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A review of boron enhanced nanoporous carbons for hydrogen adsorption: numerical perspective

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Abstract We review the current achievements in the numerical studies of adsorption of molecular hydrogen in boron substituted nanoporous carbons. We show that the enhanced attraction of H_2 by boron-substituted all-carbon structures may allow designing new porous materials with modulated capacity for hydrogen adsorption. Such new structures are characterized by modification of energy landscape of adsorbing surfaces extending beyond the vicinity of substituted atom over several graphene carbon sites, and show strong surface heterogeneity. Although the theoretical conception and description of boron-substituted carbons made a considerable progress during the last decade, the preparation of these materials involves tedious procedures and still needs to be improved.

Keywords Hydrogen · micro-pores · Boron · Adsorption

1 Introduction

Hydrogen has been for long considered as an alternative to fossil fuels. However, molecular hydrogen has low critical temperature (32.97 K) and for practical applications it cannot be handled in liquid state. Therefore, a development of hydrogen storage technology is crucial for the advancement of its practical use in stationary and portable devices, and, in particular, in transportation. Beside storage capacity of hydrogen tanks, many other aspects are crucial for successful development of practical applications: packaging, cost, safety and performance. Several options are being studied and three main alternatives emerged for hydrogen storage: (i) compressed and cryo-compressed hydrogen tanks, (ii) advanced metal hydrides for chemical hydrogen storage, (iii) high surface area sorbents. This last option requires a development of highly porous nanostructures of light weight adsorbing hydrogen through physisorption. In such materials, the relative weakness of the physical interactions between sorbent and hydrogen should guarantee the process reversibility which is necessary for the effective application in real devices.

Two parameters appear to be crucial and should be optimized for H_2 storage in porous solids: a gravimetric storage density (the percentage of the mass of stored gas with respect to the whole gas-sorbent system) and a heat of adsorption. The target of 6–9 wt% of adsorbed H_2 has been defined by DOE (US Department of Energy, http://www.sc.doe.gov/bes/hydrogen.pdf) to preserve a reasonable volume and weight of the host solid feeling fuel tank and allowing ~500 km vehicle autonomy. The modulation of the heat of adsorption in the range of 15–25 kJ/mole (Bhatia and Myers 2006) is required in order to maintain the hydrogen molecule physisorbed even at the conditions close to atmospheric (298 K and ~1 atm.) and, at the same time, allow hydrogen to be easily desorbed by temperature/pressure swing. For now, the reported experimental results on the hydrogen storage in porous solids remain far below these targets. At the same time, several numerical calculations es-

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timate the theoretical limits that could be achieved within experimental systems.

The control of the adsorbing properties of a given sorbent can be realized by modification of sorbent topology either by its fragmentation, intercalation or substitutional doping. In particular, the doping attracts a lot of attention as it may influence the characteristics of sorbent in many ways, by introducing simultaneously surface heterogeneity and modification of intermolecular interactions. In the category of high surface area carbon-based sorbents, substitution with boron appears the most promising. The extensive current experimental search for synthesis of highly B-substituted activated carbons is based on theoretical predictions that B-doping raises the binding energy of H_2 from 4–7 kJ/mol (for purely carbon materials) to 15–35 kJ/mol (Kim et al. 2006) by interactions of electrons from the occupied σ orbital of H_2 to the empty p_z orbital of B, making B-doped carbon an outstanding candidate for high-capacity H_2 sorbent.

Theoretical investigations of carbon-based structures substituted by boron are already available. They play a crucial role in the process of development of the final product. As the experimental progress is technologically demanding, the theoretical calculations give an estimation of technological limits and help to orient the experimental effort towards the most promising strategies. DFT calculations revealed a non-dissociative H_2 chemisorption on B and Be doped fullerenes. The coupling between a localized empty p_z orbital of the dopant and the H_2 σ orbital was essential for the enhanced interactions (Kim et al. 2006). Substitution of boron atoms into the benzene ring of the metal-organic frameworks (MOF) linkers substantially enhanced the Ca binding energy to the linker as well as the H_2 binding energy to Ca (Zou et al. 2010). The Kubas interaction between H_2 and Ca gave rise to a large number of bounded H_2 molecules (8 per linker), with the binding energy of 20 kJ/mol, making the system promising for reversible hydrogen storage at ambient conditions. The theoretical exploration has also been made for boron carbide nanotubes coated by lithium atoms (Wu et al. 2008). According to Authors, the enhanced energetical parameters of adsorbent for hydrogen physisorption should stimulate future experimental tests. Our recent papers (Firlej et al. 2009; Kuchta and Firlej 2010c) have shown that substitution of ~10% of atoms in graphene-like activated carbons by boron dramatically increases hydrogen adsorption and leads to a record uptake ~5 wt% at room temperature and gas pressure of 100 bars. However, most probably even higher B-content (between 10% and 20% of boron atoms) is required for practical applications.

In this review we summarize the state of the art of modeling hydrogen adsorption in carbon-based nanoporous sorbents containing substitutional boron atoms. After a brief overview of experimentally prepared structures, we focus on the theoretical/numerical results estimating potential hydrogen storage in such systems. From this perspective we discuss in conclusions the possible orientations in further designing of hydrogen nanosorbents showing properties desired for future applications.

