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Grand canonical monte carlo modeling of hydrogen adsorption on phosphorus-doped open carbon framework

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Abstract Mechanism of hydrogen adsorption in high surface area carbon-based porous materials has been studied. Influence of chemical modification of the adsorbing surface has been simulated using grand canonical Monte Carlo method. Special attention has been paid to the competition between increasing the surface of open carbon frameworks and heterogeneous distribution of the energy of adsorption. Additionally, it has been shown that the molecular mass of atoms which substitute carbon atoms is an important factor determining the final hydrogen uptake.

Keywords Hydrogen adsorption · Carbon-based adsorbents · Polycyclic aromatic hydrocarbons (PAHs) · Density functional theory (DFT) · Grand-canonical Monte Carlo simulation · Phosphorus

1 Introduction

The low weight of carbon-based porous materials makes them one of the most important candidates for hydrogen storage applications. Nevertheless, their storage capacity is not sufficient for mobile application and a lot of effort has been done to increase their hydrogen storage capacity. Two main modifications have been proposed: increasing the interaction energy of the adsorption sites (Xia et al. 2009; Miwa et al. 2008; Kuchta et al. 2010a, b; WU et al. 2010) or increasing the surface area (Ma et al. 2001).

Insertion of dopants such as nitrogen (Badzian et al. 2001), boron (Miwa et al. 2008; Sankaran and Viswanathan 2007; Firlej et al. 2009) and sulfur (Sankaran and Viswanathan 2006) into carbon hydrogen storage materials have been studied theoretically and experimentally. The results show positive effect of dopants on hydrogen adsorption capacity compare to the non-doped structures. However, the hydrogen storage capacity is still far from the goal for mobile applications and extra effort to modify the structure of the porous material is necessary.

Current progress to increase the surface area in material such as metal organic frameworks (MOFs), covalent organic frameworks (COFs) and porous aromatic frameworks (PAFs) is the evidence for such efforts. MOF constitutes large group of materials which have specific surface greater than 3,000 m^2/g (Rosi et al. 2003; Sculley et al. 2011). Starting from the landmark MOF-177 (Wong-Foy et al. 2006) with a surface area of 4,750 m^2/g, several high surface area structures have been successively proposed such as e.g. MIL-101 with surface area of 5,900 m^2/g (Férey et al. 2005), NOTT with surface area of 4,000 m^2/g (Yan et al. 2010) and porous coordinate polymers with surface area over 5,000 m^2/g (Koh et al. 2009). The record surfaces within MOF structures belongs to MOF-210 with surface area of 6,240 m^2/g (Furukawa et al. 2010), NU-100 with 6,140 m^2/g (Farha et al. 2010) and a polymer network with diamond structure PPN-4 with 6,460 m^2/g (Yuan et al. 2011). COFs have similar structures to MOFs. Their surface area, however, are below 4,500 m^2/g (El-Kaderi et al. 2007; Furukawa et al. 2009). Another promising group of materials with high surface area for gas storage are the family of materials with scaffold type structure. Structures such as PAFs, showing the experimental surfaces above 5,000 m^2/g (Ben et al.2009; Lan et al. 2010), pillared graphene (Dimitrakakis et al. 2008) and graphene-oxide

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frameworks (Srinivas et al. 2011; Burress et al. 2010) are among this group. Although many of such structures have been studied, still the problem of hydrogen storage has not been solved.

These newly proposed structures (Lan et al. 2010; Dimitrakakis et al. 2008; Srinivas et al. 2011) including our previous work on open carbon frameworks (OCF) (Kuchta et al. 2012) are often built from different Polycyclic Aromatic Hydrocarbons (PAHs) and finite-size graphene-based fragments. Compared to an infinite graphene layer, these building block fragments, ranging from benzene to the larger nanometric fragments, have high accessible surfaces due to the presence of edges. However, the interaction energy on the edge surface is always lower than on graphene surface. Hence, the PAH fragments makes the system strongly heterogeneous because of their finite size and wide distributions of the interaction energy. This structural and energetic heterogeneity are among the most important factors determining the hydrogen storage capacity in these group of materials in which the competition between having higher specific surface and lower interaction energy at the edge area determines the final capacity of these porous systems. This aspect is studied in this paper using DFT methodology. We show how the adsorption energy depends on the size of the building blocks and how it is modulated on edge of the surface.

Materials with large surface areas and low densities, such as MOFs (Leslie et al. 2009), COFs and PAFs are good candidates for hydrogen storage applications but their energy of adsorption is still too low. Obviously, specific surface of porous materials plays very important role on the adsorption on carbon-based adsorbents (Firlej et al. 2009; Kuchta et al. 2010a, b, c) and MOFs (Mellot-Draznieks et al. 2004). However, high surface is not enough to obtain required hydrogen storage capacity. This is the second important aspect studied in this paper. We examine the influence of chemical modification on the adsorption capacity in such high surface carbon-based systems made of PAH fragments.

