Fullerene-intercalated Graphene Nano-containers — Mechanism of Argon Adsorption and High-pressure CH₄ and CO₂ Storage Capacities

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ABSTRACT: Using GCMC simulations, we discuss the mechanism of argon adsorption onto intercalated graphene nano-containers (NanoBuds). The mechanism is related to the shapes of the high-resolution $\alpha_S$-plots. Next, we have tested the applicability of these materials to the storage of methane and carbon dioxide. We show that intercalation improves the storage, especially in the range of low pressures where the effect of volume does not dominate. The results obtained may be of interest in the design of new carbon materials.

1. INTRODUCTION AND AIMS OF THE STUDY

Considerable progress has been achieved in nanotechnology and, although still new, it has led to the theoretical prediction or laboratory synthesis of very interesting carbon materials. One such example is fullerene-intercalated graphite. The stability of such forms was first predicted theoretically by Saito and Oshiyama (1994) and Savin and Harris (1995, 1996), while the direct intercalation of $\text{C}_{60}$ into graphite was first reported 10 years later by Gupta and co-workers (2004). Recently, Kuc et al. (2007) and Heine et al. (2007) have reported that these materials may be promising for hydrogen storage. Nasibulin et al. (2006, 2007) discovered a novel hybrid material that combines fullerenes and single-walled nanotubes (SWNTs) into a single structure in which the fullerenes are covalently bonded to the outer surface of the SWNTs. These fullerene-functionalized SWNTs, termed NanoBuds, were selectively synthesized via two different one-step continuous methods, during which fullerenes were formed on iron catalyst particles together with SWNTs during CO disproportionation. The field-emission characteristics of NanoBuds suggest that they may possess advantageous properties compared with SWNTs or fullerenes alone, or in their non-bonded configurations.

Recently, Wu and Zeng (2009) studied structures called “periodic graphene nanobuds” (PGNBs) which were similar to those considered by Nasibulin et al. (2006). PGNBs are hybrid zero-dimensional/two-dimensional carbon materials in which $\text{C}_{60}$ buckyballs are covalently attached to a graphene monolayer or, alternatively, fragmented buckyballs are fused onto the graphene monolayer forming a periodic lattice on that layer. The structures studied by these authors possessed chemical bonds between fullerenes and graphene walls and were composed of closed fullerenes. At the end of their interesting study they concluded: “...multilayer PGNBs are a porous network structure and may be exploited for gas storage. The much enhanced interlayer distance

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due to the nanobuds allows gases such as methane or hydrogen to be physisorbed within the slit pores at low temperature or under high external pressure”. It seemed worthwhile to check this hypothesis, and this is the major subject of this study.

Since adsorption isotherm measurements provide a fast method of determining the structural parameters of adsorbents, it would be interesting to check the adsorption mechanisms of argon (the “standard” molecule used for the characterization of adsorbents) onto PGNBs samples. In this respect, we have paid attention to the high-resolution $\alpha_S$-plot method, this being a simple and fast comparative method of porosity characterization. In the first part of this report, we present the results of GCMC simulations of Ar adsorption onto different PGNBs and discuss the adsorption mechanisms. Next, we propose new parameters for the fluid–fluid potential for the simulation of the high-pressure adsorption of methane. Finally, we check the applicability of PGNBs for methane and carbon dioxide adsorption and storage. Since the major contribution to the potential energy of solid–fluid interactions in the graphite slit-like pores is from interactions with the first wall, the results of our study could also be useful for the case of fullerene-intercalated graphites.

2. SIMULATION METHODOLOGY — CONSTRUCTION OF THE BOXES

To construct PGNBs, the fullerenes $C_{180}$, $C_{240}$, $C_{260}$, $C_{320}$ and $C_{500}$ (generated using the Nanotube Modeller software http://www.jcrystal.com/products/wincnt/) were studied. In each fullerene, the entrance was adjusted so that its diameter was close to that for the CH$_4$ molecule, i.e. ca. 0.5 nm, to allow penetration of the internal space by the adsorbed molecules$^1$. The value of the entrance radius was adjusted in such a way that only carbon atoms belonging to five- or six-member rings were present at the edges. These fullerenes were then used to intercalate slit-like graphene pores.

Figure 1. Schematic representation of simulation boxes and applied notations.