2 Synthesis and structures of boron-substituted nanoporous carbons

2.1 Layered BC_n structures

Graphite-like layered structures of *bulk* BC_n (Fig. 1) were successfully synthesized more than 20 years ago by the chemical reaction of benzene and boron trichloride at 800 °C

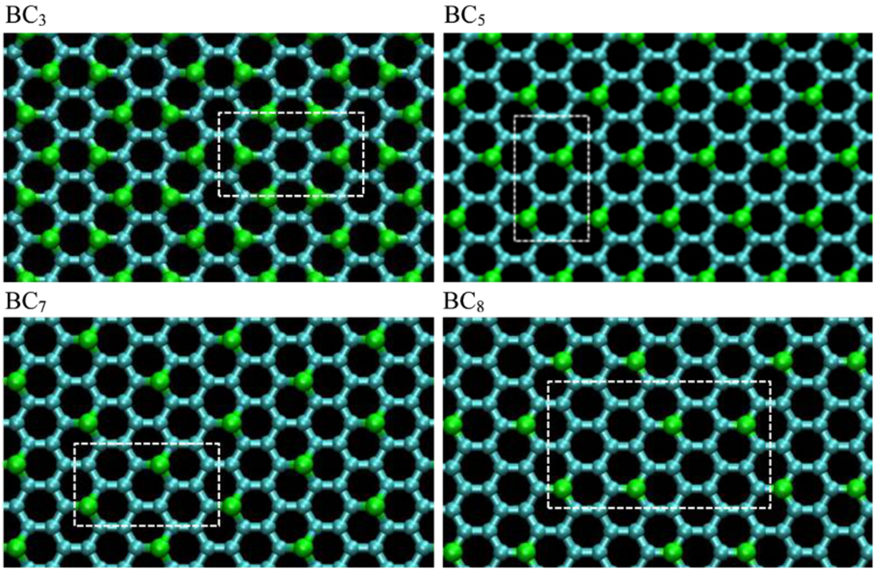

Fig. 1 Regular structures of BC_n ($n = 3, 5, 6, 7$) layers prepared experimentally. The *dashed lines* delimit the unit cell

(Kouvetakis et al. 1986). Experiments (Krishnan 1991) and ab initio calculations (Tomanek et al. 1988; Wang et al. 1996, 1997) suggested that the synthesized material consists of BC_3 layers of hexagonal symmetry. Different stacking arrangements of BC_3 crystals are studied with using ab initio pseudopotential density-functional method (Sun et al. 2004; Yanagisawa et al. 2004). Two stable BC_3 structures, one semiconducting and the other metallic, have been identified.

Boron atoms can be substituted for carbons in the basal hexagonal graphite plane (Endo et al. 2001) by annealing highly oriented pyrolytic graphite in presence of boron carbide B_4C at high temperature ($T \sim 2500\,^\circ\mathrm{C}$). The presence of substitutional boron has been confirmed using scanning tunneling microscopy (STM). The boron was substituted at random positions, with an average substitution ratio 1 : 27. The B–C_α distance estimated from STM images was 0.159 nm (C_α-carbon directly connected to substitutional boron) and only 0.141 nm between nearest carbon atoms located far from substitution site. This result has been interpreted as a signature of a distortion of the graphene plane upon substitution, and the improper angle at substitution site was estimated to be $\sim 164^\circ$. Molecular orbital calculations reveal that substituted boron hold high electron density, in agreement with STM results. However, the out-of-plane location of substitutional boron has not been confirmed by recent ab initio calculations (Firlej et al. 2009).

Solid-solution technique to prepare BC_n compounds require heat treatment at temperatures close to carbon graphitization and lead to relatively low substitution ratio ($<2.35\%$) (Radovic et al. 1998; Lowell 1966; Lee et al. 2002). Therefore, to prepare BC_n layers or thin films, chemical vapor deposition (CVD) is being frequently used, as it operates at lower temperatures (700–900 °C) and leads to higher boron uptake (Hach et al. 1999; Shirasaki et al. 2000). Usually, C_6H_6 or C_2H_2 and BCl_3 are used as BC_n precursors. During deposition boron is incorporated into the structure via electrophilic attack on individual benzene rings. The cumulative addition of rings occurs in the gas phase, where both: in-plane and inter-plane diffusion constant of boron are larger than that of carbon (Hach et al. 1999). Deposition rates are extremely slow and a thin film grows only to a thickness of ~ 1 mm (Hach et al. 1999). The material consists of interconnected platelets of hexagonal morphology observable via TEM. X-ray diffraction measurements showed that the distance between layers of thin films prepared in this way varies with boron concentration in the deposits and with reaction temperature. Moreover, addition of boron improves films crystallinity up to a boron concentration of $\sim 25\%$; beyond this critical value, the film crystallinity deteriorates, mainly because of interlayer intercalation of boron-containing precursor (Shirasaki et al. 2000). According to ^{11}B-NMR measurements (Lee et al. 2002), boron atoms are isolated from each other in samples with low-boron content; boron-boron contacts appear only in samples of high-boron content. Thin films obtained by CVD have been identified as BC_5 (Naeni et al. 1996) and BC_6 (Hach et al. 1999). In the later case, the interlayer spacing was nearly identical to that of perfect graphite but an ABAB stacking of layer planes was missing.

Recently, a carbonization of B-containing polymeric precursors has been developed to prepare microporous boron-containing carbons (Chung et al. 2008). The materials with a high B content (7.2%) and surface area (780 $\mathrm{m^2/g}$) exhibit enhanced hydrogen binding energy (~ 11 kJ/mol), twice as high as in pure microporous carbons.

2.2 B–C nanoporous structures with cylindrical pores: nanotubes and templated carbons

Boron-containing carbon nanotubes have been prepared using variety of techniques, including arc discharge, laser ablation, substitution reaction (Borowiak-Palen et al. 2003; Han et al. 1999; Golberg et al. 1999), CVD (Ceragioli et al. 2008), and precursors pyrolysis (Borowiak-Palen et al. 2003; Han et al. 1999; Golberg et al. 1999). All these methods do not allow a control of structural properties of the material (tube size, chirality and relative orientations); only CVD techniques aiming to produce tubes of less dispersed parameters are still under development.