2 Computational methodology

The methodology applied in this paper aims to contribute to the search of optimal porous structure from the point of view of hydrogen storage capacity. Therefore, before we start to simulate the adsorption capacity of OCF structures, we have performed the adsorption analysis of nanometric graphene-based fragments and PAHs, (see Fig. 1a) which are the building blocks of the OCF structures. The main methodology applied to the calculation of interaction energy on PAHs is DFT calculations which allows us to model distributions of the adsorption energy on these fragments. The DFT calculations (Hohenberg and Kohn 1964; Kohn and Sham 1965) have been performed with the CPMD program (CPMD 2001) that implements the plane wave basis set approach to expand the electronic wave-function. DFT calculations have been performed along with BLYP exchange–correlation functionals (Becke 1988) of the generalized gradient approximation. The plane wave type of the basis set is the most appropriate one for the problems of adsorption in solids because these systems are extended by nature. For the calculations, we employed Goedecker–Teter–Hutter (GTH) norm-conserving pseudo-potentials in conjugation with dispersion-corrected atom-centered effective potentials (DCACPs) (Lin et al. 2007). The use of DCACPs is one of the techniques that permits to include London dispersion forces within the framework of DFT which is essential in the study of hydrogen adsorption on the physisorption domain. The quality of the plane wave basis set is defined by the kinetic energy cut-off. In order to select appropriate cut-off energy (E_{cut}), a preliminary analysis of interaction energy dependency on E_{cut} has been performed for hydrogen interaction with coronene. E_{cut} value of 100 Ry has been selected for the calculations to limit the length of the calculations for both single point and geometry optimization calculations. This value of E_{cut} ensures that the basis set is of good quality and allows us to provide accurate DFT results. The convergence criteria on the total energy has been fixed to 5.10^{-7} Hartree. To calculate the interaction energies between H_2 molecule and PAHs (Fig. 1a), the molecules are placed in a simulation box that is large enough to prevent the interaction of hydrogen and PAH with their neighboring periodic images. For the calculation of interaction energies between H_2 molecule and infinite graphene, the infinite graphene layer is constructed from the periodic graphene model (PGM) unit cell as defined in the Fig. 1b. From these calculations, the analysis of the interaction properties of hydrogen molecules adsorbed on fragmented graphene surface has been performed. In fact, the DFT calculations allowed us to find the position and energy of adsorbed hydrogen molecule at 0 K and the hydrogen interaction energy dependency on the fragment size.

The methodology applied to calculate the theoretical storage capacity of the 3D porous OCF structures is a Monte Carlo (MC) approach. The MC simulations carried out in this paper are based on the Metropolis algorithm (Allen and Tildesley 1990). The grand canonical ensemble has been applied where temperature, volume and chemical potential are constant parameters. We have performed the calculation at two temperatures, namely 77 and 298 K. Adsorption isotherms are calculated for various values of

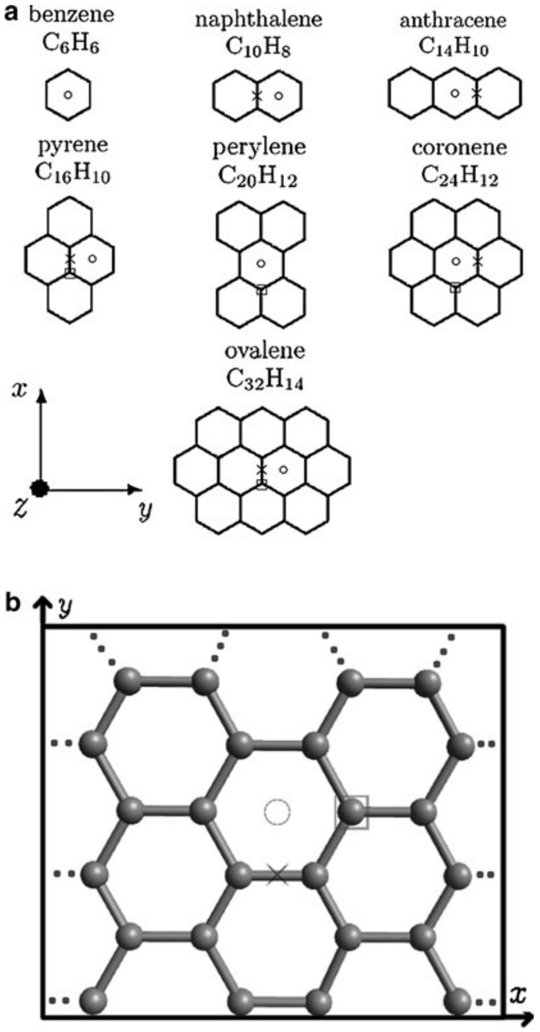

Fig. 1 **a** Structures of polycyclic aromatic hydrocarbons (PAHs). The position of three different adsorption sites α (*square*), β (*cross*) and ρ (*open circle*) have been indicated and; **b** periodic graphene model (PGM) unit cell defined in the calculation of infinite graphene layer (the *dotted lines* indicate the directions to the nearest neighbors in the periodic system)

chemical potential which is recalculated into pressure using the ideal gas model. The hydrogen molecules are modeled by the super-atom approach. This approach and the pertaining interaction model have been tested in the previous papers (Firlej et al. 2009; Kuchta et al. 2010c). In general, the interactions have been modeled by atom–atom Lennard-Jones potential function.