$^1$Terrones et al. (2002) have shown that fullerenes with holes can be stable energetically.
Each graphene pore was generated in an atomistic way so as to allow the application of the periodic boundary conditions (PBC) in the xy-plane. The diameter of each slit was assigned to allow osculation between the layer and a fullerene (the distance between the centres of the C atoms, $\Delta$, was 0.34 nm). The slits were placed in the simulation box in such a way that the bottom layer of one slit was the upper layer of the next. The simulation box with the PBC in all directions contained three slits of this kind (see Figure 1). Two dimensions of the simulation box were employed depending on the type of fullerene considered (Table 1). For one type of fullerene, two boxes were studied: the first contained only one fullerene molecule (labelled as “_1”), while the second contained four equally placed fullerenes (labelled as “_4”). Exactly the same boxes were used as a reference, but with non-intercalated graphene slits (denoted as “_0”). Figure 1 shows further details regarding the construction of the simulation boxes.

### 3. SIMULATIONS USING THE GCMC METHOD

Simulations of the adsorption of Ar (at its boiling point temperature of 87 K), of CH$_4$ (at 298 K) and of CO$_2$ (at 298 K) were performed using the standard GCMC method (Frenkel and Smit 1996). For each adsorption point, $25 \times 10^6$ iterations were performed (to attain an equilibrium state), following which $25 \times 10^6$ iterations were performed at equilibrium (the average values were calculated from these results). A single iteration represents an attempt at changing the state of a system via displacement, creation, annihilation and rotation of the adsorbate. The probabilities of creation, displacement and annihilation for all three molecules were the same (= 1/3). For CH$_4$ and CO$_2$ (where the molecules were modelled as multi-sites), the probabilities of displacement or rotation were equal to 1/6 (note that the displacement of a molecule in this case is connected with the change in the angular position).

### 4. INTERMOLECULAR INTERACTIONS

Argon atoms were modelled as Lennard-Jones centres, methane molecules using the revised five-site model proposed by Sun et al. (1992) (see below) and carbon dioxide by three-centre models of the TraPPE types (Potoff and Siepmann 2001). The lengths of the bonds in the molecules were $l_{\text{C-H}} = 0.109$ nm and $l_{\text{C-O}} = 0.116$ nm. Each centre was the LJ centre as well as the point charge.

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**TABLE 1. Parameters of the Simulation Boxes**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Fullerene type</th>
<th>No. of C atoms deleted from a single fullerene</th>
<th>Distance between C layers* (nm)</th>
<th>$L_{\text{box,x}}$ (nm)</th>
<th>$L_{\text{box,y}}$ (nm)</th>
<th>$L_{\text{box,z}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_180</td>
<td>C$_{180}$</td>
<td>18</td>
<td>1.8968</td>
<td>4.3959</td>
<td>4.2300</td>
<td>5.6904</td>
</tr>
<tr>
<td>S_240</td>
<td>C$_{240}$</td>
<td>25</td>
<td>2.0950</td>
<td>4.3959</td>
<td>4.2300</td>
<td>6.2850</td>
</tr>
<tr>
<td>S_260</td>
<td>C$_{260}$</td>
<td>21</td>
<td>2.1552</td>
<td>6.5939</td>
<td>6.3450</td>
<td>6.4656</td>
</tr>
<tr>
<td>S_320</td>
<td>C$_{320}$</td>
<td>24</td>
<td>2.3132</td>
<td>6.5939</td>
<td>6.3450</td>
<td>6.9396</td>
</tr>
<tr>
<td>S_500</td>
<td>C$_{500}$</td>
<td>20</td>
<td>2.7448</td>
<td>6.5939</td>
<td>6.3450</td>
<td>8.2344</td>
</tr>
</tbody>
</table>

*Distance between the centres of the layers.
Generally, the energy of interaction between a pair of molecules at a distance $r$ can be written as:

$$U(r) = \sum_{i=1}^{N} \sum_{j=1}^{N} U_{LJ}^{ij}(r_{ij}) + U_{\text{electr}}(r)$$

(1)

where $N$ denotes the number of LJ centres ($N = 1$ for Ar, $N = 5$ for CH$_4$ and $N = 3$ for CO$_2$), $U_{LJ}^{ij}(r_{ij})$ is the energy of the dispersion interactions between a pair of centres $i$ and $j$ placed at a distance $r_{ij}$ and calculated from the truncated LJ potential:

$$U_{LJ}^{ij}(r_{ij}) = \begin{cases} 
4\epsilon_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}, & \text{if } r_{ij} < r_{\text{cut,ij}} \\
0, & \text{if } r_{ij} \geq r_{\text{cut,ij}}
\end{cases}$$

(2)

where $\sigma_{ij}$ and $\epsilon_{ij}$ are the collision diameter and the potential energy well depth for interactions between $i$ and $j$.