An alternative method to produce nanoporous carbons with cylindrical pores of uniform diameter consists in building them around appropriate templates (Martin 1994). The template synthesis is widely used for preparing various micro- and nanoporous materials as it offers the possibility of full controlling of pores morphology and pore walls composition. The method has been successfully used to synthesize carbon nanotubes by Che et al. (1998) and Kyotani et al. (1996) Combination of CVD and template synthesis allowed to prepare nanoporous carbons with cylindrical pores that were highly aligned, uniform in diameter, hollow and open ended (suitable for filling with other materials). Depending on template used, the pore diameters varied from 20 to 200 nm. Using this approach boron substituted carbon nanotubes has been also synthesized. Two procedures have been developed: carbonization of hydroborane polymer formed in situ during the polymerisation of divinyl benzene and BH_3 in alumina membrane template and carbonization of acetylene in the presence of borane gas in NaY zeolite template (Ceragioli et al. 2008; Sankaran and Viswanathan 2007). Structural analysis of the tubes prepared in this way clearly showed that the boron atoms are bonded to carbon atom in two different chemical environments, BC_3 and BC_4 type. The ^{11}B MAS NMR study confirmed this result and additionally showed that there is no possible quadrupole interaction due to B–B bond. However, the substitution ratio has not been estimated.

2.3 Metal-organic and covalent-organic frameworks

Metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) constitute a new class of ultra-light nanoporous networks with large specific surface area. They are very promising sorbents for gas storage in general and hydrogen in particular. The boron-rich components are often used as structure building blocks (Farha et al. 2007; Li et al. 2010; Klontzas et al. 2010; Han et al. 2008; Zhao et al. 2008; Chen and Wu 2004). This large and rapidly developing area exit the frame of this review devoted to only B/C sorbents and will not be discussed here in details.

3 Quantum chemical calculations

The available quantum-chemical studies regard two groups of problems. One is concerned with boron induced effects to the hydrogen adsorption template, the second collects studies of direct interactions between adsorbent constituted by boron substituted carbons and hydrogen (atom or molecule). The quantum-chemical models falls into two general methodological categories: methods utilizing periodic boundary conditions and the cluster approach. Both of these approaches possess limitations and are complementary to each other. At present, available realizations of "periodic" methods are based exclusively on density functional theory (DFT) formalism (Parr and Yang 1994). Despite extensive search, available functionals do not account adequately for dispersion interaction energy which constitutes major component for physisorption of H_2. The majority of "cluster" calculations were also performed within the DFT approach. However, although computationally demanding, many methods for inclusion of correlation energy are available for confined conditions (Schleyer 1998). The second order Møller-Plesset perturbation theory (MP2) (Møller and Plesset 1934) is the simplest approach leading to reasonable results. More advanced methods (higher order MP perturbation, coupled cluster, configuration interaction methods) are also available. The obvious restrictions of cluster models originate of nonphysical effects due to the reduction of size of studied systems.

The results of density functional theory studies for boron substitution indicate that such process leads to low spin nanographene sheets, unlike all carbon sheets (Redfern et al. 2009). This implies that boron lowers the energy of the highest occupied orbital resulting in holes in the valence orbital energy levels. These results are consistent with a number of experimental findings. The theoretical studies applying "periodic" calculations for the boron exchange in bulk graphite, nanotubes or graphene nanoribbons show that boron creates holes at the top of valence band and lowers the Fermi level (McGuire et al. 2005; Carroll et al. 1998). Each boron "configuration" gives rise to a unique electronic state signature reflecting subtle changes in orbital energies.

In the last 15 years the infinite graphite-like structures substituted by boron have been studied theoretically applying density functional theory within the periodic boundary conditions approach. The cohesion energies of random alloys at all compositions were calculated and studies showed that the random distribution of boron in B_xC_{1-x} was discouraged mostly because of the repulsive boron-boron first neighbor interactions (Magri 1994). The results supported experimentally suggested observations that ordered B_xC_{1-x} structures were formed with x ranging from 0.15 to 0.25. Several calculations (Wang et al. 1996, 1997; Magri 1994) confirmed that the ordered structure with the hexagonal symmetry within the layer is the most stable structure for the C_3B compound. The BC stacking sequence along the normal to the layer is stable with a c-lattice parameter 6.85–6.90 Å (Wang et al. 1996, 1997). Also, the ordered structures of C_5B can be stable in both stacking sequences with the c-lattice parameter 6.00 Å, which is significantly smaller compared to 6.60–6.70 Å of pure graphite (Wang et al. 1996, 1997; Hu et al. 2006).

For confined graphene-like clusters it is convenient to apply "cluster" models. In this case, the explanation in terms of an empty p orbital which is expected to change the electron acceptor level has been found insufficient for understanding the modification of carbon reactivity. Especially, the enhancement of oxidation resistance at relatively high levels of boron doping and a catalytic effect at low levels of boron doping (Serin et al. 2000) require a theoretical explanation. The theoretical ab initio analysis (Wu and Radovic 2004) confirmed that boron substitution in the carbon network can result in two opposite effects on carbon oxidation: catalysis and inhibition. Boron substitution was found to decrease the global cluster stability and to affect the local reactivity of its edge sites. This phenomenon must also change the interaction properties important for H_2 adsorption. The functionalization as well as reactivity of particular atom within the B/C structure depends on the boron substitution site. The loss of electron, due to the B presence, allows for different π-bonding conjugation as the function of B/C exchange site. Such a conjugation in case of boron nanotubes leads to two possible organizations (local or global) of electron spin density (Saloni et al. 2010) and in an effect to different reactivity regarding the H_2 physisorption.