In the case of porous structures built of PAH fragments, a periodic OCF structure is represented by a MC box. The total adsorption is extracted directly from the raw MC data and represented as the mass of hydrogen adsorbed in the MC box divided by the mass of the adsorbent. The excess adsorption is calculated by subtracting the amount of gas which would be present in the pore volume (that is in the MC box), if there was no adsorption.

3 Structure design principles and adsorbent geometry

When designing structures such as OCF, principal questions arise: How far can we increase the surface area and what is the optimum fragment size?

Keeping in mind that the specific surface of ideal graphene sheet is about 2,600 m^2/g, fragmentation of the pore walls becomes necessary to have higher accessible surface for adsorption. So, as the first step, we have calculated the geometric accessible surfaces area of PAHs and finite-size graphene-based fragments, shown in Fig. 2, using the methodology proposed by Tina Düren (2007).

In this analysis, surface area as one of the major parameters that influences the hydrogen adsorption capacity, and it has been studied for PAHs and finite-size graphene-based fragments (Fig. 2). Results have been analyzed to design OCFs with high hydrogen storage performance.

As expected, the results are showing a significant dependency of the surface area with respect to the size of fragment: the smaller the fragment the larger the surface area, the smallest tested fragment being the benzene molecule. This size dependency is the contribution of edges to the surface area. The difference between the surface area for PAHs and infinite graphene layer is large. The specific surface area for the finite-size graphene-based fragments (PGM-X series e.g. PGM-216 & PGM-3280) is also high and they can be used for the design of OCF structure. The numerical values of the surface area of the fragments depend on probe molecule used where the minimal value is defined by the van der Waals radii (see Fig. 2, size of the probe $d = 0.0$ Å). Larger probe sizes (which physically

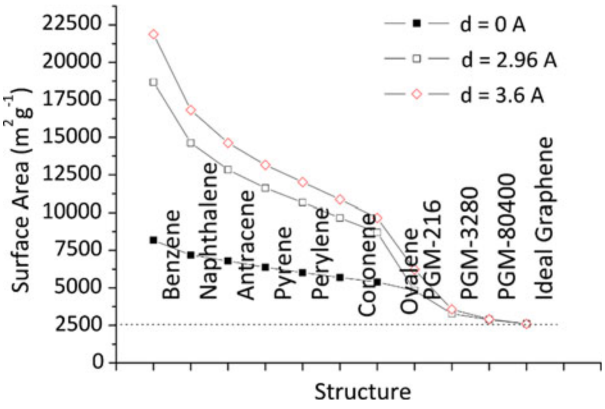

Fig. 2 The geometrical accessible surface area for common sets of PAHs and finite-size graphene-based fragments have been analyzed. Three different probe sizes have been used to estimate the accessible surfaces: $d = 0$ Å estimates the van der Waals surface, $d = 2.96$ and 3.6 Å represent H_2 and N_2 molecules as the probes. Where PGM-X, X defines the number of carbon in the structure e.g. PGM-216 is a finite-size graphene-based fragment with 216 carbons in the structure consist of 24 hexagonal rings

should represent the size of adsorbed molecules) gives larger surface.

On the contrary, the interaction energy of PAH fragments with hydrogen is dependent on the fragment size and it is higher for larger fragments (Fig. 3a). The lowest interaction energy belongs to the smallest fragment which is an opposite behavior to the surface area. The average interaction energies presented in Fig. 3a is that of hydrogen with three adsorption sites on the fragment. The interaction energies are calculated for hydrogen at its optimum distance from the surface.

In another effort, we have also calculated the potential energy surface (PES) of a single hydrogen (Fig. 3b), to analyze the energy heterogeneity on the surface of fragments. The calculation has been performed for hydrogen being in its attractive interaction distance (3 Å) and normal to the surface. We have observed that the energy decreases for the sites closer to the fragment edge.

Therefore, there is always a competition between two factors, namely surface area and average interaction energy for different fragment size. The balance between the two factors is the key feature to design adsorbents with high capacity of hydrogen storage and it has to be found to get the maximal storage capacity.

Thus, we have analyzed adsorption of one H_2 molecule on these fragments (isolated) in order to see how the above mentioned factors affect the hydrogen storage capacity. The results obtained from the GCMC simulations of the adsorption of H_2 on the separate PAHs fragments are shown in Fig. 4. We have observed the increase of adsorption capacity, when decreasing the fragment size. This analysis demonstrates that the surface area prevails over the variation of interaction energy.