The second term in equation (1), viz. $U_{\text{electr}}(r)$, is the energy of the electrostatic interactions between a pair of molecules which can be written as:

$$U_{\text{electr}}(r) = \begin{cases} 
\frac{1}{4\pi\epsilon_0} \sum_{i=1}^{M} \sum_{j=1}^{M} \frac{q_i q_j}{r_{ij}}, & \text{if } r_{ij} < r_{\text{cut,C}} \\
0, & \text{if } r_{ij} \geq r_{\text{cut,C}}
\end{cases}$$

(3)

where $M$ is the number of point charges in the molecule ($M = 0$ for Ar, $M = 5$ for CH$_4$ and $M = 3$ for CO$_2$), $q_i$ and $q_j$ denote the values of the charges on the centres, and $\epsilon_0 [8.8543 \times 10^{-12} \text{ C}^2/(\text{J m})]$ is the permittivity of the free space. We use the cut-offs for electrostatic interactions but for all molecules (Ungerer et al. 2005) and, especially if the centres of the mass of two molecules are located at a distance smaller than the cut-off for electrostatic interactions ($r_{\text{cut,C}}$ assumed as equal to 1.5 nm), the sum of the energy of interactions between all pairs of charges occurring in the molecules is calculated, otherwise the electrostatic interactions are neglected. At the cut-off distance, the energy of interaction of a pair of molecules is negligibly small — the energy of electrostatic interaction for molecules (having quadrupole or larger moments) decreases in proportion to the fifth (or larger) power of the distance (Gray and Gubbins 1984).

The interactions between the studied molecules and the structure of the adsorbent can be written as:

$$U_{\text{sf}} = \sum_{i=1}^{N_{\text{C}}} \sum_{j=1}^{N} U_{LJ}^{ij}(r_{ij})$$

(4)

where $N_{\text{C}}$ is the number of carbon atoms in the simulation box.

For all LJ interactions, the cut-offs were placed at $r_{\text{cut,ij}} = 5\sigma_{ij}$. Table 2 shows the values of the parameters applied (we used the Lorentz–Berthelot mixing rules, except for the case of CH$_4$ – see below).
To model the intermolecular interactions between methane molecules at high pressures and temperatures, we revised the five-site model proposed by Sun et al. (1992). These authors parameterized the methane force field using the experimental data for the free energy of solvation of methane in water under normal conditions. This model has often been applied by other authors, for example for modelling the high-pressure adsorption of methane onto graphite and in graphitic slit pores (it is sometimes called the Kolmann model). However, the many-body effect embedded in 12–6 Lennard-Jones (LJ) effective parameters is different for pure methane fluid at high pressures and temperatures from that for methane interacting with polarized water molecules under normal conditions. Indeed we found that the five-site model of Sun et al. (1992) is unable to reproduce the experimental density data of methane at high pressures and temperatures because the Lorentz–Berthelot mixing rule does not predict the correct interactions between the hydrogen and carbon of methane. Thus, for the purpose of this study, we refined the LJ interactions between the hydrogen and carbon in the five-site methane model of Sun et al. to reproduce the experimental data at 298, 320 and 340 K, respectively, and pressures up to 20 MPa. The values of the parameters of the revised five-site model of Sun et al. for methane are as follows: \( \sigma_{\text{C-C}} = 0.34 \text{ nm}, \sigma_{\text{H-H}} = 0.265 \text{ nm}, \sigma_{\text{C-H}} = 0.3025 \text{ nm}, \varepsilon_{\text{C-C}}/k_B = 55.055 \text{ K}, \varepsilon_{\text{H-H}}/k_B = 7.901 \text{ K}, \varepsilon_{\text{C-H}}/k_B = 30.6 \text{ K}, q_{\text{C}}/e = -0.66 \) and \( q_{\text{H}}/e = 0.165 \).