The chemisorption of hydrogen has been studied within both "periodic" (Zhou et al. 2009; Miwa et al. 2008; Zhang 2007; Zhu et al. 2006; Ferro et al. 2004a) and "cluster" models (Ferro et al. 2003, 2004a, 2004b; Zheng and Zeng 1998). The studies were performed applying exclusively density functional theory approaches. These results constitute part of information needed to design the hydrogen storage media based on chemisorption. Such properties of boron substituted carbons make them attractive as potential storage material based on the spillover (that is, dissociative chemisorption and migration along graphene plane) mechanism. Since some metal cluster are known for dissociative adsorption of hydrogen molecules, such clusters can be themselves adsorbed on B/C carbons. The balanced energetics of B/C material-metal cluster-H_2 system can lead to hydrogen storage with assumed physicochemical parameters. Preliminary studies of palladium adsorption are available (Chen et al. 2009). New DFT calculations showed (Zhu et al. 2006) that there is a correlation between the stability of the graphene sheet, the distribution of π electrons, and the electrostatic potential. After boron substitution, the distribution of the HOMO electron wave is no longer uniform; rather, the whole aromatic rings adjacent to the boron atoms are covered by the HOMO electron wave, and the π electron density around the substitutional boron is much higher than that in other areas. Boron substitution makes the graphene structure less stable and the off-plane π electrons around the substitutional boron atoms more concentrated, thus lowering the electrostatic potential. As a result, the hydrogen adsorption energy on carbon is improved.

The hetero-atoms doped to carbons create possible activation centers for molecular hydrogen adsorption. The DFT studies for boron modified carbon nanotubes and fullerenes are available (Kim et al. 2006; Viswanathan and Sankaran 2008; Sankaran et al. 2005, 2008; Sankaran and Viswanathan 2006; Ni et al. 2009). However, because of the importance of dispersion forces as leading component of interactions involving H_2 (Lochan and Head-Gordon 2006) one should consider these results with a caution. The second order Møller-Plesset perturbation or higher level theories have to be applied for the reasonable accounting for correlation energy. The calculations involving model boron doped graphenes interacting with H_2 were performed with the aim to determine of atom-atom potentials (Firlej et al. 2009). The Monte-Carlo simulations, applying above mentioned potential functions, suggest the promising properties of studied boron substituted carbon nanospaces.

4 Numerical studies of adsorption in B/C nanostructures

Hydrogen can adsorb in a host matrix in molecular form (physical adsorption) or as atoms bonded to surface (chemical adsorption).

Physisorption in nanoporous carbons is particularly appealing way of hydrogen storage because its mechanism is simple. However, the main obstacle for widespread application of this option is the weak energy of hydrogen adsorption on all-carbon surfaces (Kuchta and Firlej 2010c; Bernard and Chahine 2007; Zubizarreta et al. 2008). Substitution of carbon atom with boron improves effectively adsorption efficiency. Numerical estimations of hydrogen physisorption in B-modified carbons are however to date almost absent, mainly because of the absence of reliable description of H_2 interaction with surfaces of different geometries and substitution ratios. Recent Grand Canonical Monte Carlo (GCMC) simulations (Firlej et al. 2009) report an enhanced H_2 uptake in a model of modified graphene slits with slit walls containing up to 10% of randomly distributed boron atoms. The energy of interaction between H_2 molecule and the boron substituted surface was calculated using the ab initio methodology (the second order Møller-Plesset level of theory utilizing restricted open Hartree-Fock wave function). An analysis of energy landscape of graphene substituted with one boron atom shows interesting features. First, the substitutional boron is not actually the location of strongest energy of adsorption, but it contributes to a dramatic enhancement of the adsorption over the neighboring hexagons of the graphite lattice. As the boron atom is larger than carbon there is a local weak maximum of the energy at the boron, and it is located farther from the surface. Second, modification of the energy landscape extends far beyond the nearest carbons and is still perceptible ∼7 Å from the substituted boron (Fig. 2). The calculations showed that the energies of hydrogen adsorption in such model systems are close to optimum at low coverage (10.0–13.5 kJ/mol for 5–10% boron concentration), but decrease at high coverage (5.0–6.0 kJ/mol), with an average of 7.5–10 kJ/mol over a 0–100 bar pressure cycle (Fig. 3). The calculations also showed that the substitution ratio of 10% is not sufficient to reach the required hypothetical optimum of heat of adsorption of ∼15 kJ/mol suggested upon theoretical (Bhatia and Myers 2006) and numerical (Kuchta and Firlej 2010c) considerations. However, it is not obvious that the higher contents of boron will proportionally increase the adsorption energy. At high substitution ratios boron atoms are not any longer independent from each other and their contribution to the surface-hydrogen interaction may not be additive. The appearance of B–B or B–C–B contacts is a qualitatively new situation and H_2 interaction with these local structures of the adsorbing surface needs separate ab initio analysis.