The geometry of the porous system that has been used in this paper was defined in our previous paper (Kuchta et al. 2012) and is briefly recalled in the following. It is an open, low density orthorhombic structure with high surface area, an open carbon framework (OCF). Based on the analysis that has been done on the effect of fragment size on the surface area (Fig. 2) and hydrogen interaction energy (Fig. 3a, b), the building blocks of OCF have been selected. The OCF structure has been designed using six PAH-like fragments linked together where the fragments size is in the range of 2 nm (Fig. 5a). In this paper we simulated

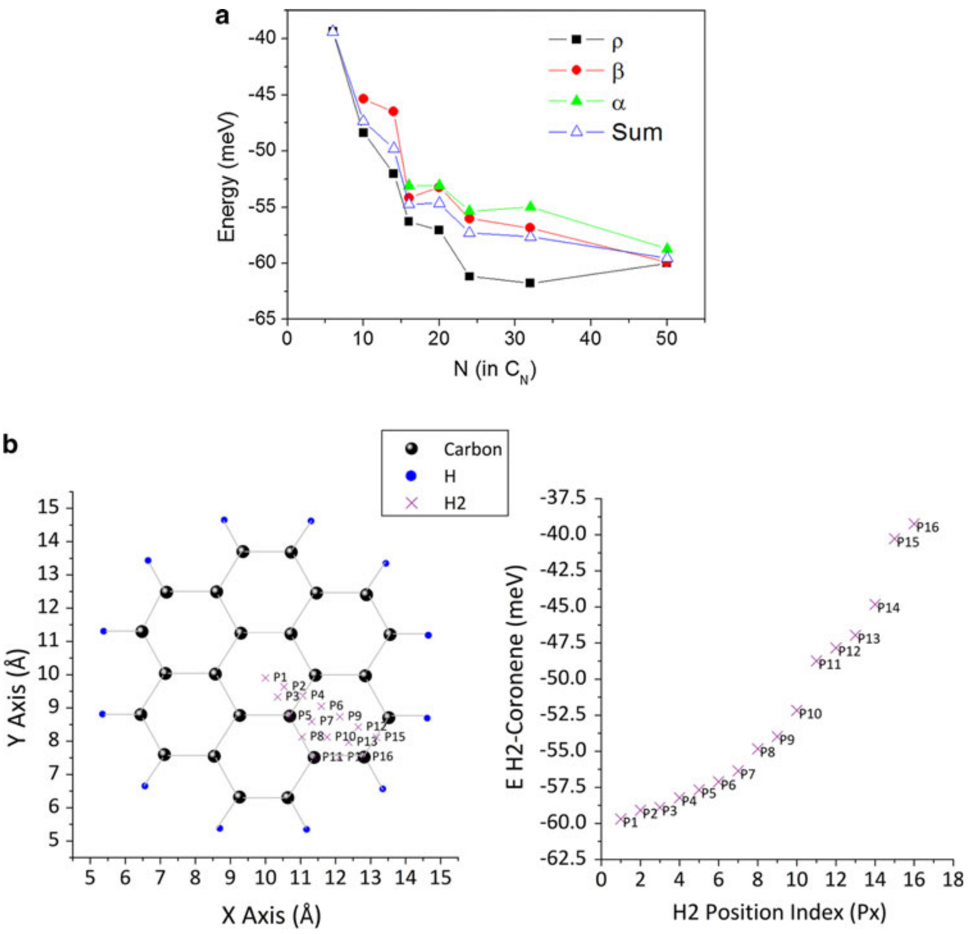

Fig. 3 The interaction energy of PAHs for different: **a** fragment size and **b** interaction site on the fragment surface. The energies have been calculated using DFT dispersion corrected methodology. For PAH size dependency calculation (**a**), interaction energies are calculated on tree different adsorption sites, α, β and ρ which are the same sites as presented in Fig. 1, for Hydrogen at its optimum interacting distance to the surface. The energies represent in (**b**) are the interaction of H_2 molecule at 3 Å distance from the fragment surface (as defined by the centers of the C atoms)

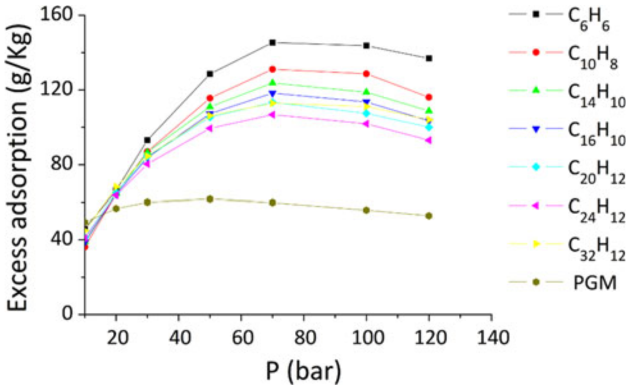

Fig. 4 Excess adsorption capacity of PAHs at 77 K calculated for isolated PAH fragments