To validate the revised intermolecular potential model, we performed a series of (N,P,T) Monte Carlo simulations of pure methane at 298, 320 and 340 K, and at operating pressures up to 22 MPa. In the isothermal/isobaric ensemble, we generated \( 6 \times 10^7 \) configurations. The first \( 1 \times 10^7 \) configurations were discarded to guarantee equilibration, whereas the latter \( 5 \times 10^7 \) configurations were used to obtain the desired properties. For arbitrarily selected points, we stored the fluctuations in the total energy. Next, the variations of the internal energy were analyzed to ensure that thermodynamic equilibrium was achieved. To characterize the structure of methane under the high-pressure and temperature conditions, we computed the radial distribution function (mass centre–mass centre) from:

\[
g(r) = \frac{\rho_l}{\rho} = \frac{N_r V}{4\pi r^2 N \Delta r}
\]

where \( r \) denotes the intermolecular distance between the mass centres of two molecules, \( \rho_l \) is the number of molecules (mass centres) in the volume element, \( \rho \) is the overall density, \( N_r \) is the number of molecules (mass centres) inside the shell, \( N \) is the total number of molecules in the system and \( V \) is the defined volume.
Finally, for selected pressures, we computed the total intermolecular bonding energies for methane at 298, 320 and 340 K. The histograms of the total intermolecular bonding energies were constructed by the algorithm described in a series of papers published by Jorgensen’s group (Jorgensen et al. 1983; Jorgensen and Madura 1985; Jorgensen and Jenson 1998).

As can be seen from Figure 2, the revised five-site model of Sun et al. correctly reproduced the pressure variation of methane density at 298, 320 and 340 K, respectively. The distributions of the total intermolecular bonding energies computed from isobaric/isothermal Monte Carlo calculations [Figure 2(c)] show that the continuous binding energy curve for methane at 20 MPa and 298 K is characterized by a single broad and smooth peak with a maximum at ca. –5.78 kJ/mol. As would be expected, the binding energy curve is systematically shifted at higher pressures.

Figure 2. Comparison of the density versus pressure computed from the revised five-centre model of Sun et al. (1992) for methane (symbols) with the measured experimental data (solid lines). (b) Mass centre–mass centre radial distribution functions [g(r)] computed from the revised five-centre model of Sun et al. for methane at 20 MPa. (c) Bonding energy (E_B) profiles computed from the same model for 20 MPa.

Only the range of pressures employed in the simulations are depicted in the figure. However, very good reproducibility was also observed for larger pressures.
temperatures to higher values of energy due to the increasing thermal energy. The radial distribution functions of methane [Figure 2(b)] are typical for supercritical fluids. The correlations between the methane molecules virtually disappear for distances greater than the second solvation shell (ca. 1 nm) due to the action of the thermal energy. The coordination number of methane at 20 MPa and 298 K is ca. 6.6. Additionally, we have evaluated the isobaric heat capacity from the standard fluctuation formula and obtained satisfactory results (data not shown). In summary, our revised five-site Sun et al. model of methane reproduced the properties of methane at 298, 320 and 340 K and pressures up to 22 MPa relatively well.

6. CALCULATIONS

In the case of methane or carbon dioxide, the most interesting method of storage from the practical viewpoint is the most effective utilization of the storage volume, apart from the way that it is filled. In accordance with this idea, the results below are presented as the density re-calculated on the basis of the volume of the whole simulation box (including the space occupied by the carbon structure):

\[ \rho_s = \frac{\langle N \rangle}{V_{\text{box}} \cdot N_{\text{Av}}} \]  

where \( \langle N \rangle \) is the average number of methane molecules present in the simulation box at a given pressure, \( N_{\text{Av}} \) is the Avogadro number and \( V_{\text{box}} \) is the volume of the simulation box:

\[ V_{\text{box}} = L_{\text{box},x} \cdot L_{\text{box},y} \cdot L_{\text{box},z} \]  

where \( L_{\text{box},i} \) is the length of the box in the direction \( i \).

The adsorption excess was calculated using the standard formula:

\[ a_{\text{exc}} = \frac{\langle N \rangle - \rho_{\text{bulk}} (V_{\text{box}} - V_A)}{N_c \cdot M_c} \]  

where \( \rho_{\text{bulk}} \) is the density of the compressed (gaseous) adsorbate at a given pressure, \( V_A \) is the volume occupied in the simulation box by the carbon structure (calculated from Monte Carlo integration) and \( M_c \) is the molar mass of carbon. The isosteric enthalpy of adsorption was calculated from the theory of fluctuations.