In MOF and COF boron-rich structures (Chung et al. 2008), although the choice of the structural elements is crucial for the system adsorption properties, there is no explicit analysis of the role of boron in a complex environment which contains many different atoms. For example, the force field parameters used for simulations of hydrogen adsorption in several COFs (Zhao et al. 2008) result from ab initio calculations of H_2 adsorption on boroxine ($B_3O_3H_3$) and silane (SiH_4). The resulting well depths ratios for H–C, H–O, H–B and H–Si interaction are 100 : 25 : 48 : 110, with relatively weak adsorption over boron site. When this article

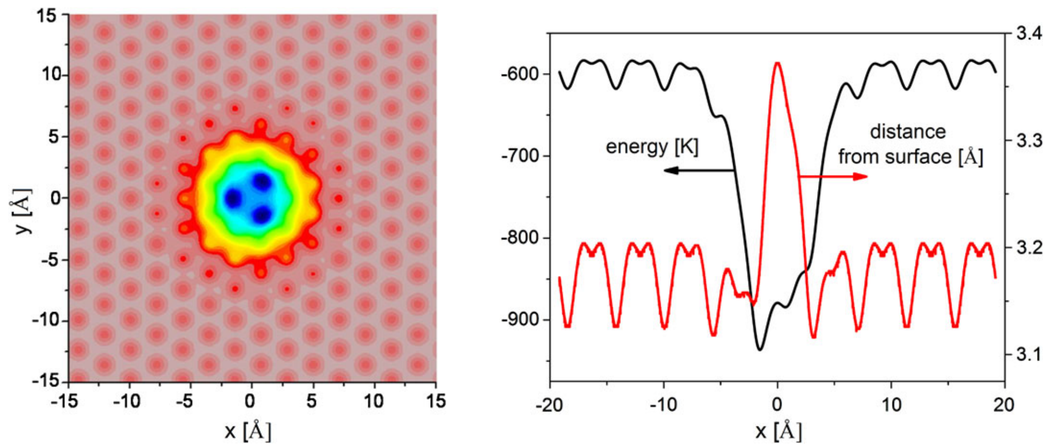

Fig. 2 (*Left panel*) Energy landscape for H_2 adsorption on graphene layer substituted by one boron atom at $x, y = (0, 0)$ location. Isoenergetic lines are separated by $\Delta E/k_B = 10$ K and go from $E/k_B = -580$ K (*pink grey*) to -940 K (*navy*). (*Right panel*) Minimum of H_2 adsorption energy and its distance from the substrate along the $(x, 0)$ line—see the original paper (Firlej et al. 2009) for details

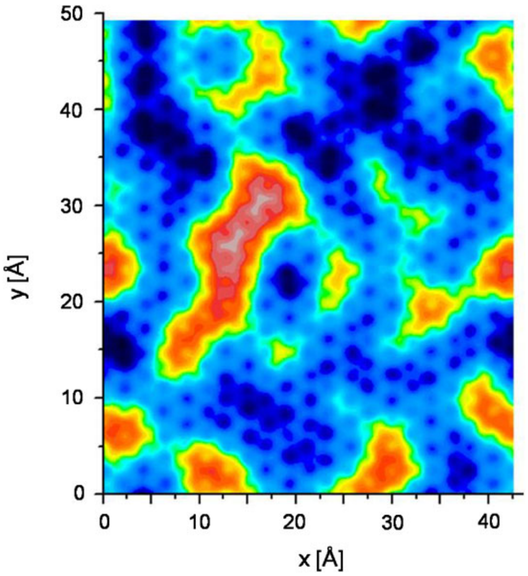

Fig. 3 Energy landscape for H_2 adsorption on graphene layer substituted by boron atoms. Substitution is random; B : C ratio is equal 5% at $x, y = (0, 0)$ location. Isoenergetic lines are separated by $\Delta E/k_B = 10$ K. The color code is the same as on Fig. 2: from $E/k_B = -580$ K (*pink grey*) to -1100 K (*dark navy*)—see the original paper (Firlej et al. 2009) for details

was written, it was unknown how universal these relations were.

Chemisorption of atomic hydrogen on graphite-like surfaces is an extensively studied alternative of hydrogen storage in the context of the spillover mechanism. Ferro et al. (2003) modeled the boron-doped graphite surfaces by modified $C_{16}H_{10}$ cluster in which one or two carbon atoms are substituted by boron. The study has shown show that the boron atom is not a stable adsorption site for hydrogen atom as it induces an increase of H binding energy. In general, such variation of surface properties is not suitable for practical applications: higher binding energy makes the recovery of hydrogen more difficult. However, at the same time, boron favors the diffusion of an isolated H atom on the surface and dramatically decreases the activation energy for atoms recombination. On BC_3 surface, the activation energy for the diffusion of an isolated atom is reduced to 50–54 kJ/mol (from 91 kJ/mol for diffusion on graphite) and is totally suppressed in the vicinity of another H (while it remains high, 46 kJ/mol, on graphite). The activation energy for the final recombination step falls down to 9 kJ/mol on BC_3 (272 kJ/mol on graphite) (Ferro et al. 2004a).

The binding energy of hydrogen to the surface is also affected by the presence of boron (Saloni et al. 2010). In graphene, the binding energy of hydrogen adatoms forming dimer-like configurations is by nearly 100 kJ/mol atom higher than the binding energy of two isolated H monomers ($E_{\mathrm{bH}} = 94.8$ kJ/mol). The presence of a single substitutional boron atom increases the hydrogen binding energy by 87 kJ/mol with respect to the binding on graphene. Chemisorbed hydrogen atom is attached to the carbon which is the nearest neighbor to the substitution site. The adsorption of two hydrogens close to other dimer-like configurations is energetically less favorable. This result indicates that the formation of hydrogen clusters on the graphene sheet may be suppressed in boron substituted carbons when the substitution ratio is low. The situation is changing when the B : C ratio increases. For boron concentration of ∼2.4%, the binding energy of hydrogen in dimer configuration becomes higher than the binding energy of two separated hydrogen atoms. In this case, boron atoms create preferential adsorption sites for hydrogen adatoms, and thus stimulate the formation of hydrogen clusters on the adsorbing surface.