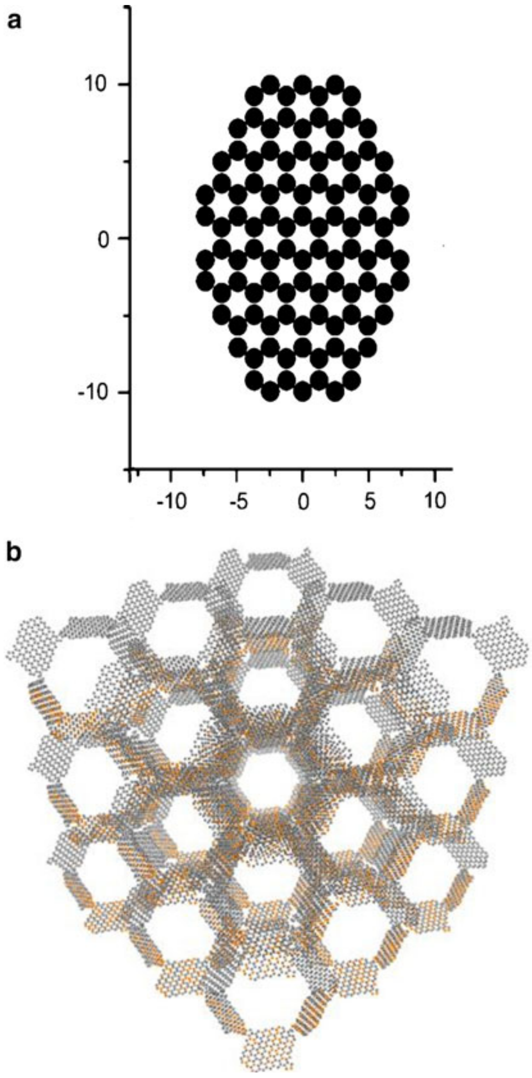

Fig. 5 **a** Finite-size graphene-based fragment used to construct hypothetical carbon porous systems. The axis scales are in angstroms. **b** Perspective projection of a doped orthorhombic open carbon framework structure, dopants are shown in *color*. The periodic purely carbon unit cell of this system was defined in our previous paper (Kuchta et al. 2012). A low density structure with high porosity (0.92)

adsorption into this OCF structure (Fig. 5). The new aspect introduced in this paper is a chemical modification of the adsorbent structure as described in the following chapter. In parallel, we used conventional slit pore geometry as a reference system. The pore walls in this case are constructed from infinite graphene layers (Kuchta et al. 2010a, b, c) called PGM in this paper. The optimal pore widths have been selected in order to maximize the hydrogen adsorption (Kuchta et al. 2010a, b, c).

4 Choice of phosphorus as dopant

It has been shown, both experimentally and theoretically (Xia et al. 2009; Miwa et al. 2008; Kuchta et al. 2010a, b; WU et al. 2010), that chemical modifications of carbon surface have a positive effect on the adsorption due to the possible increase in the local attractive forces of the surface by substituted atoms. The main stabilizing forces in hydrogen adsorption are due to the London dispersion interaction which depends on the polarizabilities of substituted elements. There are varieties of dopants which have been used in planar and curved carbon-based structures such as N and B atoms (Xia et al. 2009; Miwa et al. 2008; Kuchta et al. 2010a, b; WU et al. 2010) and there exist potentially more attractive elements such as phosphorus (Cho et al. 2011; Garcia et al. 2008) and silicon (Cho et al. 2011). However, mass increase of the system is evident when heavier dopant such as phosphorus is used. Therefore, a careful analysis of the impact of the dopant on the adsorption capacity must be carried out. The important physical properties of some common dopants and phosphorus are shown in Table 1. It is important to emphasize that phosphorus atoms show the strongest interaction parameter **ε/k** but it is also the heaviest among the listed atoms.

Table 1 Properties of common dopants in comparison with carbon (Cho et al. 2011; Mattera et al. 1980; Rappe et al. 1992). ε/k (K) is the parameter of the Lennard-Jones interaction model

Structure	Dopant molar mass/polarizability (Å^3)	ε/k (K)
C	12/1.76	45.1
N	14/1.1	34.46
B	10.8/3.03	55.66
P	31/3.63	72.45

In this paper, we have selected phosphorus as a potential candidate having strong interaction property and medium mass. Although, according to the theoretical work of Cho et al. (2011), silicon is seemingly more attractive, there exist experimental and theoretical investigations on phosphorus doping show that phosphorous deserves more attention as a potential dopant (Cruz-Silva et al. 2008; Puziy et al. 2002, 2008). For the computational purpose, we distributed phosphorus atoms uniformly on the surface as it would be expected in practical approach. We have also imposed constraints to keep phosphorus atoms separated from each other to avoid deformed or unstable structures.

