures (distance between walls $H=1.2 \text{ nm}$). Excess uptake means the maximum value (from Fig.6b) at $T=77 \text{ K}$. Total uptake is given at 100 bar (Fig. 6a) at $T=77 \text{ K}$ (in parenthesis $T=298 \text{ K}$). Graphene slit properties have been

shown as a reference. Volumetric density ($T=77 \text{ K}$) is given for the pressure $P=100 \text{ bar}$. Energy means absolute average energy (from Monte Carlo simulations) of H_2 -walls interaction

OCF structure	Surface ($\text{m}^2 \text{ g}^{-1}$)	Density ($\text{g} (\text{cm}^3)^{-1}$)	Excess (g kg^{-1})	Total (g kg^{-1})	Volumetric (g L^{-1})	Energy (from MC) (kJ mol^{-1})
Cor_Benz	6500	0.39	84	131 (23)	50	2.38
Cor_Benz decorated	6500	0.39	109	149 (37)	57	3.71
Cor_Cor	5500	0.45	74	113	30	2.83
Cor_Cor decorated	5500	0.45	100	130	35	4.28
Graphene slit	2600	0.63	73	96 (20)	60	3.20

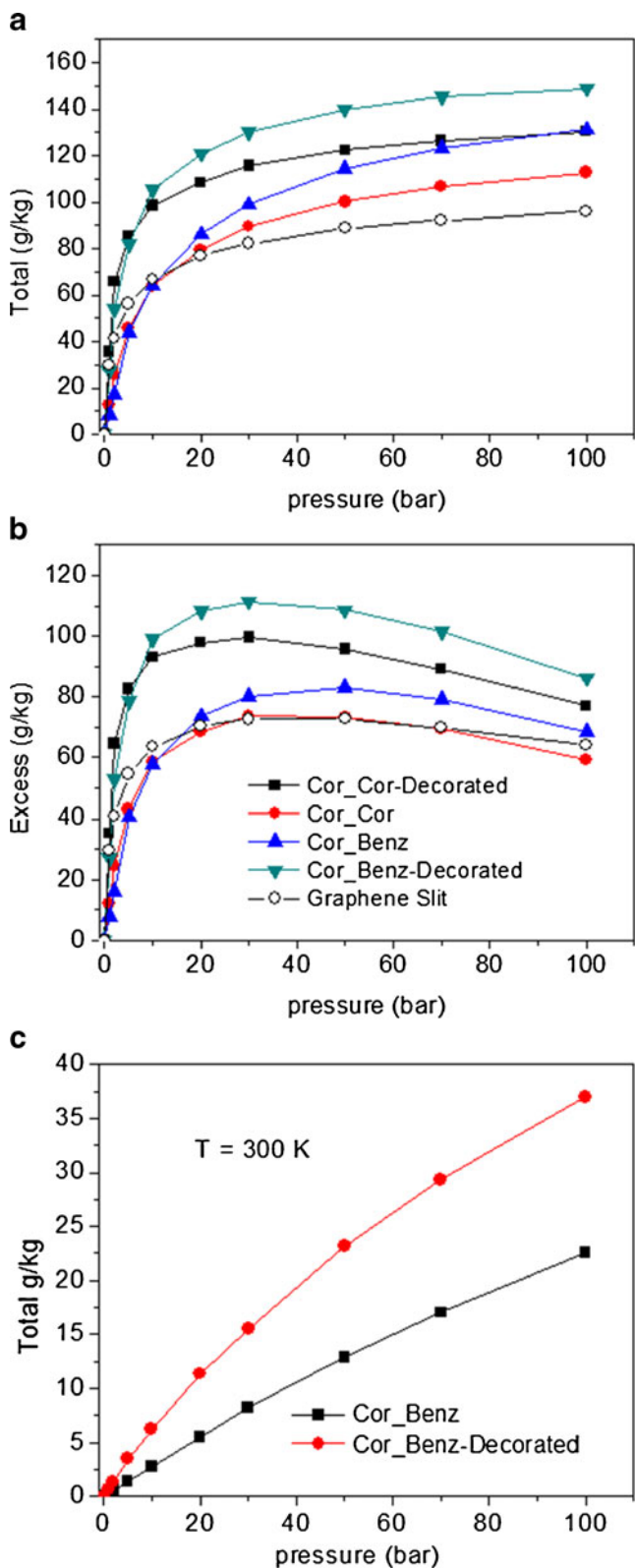


Fig. 6 Adsorption isotherms for OCF structures compared to the infinite graphene slit pore uptake. Cor_Cor and Cor_Benz are the structures presented in Fig. 5a and b, respectively. Figure 6a and b show adsorption at T=77 K. Figure 6c show T=300 K isotherms for the best performing structure (Cor_Benz). ‘Decorated’ indicate models where the hydrogen atoms have been substituted with hypothetical atoms which interact with adsorbed hydrogen molecules two times stronger than the carbon atoms do (that is, with the corresponding Lennard-Jones parameter ϵ taken as the C-H₂ parameter multiplied by 2)