5 Conclusions

Although boron containing carbons show properties that make them promising for a variety of applications (Radovic et al. 1998; Wei et al. 1999) and, in particular, for hydrogen storage, preparation of these materials seems to be involving tedious procedure. The preparation of boron containing carbon materials is an art by itself. Moreover, an additional experimental effort is necessary to prepare BC_n materials in the form of porous matrices with the pore sizes adapted for an efficient and reversible adsorption of hydrogen. Therefore, the theoretical calculations and numerical simulations give an estimation of technological limits and help to focus the experimental effort on the most promising strategies.

The main conclusions from the current state of both theoretical and numerical calculations are the following:

(1) High surface area microporous carbon structures are required to reach the generally accepted goals. However, structural modifications creating additional adsorption surface do not automatically increase the amount adsorbed (Kuchta et al. 2010a, 2010b). By themselves, these structural modifications lead to a strong structural heterogeneity and (usually) to a lower uptake. The only way to compensate the heterogeneity effect is to couple surface modification with the additional source of enhanced hydrogen-wall interaction.

(2) Activated carbons, chemically modified by boron, appear as potentially applicable systems, if prepared as high quality microporous structures. Calculations based on a high quality force field obtained from the extensive ab initio calculations prove that the amount of adsorbed hydrogen may double in boron substituted carbons (as compared to pristine graphene) (Firlej et al. 2009; Wei et al. 1999).

(3) The MOFs and COFs structures define an alternative approach and can potentially reach the energy and surface requirement. However they need to be engineered to limit the free volume inside the pores and optimize hydrogen-pore wall interaction. It is not clear whether the high hydrogen uptake in MOFs reported recently (Collins and Zhou 2007) is mostly a consequence of high surface area of MOFs structures, or it is also related to the presence of boron which may increase the adsorption energy. The existing results point rather to the first option (Li et al. 2010; Klontzas et al. 2010; Han et al. 2008; Zhao et al. 2008; Chen and Wu 2004).

(4) Catalytic properties of boron for molecular hydrogen dissociation coupled to carbon capacity to enhance hydrogen diffusion across the adsorbing surface made boron-doped carbons good candidates to improve hydrogen sorption via spillover mechanism.

(5) Other similar systems, such as boron-nitride compounds, are also potentially interesting as storage materials (for example, boron-nitride nanotubes, which show enhanced selectivity of deuterium over hydrogen adsorption (Kowalczyk et al. 2008)).

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References

Bernard, P., Chahine, R.: Storage of hydrogen by physisorption on carbon and nanostructured materials. Scr. Mater. **56**, 803–808 (2007)

Bhatia, S.K., Myers, A.L.: Optimal conditions for adsorptive storage. Langmuir **22**, 1688–1700 (2006)

Borowiak-Palen, E., Pichler, T., Fuentes, G.G., Graff, A., Kalenczuk, R.J., Knupfer, M., et al.: Efficient production of B-substituted single wall carbon nanotubes. Chem. Phys. Lett. **378**, 516–520 (2003)

Carroll, D.L., Redlich, P., Blase, X., Charlier, J.C., Curran, S., Ajayan, P.M., Roth, S., Ruhle, M.: Effects of nanodomain formation on the electronic structure of doped carbon nanotubes. Phys. Rev. Lett. **81**, 2332–2335 (1998)

Ceragioli, H.J., Peterlevitz, C., Quispe, J.C.R., Larena, A., Pasquetto, M.P., Sampaio, M.P., Baranauskas, V.: Synthesis and characterization of boron-doped carbon nanotubes. J. Phys. **100**, 052029 (2008)

Che, G., Lakshmi, B.B., Martin, C.R., Fisher, E.R., Martin, C.R., Ruoff, R.A.: Chemical vapor deposition based synthesis of carbon nanotubes and nanofibers using a template method. Chem. Mater. **10**, 260–267 (1998)

Chen, J., Wu, F.: Review of hydrogen storage in inorganic fullerene-like nanotubes. Appl. Phys. A **78**, 989 (2004)

Chen, G.-X., Zhang, J.-M., Wang, D.-D., Xu, K.-W.: First-principles study of palladium atom adsorption on the boron- or nitrogen-doped carbon nanotubes. Physica B **404**, 4173 (2009)

Chung, T.C.M., Jeong, Y., Chen, Q., Kleinhammes, A., Wu, Y.: Synthesis of microporous boron-substituted carbon (B/C) materials using polymeric precursors for hydrogen physisorption. J. Am. Chem. Soc. **130**, 6668–6669 (2008)

Collins, D.J., Zhou, H.C.: Hydrogen storage in metal–organic frameworks. J. Mater. Chem. **17**, 3154 (2007)

Endo, M., Hayashi, T., Hong, S.-H., Enoki, J.T., Dresselhaus, M.S.: Scanning tunneling microscope study of boron-doped highly oriented pyrolytic graphite. J. Appl. Phys. **90**, 5670–5674 (2001)

Farha, O.K., Spokoyny, A.M., Mulfort, K.L., Hawthorne, M.F., Mirkin, C.A., Hupp, J.T.: Synthesis and hydrogen sorption properties of carborane based metal-organic framework materials. J. Am. Chem. Soc. **129**, 12680–12681 (2007)

Ferro, Y., Marinelli, F., Allouche, A., Broset, C.: Density functional theory investigation of H adsorption on the basal plane of boron-doped graphite. J. Chem. Phys. **118**, 5650 (2003)

Ferro, Y., Marinelli, F., Jelea, A., Allouche, A.: Adsorption, diffusion, and recombination of hydrogen on pure and boron-doped graphite surfaces. J. Chem. Phys. **120**, 11882 (2004a)