The choice of the substituted atoms is a crucial factor. They obviously should enhance the attraction properties of the surface but at the same time they cannot be too heavy. The mass of phosphorus atom seems to be within acceptable limits. There exist already some ways to prepare porous structures modified by phosphorous substitution. Chemical activation of various carbonaceous precursors with phosphoric acid has long been known and used for the production of active carbons in industry (Smíšek and Černeý 1970). This approach is used for the production of phosphorus doped carbon-based materials. Also deposition of phosphorus in carbon material has been performed in vapour phase by Marinkovic et al. (1973) which is an alternative method for the doping process. It seems that the combination of this techniques with template method (Ma et al. 2001), which is generally used for synthesis of high surface area microporous carbon, can be the possible approach to synthesize the OCF structures. The experimental evidence of synthetic phosphorus doped carbon and its property has been investigated by A.M. Puziy et. al. in several articles (Puziy et al. 2002, 2008).

In this paper, we have not analyzed the effect of the oxygen on the structure and we did not include bonds such as P–O–P and P–O–C in the simulation box. One reason to neglect oxygen in the GCMC calculations is that the Lennard-Jones parameters of oxygen are quite similar to those of phosphorus and the other reason is the low percentage of oxygen that can exist in the final synthesized structure.

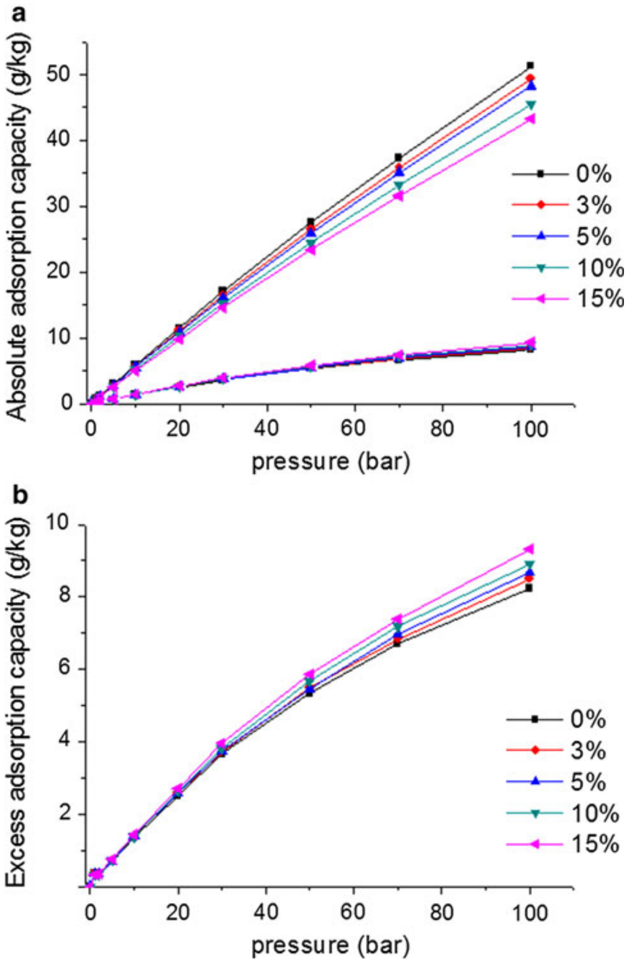

Fig. 6 Hydrogen adsorption isotherm at 298 K for OCF structure with 3–15 % of P atoms doping in atomic % basis: **a** Comparison of total and excess (*lower curves*) adsorption capacity, **b** Excess adsorption capacity. The absolute and excess capacities are related by the standard formula $N_{exc} = N_{abs} - \rho V_{pore}$, where ρ is the hydrogen density and V_{pore},is the pore volume. The OCF structure studied in this paper is characterized by very high porosity (0.92) which means that there is a relatively high contribution of gas molecules in the total adsorption. The statistical errors are smaller than the size of the symbols

5 Results and discussion

The results obtained from GCMC simulations for the adsorption at ambient temperature of H_2 in doped OCF structure, with phosphorus content of 3–15 atomic percent, are shown in Fig. 6.

Figure 6a shows the absolute adsorption capacity derived from GCMC simulation and the excess adsorption capacity (Fig. 6b) which is calculated using the data on absolute adsorption (Fig. 6a). We applied experimental bulk hydrogen density at 298 K as published by the National Institute of Standards and Technology (NIST), for the calculation of excess storage capacity in our calculations. It is important to emphasize that in the absolute adsorption isotherm (Fig. 6a), the total storage capacity decreases when the dopant content increases. However, looking at the excess adsorption isotherm, Fig. 6b, an increase on the uptake is observed for all levels of doping which shows that the amount of adsorbed hydrogen grows faster than the extra weight introduced by the dopant.