7. ARGON ADSORPTION MECHANISMS

The simulated Ar adsorption isotherms depicted in Figure 3 were converted into the high-resolution \( \alpha_s \)-plots (Figure 4) by taking the slit-like graphene pore (effective diameter = 6.0 nm) as the reference. Although small differences may be observed in the shapes of the adsorption isotherms in the low-pressure range (an increase in adsorption is observed as the number of intercalating fullerenes increases), as expected, however, the intercalation process had a considerable influence on the maximum adsorption capacities of the studied materials.
Figure 3. Simulated argon adsorption isotherms (at 87 K) on the studied structures.

Figure 4. Comparison of the high-resolution $\alpha_S$-plots generated from the argon adsorption isotherms depicted in Figure 3.
It will be seen from Figure 4 that the high-resolution $\alpha_S$-plots obtained possessed at least three changes in course (swings) which became more pronounced as the number of intercalated fullerenes in the structure increased. The values characterizing the swings and the linear ranges, together with the related snapshots are shown in Figures 5–7 and in Figures S1 and S2 (available in the supporting information — see below), where the atoms forming monolayers are shown in green. It is interesting that, generally, four characteristic areas may be observed in these plots. Thus, at very low pressures ($\alpha_S$ smaller than ca. 0.042), a slight swing may be observed related to the filling of the internal spaces of intercalated fullerenes [snapshots (a) in Figures 5–7 and Figures S1 and S2] and to adsorption on the graphene sheets around the contact points between both sub-structures. The second, strongly marked swing [in the range $0.042 < \alpha_S < 0.12$, labelled (b) in Figures 5–7 and Figures S1 and S2] may be related to adsorption on the external surface of the fullerenes (commencing from the corners of the first layer of graphene sheets intercalated with fullerenes) and to further adsorption on the graphene sheets. The next characteristic point (where the linear part of the $\alpha_S$-plots occurs — point (c) in Figures 5–7, $0.35 < \alpha_S < 0.5$) is where a monolayer exists (where the Ar atoms shown in white are virtually absent from the snapshots), and finally the second strongly marked swing is related to the creation of “multilayers” where pore-filling occurs [point (d), $0.5 < \alpha_S < 0.8$].

![Figure 5. Snapshots related to the characteristic points of the Ar $\alpha_S$-plots (shown in Figure 4) for the structures 180.](image-url)
In summary, a four-stage adsorption mechanism is observed, involving the filling of the internal spaces of fullerenes and adsorption onto graphene sheets at the contact points (at low pressures), adsorption onto the external surfaces of fullerenes and the further creation of monolayers on the graphene walls, the packing of monolayers and finally pore filling. This mechanism can be observed on the movies (see http://www.chem.uni.torun.pl/~gaudip/wegiel/graphics/graphics_2009.html). Movie_1 shows an animation of Ar adsorption for structures of 240 type (240_0, 240_1 and 240_4, monolayer atoms marked in green, multilayer in white) while Movie_2 compares the mechanisms for three of the four structures studied [the movies and snapshots were prepared using the VMD program (Humphrey et al. 1996), http://www.ks.uiuc.edu/Research/vmd/].

8. TESTING THE ADSORPTION AND STORAGE OF METHANE AND CARBON DIOXIDE

Figure 8 shows the effect of intercalation on the density of methane. For all the cases studied, a higher value relative to that of the reference graphene slit is observed. However, Figure S3 indicates that only a small increase in excess adsorption compared to the graphene slit occurred at low pressures, while a decrease in adsorption excess occurred at high pressures due to exclusion.
of the adsorption space by fullerenes. The intercalation of graphene leads to a remarkable rise (by ca. 50%) in the value of the isosteric adsorption enthalpy of methane (see Figure S4). Normally, the plots obtained increase linearly with increasing methane density (due to the increase in fluid–fluid interaction energy); however, for structures intercalated with even the smallest fullerenes, interactions between adsorbed molecules and the high-energy sites inside fullerenes appear at small loadings. The mechanism of methane storage for structures 240 is shown in Movie_3 (where the molecules forming monolayers are indicated in red), while a comparison for different structures (180, 240 and 320) is shown in Movie_4. These animations demonstrate a similarity between the mechanisms of methane and argon adsorption.

It follows from the above that intercalated graphenes are promising materials for methane storage. However, it is well known that the optimal diameter of carbon slit-like pores for methane storage is ca. 0.8 nm (Chen et al. 1997; Sosin and Quinn 1995; Urabe et al. 2008). In Figure 9, the results of simulations in graphene slit-like pores (diameter = 0.7–0.9 nm) are depicted. This

\[ \text{Figure 7. Snapshots related to the characteristic points of the Ar } \alpha_s \text{-plots (shown in Figure 4) for the structures 260.} \]
Figure 8. Comparison of methane densities [equation (6)] at different equilibrium pressures. Crosses show the density for compressed methane.