Ferro, Y., Brosset, C., Allouche, A.: Quantum study of hydrogen interaction with plasma-facing graphite and boron doped graphite surfaces. Phys. Scr. T **108**, 76 (2004b)

Firlej, L., Roszak, Sz., Kuchta, B., Pfeifer, P., Wexler, C.: Enhanced hydrogen adsorption in boron substituted carbon nanospaces. J. Chem. Phys. **131**, 164702 (2009)

Golberg, D., Bando, Y., Han, W., Kurashima, K., Sato, T.: Single-walled B-doped carbon, B/N-doped carbon and BN nanotubes synthesized from single-walled carbon nanotubes through a substitution reaction. Chem. Phys. Lett. **308**, 337–342 (1999)

Hach, C.T., Jones, L.E., Crossland, C., Thrower, P.A.: An investigation of vapor deposited boron rich carbon—a novel graphite-like material—part I: the structure of $BC_x(C_6B)$ thin films. Carbon **37**, 221–230 (1999)

Han, W., Bando, Y., Kurashima, K., Sato, T.: Boron-doped carbon nanotubes prepared through a substitution reaction. Chem. Phys. Lett. **299**, 368–373 (1999)

Han, S.S., Furukawa, H., Yaghi, O.M., Goddard, W.A. III: Covalent organic frameworks as exceptional hydrogen storage materials. J. Am. Chem. Soc. **130**, 11580–11581 (2008)

Hu, Q., Wu, Q., Ma, Y., Zhang, L., Liu, Z., He, J., Sun, H., Wang, H.-T., Tian, Y.: First-principles studies of structural and electronic properties of hexagonal BC_5. Phys. Rev. B **73**, 214116 (2006)

Kim, Y.-H., Zhao, Y., Williamson, A., Heben, M.J., Zhang, S.B.: Nondissociative adsorption of H_2 molecules in light-element doped fullerenes. Phys. Rev. Lett. **96**, 016102 (2006)

Klontzas, E., Tylianakis, E., Froudakis, G.E.: Designing 3D COFs with enhanced hydrogen storage capacity. Nano Lett. **10**, 452–454 (2010)

Kouvetakis, J., Kaner, R.B., Sattler, M.L., Bartlett, N.: A novel graphite-like material of composition BC_3, and nitrogen–carbon graphites. J. Chem. Soc., Chem. Commun. **1986**, 1758 (1986)

Kowalczyk, P., Gauden, P.A., Terzyk, A.P.: Cryogenic separation of hydrogen isotopes in single-walled carbon and coron-nitride nanotubes : insight into mechanism of equilibrium quantum sieving in quasi-one-dimensional pores. J. Phys. Chem. B **112**, 8275–8284 (2008)

Krishnan, K.M.: Structure of newly synthesized BC_3 films. Appl. Phys. Lett. **58**, 1857 (1991)

Kuchta, B., Firlej, L., Wexler, C., Pfeifer, P.: Influence of structural heterogeneity of nano-porous sorbent walls on hydrogen storage. Appl. Surf. Sci. (2010a). doi:10.1016/j.apsusc.2009.12.116

Kuchta, B., Firlej, L., Cepel, R., Pfeifer, P., Wexler, C.: Structural and energetic factors in designing a nanoporous sorbent for hydrogen storage. Colloids Surf. A **357**, 61–66 (2010b)

Kuchta, B., Firlej, L., Pfeifer, P., Wexler, C.: Numerical estimation of hydrogen storage limits in carbon-based nanospaces. Carbon **48**, 223–231 (2010c)

Kyotani, T., Tsai, L.F., Tomita, A.: Preparation of ultrafine carbon tubes in nanochannels of an anodic aluminum oxide film. Chem. Mater. **8**, 2109–2113 (1996)

Lee, Y., Han, D.-Y., Lee, D., Woo, A.J., Lee, S.H., Lee, D., Kim, Y.K.: ^{11}B NMR of boron-doped graphite as the negative electrode of a lithium secondary battery. Carbon **40**, 403–408 (2002)

Li, Z., Zhu, G., Lu, G., Qiu, S., Yao, X.: Ammonia borane confined by a metal-organic framework for chemical hydrogen storage: enhancing kinetics and eliminating ammonia. J. Am. Chem. Soc. **132**, 1490–1491 (2010)

Lochan, R.C., Head-Gordon, M.: Computational studies of molecular binding affinities: the role of dispersion forces, electrostatics, and orbital interactions. Phys. Chem. Chem. Phys. **8**, 1357 (2006)

Lowell, C.E.: Solid solution of boron in graphite. J. Am. Ceram. Soc. **50**, 142–144 (1966)

Magri, R.: Ordering in B_xC_{1-x} compounds with the graphite structure. Phys. Rev. B **49**, 2805–2815 (1994)

Martin, C.R.: Nanomaterials: a membrane-based synthetic approach. Science **266**, 1961–1966 (1994)

McGuire, K., Gothard, N., Gai, P.L., Dresselhaus, M.S., Sumanasekera, G., Rao, A.M.: Synthesis and Raman characterization of boron-doped single-walled carbon nanotubes. Carbon **43**, 219–227 (2005)

Miwa, R.H., Martins, T.B., Fazzio, A.: Hydrogen adsorption on boron doped grapheme: an ab initio study. Nanotechnology **19**, 155708 (2008)

Møller, C., Plesset, M.S.: Note on an approximation treatment for many-electron systems. Phys. Rev. **46**, 618 (1934)

Naeni, Z.G., Way, B.M., Dahn, J.R., Irwin, J.C.: Raman scattering from boron-substituted carbon films. Phys. Rev. B **54**, 144–150 (1996)