Opposite behavior has been observed at low temperature. At 77 K, the storage capacity of the material decreases when dopant content increases, even in terms of the excess adsorption (Fig. 7). It clearly shows that the effect of extra weight of the dopant is to reduce the gravimetric hydrogen storage capacity and it constitutes one of the critical factors to be taken into account when designing new adsorbents. Fig. 7 also shows that this trend is observed in slit pore geometry.

The average adsorption energy of hydrogen in OCF in its pure form is lower than in slits built from infinite graphene layers. It is caused by the heterogeneity imposed by the wall fragmentation which leads to wider energy distribution in these structures (that is, extending to lower energies than the one representative for graphene surface). In general, the total interaction energy of an OCF depends on the size and shape of the fragment. The dependency of interaction energy versus PAHs size is much stronger for smaller fragments than for the larger fragments (Fig. 8). This suggests that a substitution of carbon atoms with more attractive elements will have more pronounced effect on the capacity of the structure built from smaller fragments and less pronounced effect on the larger fragments.

Figures 9 and 10 compare the performance of doped PGM and OCF at room and cryogenic temperatures. The influence of the dopant can be estimated easier by looking at variations of the mass storage capacity. It is shown in Figs. 9, 10 as a change on mass storage calculated with respect to non-doped samples. There is a moderate increase with increasing pressure (below 10 % in the range of pressure below 100 bar) at 298 K (Fig. 9a) for the slits built from infinite graphene layers. At the same time, the low temperature variation shows radically different behavior (Fig. 9b). The variation is large at low pressure but nearly negligible above 50–60 bar. Similar tendency can also be observed for the OCF (Fig. 10a, b).

However, in the case of OCF, one can see that the difference between the ambient and the low temperature is more pronounced. Again, at 298 K, the variation increases considerably with pressure (up to 60 % in the studied ranges of pressures and dopant content) and drops to negative values at low pressure. These negative changes show that the total mass of adsorbent is increasing faster than the gravimetric capacity.

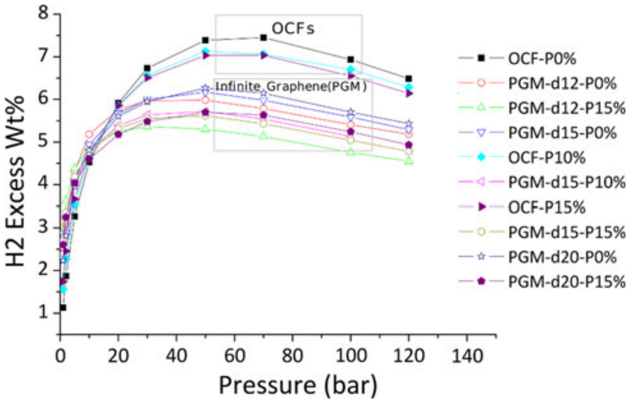

Fig. 7 Comparison of excess adsorption capacity for doped and pristine (OCF and slit pores) type structures at cryogenic temperature (77 K)

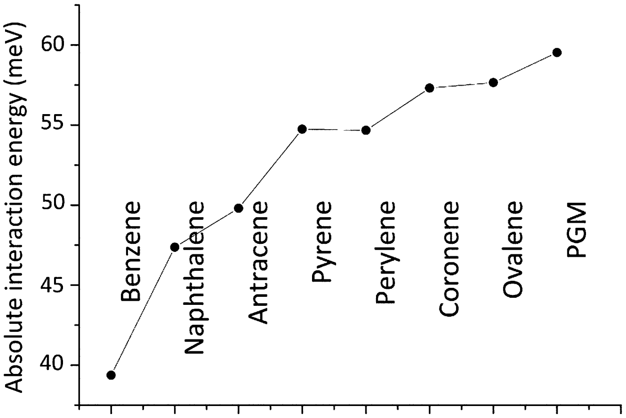

Fig. 8 Dependency of average interaction energy versus PAH size calculated using DFT. PAH size increases from *left* (benzene) to *right* (PGM)