It is interesting to observe that the graphene slit pore and our Cor_Cor model show nearly identical excess adsorption (see Fig. 6b). It is an example of perfect compensation of the higher specific surface (2600 and 6500 m² g⁻¹, respectively) by lower energy of adsorption (3.20 and 2.83 kJ mol⁻¹, respectively). At the same time, the Cor_Benz structure (average energy of adsorption: 2.38 kJ mol⁻¹) adsorbs more because of its larger accessible surface. It is important to emphasize that average energies from Table 1 do not fully characterize the adsorbing surface; in the OCF structures there is a wide distribution of energies of adsorption which must be taken into account when designing such structures.

The results can be interpreted within the analytical model discussed above. One can observe that the smaller fragments are performing only about 10 % better than the bigger ones because the influence of higher surface is compensated by the decreasing energy of adsorption for small fragments. In general, the adsorption uptake in fragmented pores is always larger than the one in the infinite pores. However, the gain is not proportional to the specific surface because the ‘edge surface’ adsorption is partially compensated by the lower ‘inside pore’ adsorption close to the edge. Additionally, part of the edge surface is not accessible for adsorption due to the bonds between fragments. In general, this effect is negligible for large fragments but becomes very important in the pore with walls built from nano-fragments.

The decorated structures have been prepared by substitution of hydrogen atoms in coronene and benzene molecules by more attractive sites. This improves the adsorption properties, that is, the average energy of adsorption is higher and the hydrogen uptake increases both for excess and total adsorption. However, it is clear that such simple change does not improve the hydrogen adsorption up to the level required for mobile application. This can be seen clearly from the room temperature adsorption simulation (see Fig. 6c and Table 1). This shows that the ultimate goal for the required porous structure will need very careful optimization of its structure, accessible surface and the distribution of adsorption energy.

the difference of specific surface values. This is the consequence of lower adsorption energy in smaller PAH structure. The difference can be seen from the average energies shown in Table 1.

Conclusions

We have analyzed adsorption properties of new model porous carbons built from nano-metric fragments of graphene

sheet which we call open carbon frameworks (OCF). Theoretically their specific surfaces may exceed $6000 \text{ m}^2 \text{ g}^{-1}$. In principle, their structures do not need to be ordered but we have not studied the influence of disorder on the adsorption properties.

We have discussed the physical limits of hydrogen adsorption in such porous structures. The most important factors are the energy of adsorption and total accessible surface for adsorption. These two characteristics strongly depend on the pore geometry and topology. For carbon based porous systems, the ideal slit pores built from graphene walls are a convenient reference system. However, if the storage capacity required for mobile applications should be attained we need to prepare materials with larger specific surface and bigger energy of adsorption. Larger specific surfaces can be achieved by fragmentation of the graphene sheet. At the same time, fragmentation leads also to heterogeneous and lower average energy of adsorption. As a consequence, there is a natural physical limit of adsorption in such structures. To obtain the maximal hydrogen uptake, the structures must be carefully optimized. It is important to emphasize that the structures analyzed in this paper are simple analogues of slit-like geometries and could be further optimized to maximize the hydrogen uptake needed for specific applications. However, due to the natural physical limit of such fragmentation the optimal size has been estimated to be between 0.5 and 1.5 nm. The analysis is supported by a simple analytical model which directly estimates the positive contribution from additional edge surface and negative one from the decreasing energy of adsorption. Additional improvement of storage capacity could be achieved if the increase of the adsorption surface was combined with the increase of adsorption energy via chemical modifications of the pore walls, especially on the edges and/or high energy defects in the carbon structure. We have shown that it effectively improves the hydrogen uptake.

Obviously, the above quantitative estimations are accurate only for H_2 -carbon interaction. The result of competition between different factors determining the adsorption in porous structures is specific for each adsorbate-adsorbent couple.

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