Figure 9. Comparison of the results for graphene slits having effective diameters ($d_{\text{eff}}$) of 0.7, 0.8 and 0.9 nm, respectively.
shows that since the energy of interaction with the second and subsequent layers of carbon slits is small, the same result as for graphite slits is observed for the graphene ones (i.e. the optimal diameter for methane storage is 0.8 nm). Unfortunately, intercalation of such pores with fullerenes is impossible. Thus, in this case, we performed the simulation of methane adsorption by intercalating a slit of 0.665 nm width with fullerene C_{20}. However, this intercalation did not improve the storage of methane (results not shown). Although a remarkable increase in the adsorption energy occurred (the enthalpy was in the range 21–14 kJ/mol), the volume excluded by fullerenes was too large relative to the pore volume.

Interesting results were also obtained for CO\textsubscript{2} storage (as shown in Figure 10). In this case, a remarkable increase in the density of CO\textsubscript{2} in the intercalated pores may be observed relative to graphene slits. In the latter case, we obtained virtually the same results as those published by Samios \textit{et al.} (2000) who simulated the isotherms of CO\textsubscript{2} in slit-like carbon pores using the GCMC. As expected, we observed an increase in CO\textsubscript{2} storage as the number of intercalating fullerenes increased. The influence of intercalation was more pronounced for CO\textsubscript{2} excess adsorption than for methane (see Figures S5 and S3), since CO\textsubscript{2} was simulated as a sub-critical gas at the studied temperatures. However, similar effects to those for methane were observed in the plots of the adsorption enthalpies (Figure S6) and also a similar adsorption mechanism (Movie_5 and Movie_6). Figure 11 shows the results of simulations of CO\textsubscript{2} storage in slit-like graphene pores. The pore with an effective diameter of ca. 0.5 nm was optimal for the compression of CO\textsubscript{2} and the largest densities at higher pressures were observed for larger slits (diameters in the range 1–2.4 nm).

Figure 10. Comparison of the CO\textsubscript{2} densities [equation (6)] at different equilibrium pressures. Crosses show the density for the compressed gas.
9. CONCLUSIONS

The mechanism of adsorption of Ar, CH\textsubscript{4} and CO\textsubscript{2} onto fullerene-intercalated graphenes was similar for all three studied adsorbates. In each case, a four-stage adsorption mechanism was observed, viz. filling of the internal spaces of fullerenes and adsorption onto graphene sheets at the contact points (at low pressures), adsorption onto the external surfaces of fullerenes and the further creation of a monolayer on the graphene walls, packing of the monolayer and, finally, pore filling. Tests of the possible application of these materials as nano-containers for methane and CO\textsubscript{2} storage led to the conclusion that better methane and CO\textsubscript{2} storage was always observed for intercalated graphenes (over the range where the volume effect did not dominate) relative to slits having the same diameters. Intercalation with defected fullerenes did not lead to an improvement in methane storage at low pressures (up to 0.8 MPa) compared to the “optimal” slit of 0.7 nm diameter. However, for this range, better storage was observed for structures S\textsubscript{240}_4 and S\textsubscript{180}_4 than for slits of 0.8 and 0.9 nm diameter.
For CO\textsubscript{2} in the low-pressure range (up to 0.02 P/P\textsubscript{s}), the optimal diameter for the slit-like graphene pore was 0.5 nm, with intercalation not improving the storage in comparison to this pore. However, a larger density was observed in the case of intercalated graphenes (S\textsubscript{240_4} and S\textsubscript{180_4}) than for pores with diameters greater than ca. 0.7 nm.

The results obtained suggest that the intercalation of a carbon structure with fullerenes is promising for methane and CO\textsubscript{2} storage, especially for activated carbons having a distributed porosity. In this case, the incorporation of fullerenes in pores having larger diameters could lead to interesting materials for methane and CO\textsubscript{2} storage.

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REFERENCES


ELECTRONIC SUPPLEMENTARY MATERIAL

The supporting information is available electronically from the following web sites:

Figures S1–S6.
Movie_1. Animation of Ar adsorption in structures 240.
Movie_2. Animation of Ar adsorption in structures 180_4, 240_4 and 320_4.
Movie_5. Mechanism of CO₂ storage in structures 240.