Ni, M.Y., Zeng, Z., Ju, X.: First-principles study of metal atom adsorption on the boron. Microelectron. J. **40**, 863 (2009)

Parr, R.G., Yang, W.: Density-functional theory of atoms and molecules. Oxford University Press, New York (1994)

Radovic, L.R., Karra, M., Skokova, K., Thrower, P.: The role of substitutional boron in carbon oxidation. Carbon **36**, 1841–1854 (1998)

Redfern, P.C., Gruen, D., Curtiss, L.A.: Effect of boron substitution on the electronic structure of nanographene and its relevance to the thermoelectric transport properties in nanocarbon ensembles. Chem. Phys. Lett. **471**, 264–268 (2009)

Saloni, J., Kolodziejczyk, W., Roszak, S., Majumdar, D., Hill, G. Jr., Leszczynski, J.: Local and global electronic effects in single and double boron-doped carbon nanotubes. J. Phys. Chem. C **114**, 1528 (2010)

Sankaran, M., Viswanathan, B.: The role of heteroatoms in carbon nanotubes for hydrogen storage. Carbon **44**, 2816 (2006)

Sankaran, M., Viswanathan, B.: Hydrogen storage in boron substituted carbon nanotubes. Carbon **45**, 1628–1635 (2007)

Sankaran, M., Muthukumar, K., Viswanathan, B.: Boron-substituted fullerens—can they be on the options for hydrogen storage? Fuller. Nanotub. Carbon Nanostruct. **13**, 43 (2005)

Sankaran, M., Viswanathan, B., Srinivasa Murthy, S.: Boron substituted carbon nanotubes—how appropriate are they for hydrogen storage? Int. J. Hydrog. Energy **33**, 393 (2008)

Schleyer, R.V.P. (ed.): Encyclopedia of Computational Chemistry. Wiley-Interscience, New York (1998)

Serin, V., Brydson, R., Scott, A., Kihn, Y., Abidate, O., Maquin, B., Derre, A.: Evidence for the solubility of boron in graphite by electron energy loss spectroscopy. Carbon **38**, 547 (2000)

Shirasaki, T., Derre, A., Menetrier, M., Tressaud, A., Flandrois, S.: Synthesis and characterization of boron-substituted carbons. Carbon **38**, 1461–1467 (2000)

Sun, H., Ribeiro, F.J., Li, J.-L., Roundy, D., Cohen, M.L., Louie, S.G.: Ab initio pseudopotential studies of equilibrium lattice structures and phonon modes of bulk BC_3. Phys. Rev. B **69**, 024110 (2004)

Tomanek, D., Wentzcovitch, R.M., Louie, S.G., Cohen, M.L.: Calculation of electronic and structural properties of BC_3. Phys. Rev. B **37**, 3134 (1988)

Viswanathan, B., Sankaran, M.: Hetero-atoms as activation centers for hydrogen absorption in carbon nanotubes. Diam. Relat. Mater. **18**, 429 (2008)

Wang, Q., Chen, L.Q., Annett, J.F.: Stability and charge transfer of C_3B ordered structures. Phys. Rev. B **54**, R2271 (1996)

Wang, Q., Chen, L.Q., Annett, J.F.: Ab initio calculation of structural properties of C_3B and C_5B compounds. Phys. Rev. B **55**, 8 (1997)

Wei, B., Spolenak, R., Kohler-Redlich, P., Ruhle, M., Arzt, E.: Electrical transport in pure and boron-doped carbon nanotubes. Appl. Phys. Lett. **74**, 3149–3151 (1999)

Wu, X., Radovic, L.R.: Ab initio molecular orbital study on the electronic structures and reactivity of boron-substituted carbon. J. Phys. Chem. A **108**, 9180–9187 (2004)

Wu, X., Gao, Y., Zeng, X.C.: Hydrogen storage in pillared Li-dispersed boron carbide nanotubes. J. Phys. Chem. C **112**, 8458 (2008)

Yanagisawa, H., Tanaka, T., Ishida, Y., Matsue, M., Rokuta, E., Otani, S., Oshima, C.: Phonon dispersion curves of a BC_3 honeycomb epitaxial sheet. Phys. Rev. Lett. **93**, 177003 (2004)

Zhang, C., Alavi, A.: Hydrogen absorption in bulk BC_3: a first-principles study. J. Chem. Phys. **127**, 214702 (2007)

Zhao, Y., Lusk, M.T., Dillon, A.C., Heben, M.J., Zhang, S.B.: Boron-based organometallic nanostructures: hydrogen storage properties and structure stability. Nano Lett. **8**, 158 (2008)

Zheng, X.M., Zeng, J.: Hydrogen chemisorption on a boron-terminated diamond (100) surface: an ab initio study. Surf. Sci. **416**, 472 (1998)

Zhou, Y.G., Zu, X.T., Gao, F., Nie, J.L., Xiao, H.Y.: Adsorption of hydrogen on boron-doped graphene: a first-principles prediction. J. Appl. Phys. **105**, 014309 (2009)

Zhu, Z.H., Lu, G.Q., Hatori, H.: New insight into the interaction of hydrogen atoms with boron-substituted carbon. J. Phys. Chem. B **110**, 1249 (2006)

Zou, X., Cha, M.-H., Kim, S., Nguyen, M.C., Zhou, G., Duan, W., Ihm, J.: Hydrogen storage in Ca-decorated, B-substituted metal organic framework. Int. J. Hydrog. Energy **35**, 198–203 (2010)

Zubizarreta, L., Gomez, E.I., Arenillas, A., Ania, C.O., Parra, J.B., Pis, J.J.: H_2 storage in carbon materials. Adsorption **14**, 557–566 (2008)