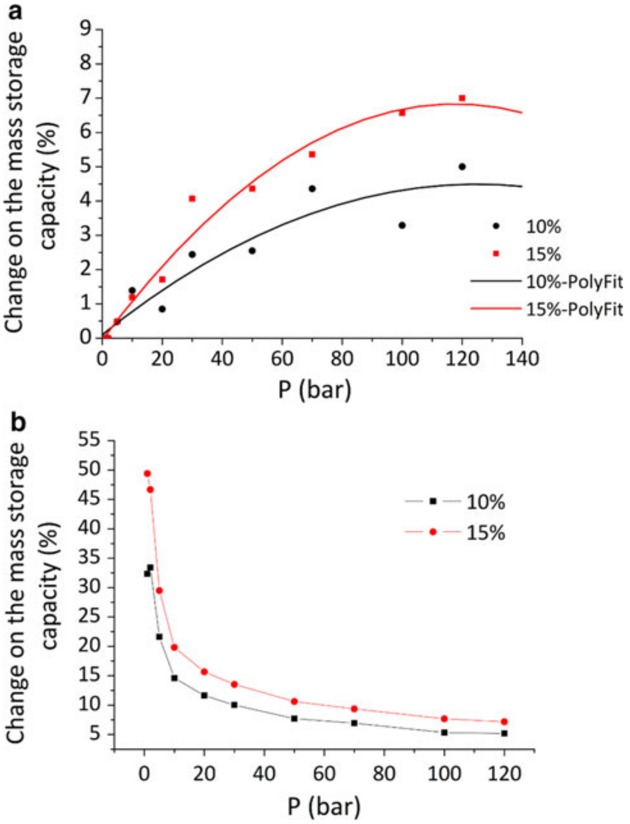

Fig. 9 Percentage of change in the excess mass adsorption capacity with the increase in the content of dopant on PGM structure at; a ambient temperature (298 K) **b** at 77 K

The results presented in the Figs. 9 and 10, show one common characteristics. The largest increase for hydrogen storage capacity due to the phosphorus dopants in the carbon adsorbent matrix is observed at low coverage, much below the monolayer formation. Therefore, it is more

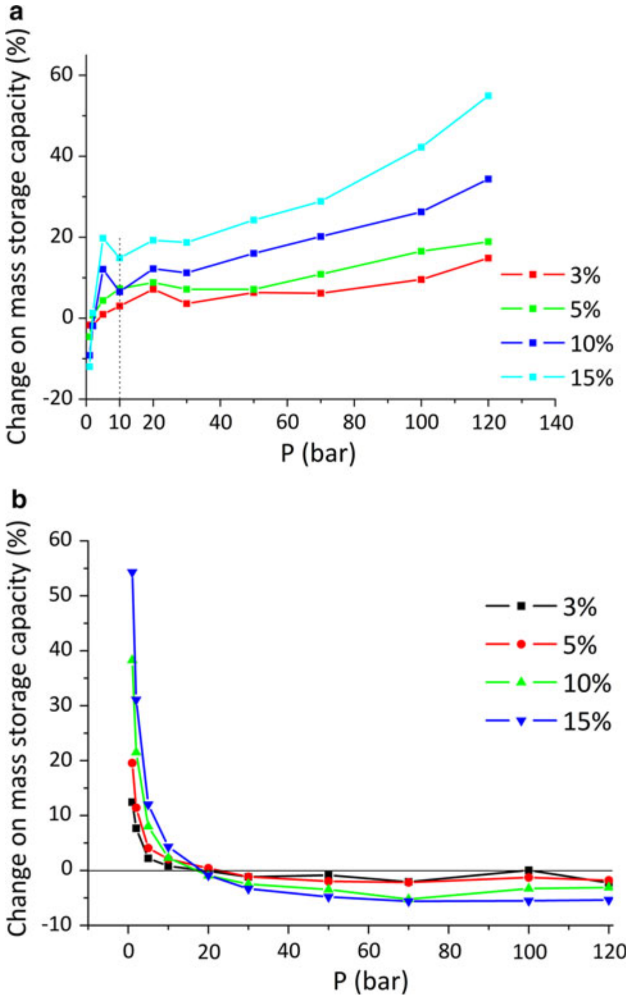

Fig. 10 Percentage of change in the excess mass adsorption capacity with the increase in the content of dopant on OCF structure at; **a** ambient temperature (298 K) and; **b** cryogenic temperature (77 K)

evident at high temperature where the total capacity is still far from the full monolayer. When the coverage is approaching the full monolayer, the change in hydrogen storage capacity starts to be negligible. This suggests that the chemical modifications can be more effective in improving adsorption capacity at room temperature than at low temperature.

6 Conclusions

We presented an analysis of porous structures (OCF structures) built from finite-size graphene fragments where some carbon atoms were substituted by phosphorus atoms. First, we show that the storage capacity of the OCF structures is not increasing proportionally to the surface of the fragments. The main reason is the distribution of the interaction energy which is very heterogeneous at the edge part of the surface. This is the important feature of the open structures made of finite-size fragments where the major part of the adsorbing surface is characterized by low energy of adsorption. It seems that the chemical modifications of the surface could be the most effective in the edge part of the surface. We have shown that performance of such chemically modified structure depends on many structural and energetic parameters which must be optimized to get the maximal hydrogen capacity. In particular, the mass of substituted atoms affect the gravimetric storage capacity. Finally, the results presented in this article for the doped OCF structure can indeed contribute to the better understanding of the fundamentals of hydrogen interaction with modified carbon-based materials and also further understanding of the limits of adsorption in such materials.

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