Sequestration and selective oxidation of carbon monoxide on graphene edges

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Abstract

The versatility of carbon nanostructures makes them attractive as possible catalytic materials, as they can be synthesized in various shapes and chemically modified by doping, functionalization, and the creation of defects in the nanostructure. Recent research has shown how the properties of carbon nanostructures can be exploited to enhance the yield of chemical reactions such as the thermal decomposition of water (Kostov *et al* 2005 *Phys. Rev. Lett.* **95**) and the dissociation of methane into carbon and hydrogen (Huang *et al* 2008 *J. Chem. Phys.* at press). In this work, we consider the carbon-mediated partial sequestration and selective oxidation of carbon monoxide (CO), both in the presence and absence of hydrogen. Using first-principles calculations we study several reactions of CO with carbon nanostructures, where the active sites can be regenerated by the deposition of carbon decomposed from the reactant (CO) to make the reactions self-sustained. Using statistical mechanics, we also study the conditions under which the conversion of CO to graphene and carbon dioxide is thermodynamically favorable, both in the presence and in the absence of hydrogen. These results are a first step toward the development of processes for the carbon-mediated partial sequestration and selective oxidation of CO in a hydrogen atmosphere.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The disproportionation reaction of carbon monoxide has recently been the focus of some attention as a means for the synthesis of carbon nanotubes [3–5]. This process has been shown to be favorable at relatively high temperatures and partial CO pressures. Favorable conditions for CO sequestration from any carbon source are highly dependent on temperature, pressure and co-reactant species. In systems where CO is the main carbon bearing species, the disproportionation ($2CO \Leftrightarrow C(s) + CO_2$) and direct reduction reactions ($CO + H_2 \Leftrightarrow C(s) + H_2O$) are the primary pathways for carbon deposition. Increasing the concentration of CO by increasing the system pressure can increase the flux of the disproportionation reaction, but it may also favor side reactions such as the direct reduction, which would be undesirable in an application such as the purification of hydrogen for use in fuel cells.

In this study, we consider the sequestration of CO through disproportionation on a graphene surface, both in the absence and in the presence of hydrogen. We find that it is possible, under certain thermodynamic conditions, to selectively deposit carbon on graphene through disproportionation rather than direct reduction, i.e. without converting hydrogen to water, which makes it possible to separate the H_2 from CO. We investigate the energetics of the sequestration of CO on a graphene edge using density functional theory calculations [6, 7], studying in detail the reaction between CO and aromatic rings on graphene surfaces. In particular, we consider the adsorption of CO on edges of graphitic materials and the desorption of CO_2. Our results are a first step toward understanding the energetics of carbon deposition from a CO

atmosphere, and can be used as a basis for obtaining the conditions under which such deposition can occur.

2. Methods

The results presented in this work were obtained using plane-wave pseudopotential [8] density functional theory [6, 7] (DFT), with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [9]. We used ultrasoft pseudopotentials [10, 11] with a plane-wave cutoff of 35 Ryd and a density cutoff of 280 Ryd, which we found sufficient for convergence. The calculations were done using the PWSCF [12] and CPMD [13] codes. Some reaction pathways were obtained using the nudged elastic band (NEB) method [14, 15] with the climbing image [16] modification to obtain the structure of the transition states and the activation barrier. All geometries have been relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [17]. The graphene walls were modeled on an orthorhombic unit cell with periodic boundary conditions. In order to prevent interaction between periodic images in the y- and z-directions, a vacuum of 10 Å was left in those directions. One end of the graphene wall was saturated with hydrogen in order to see the interactions between the gas molecules and a single edge. We considered graphene edges with different numbers of rings in order to ensure that our results were reasonably independent of the system size.

We also estimated the equilibrium constants for the various reactions in the low-pressure limit as functions of temperature. In order to do so, we computed the vibrational spectrum for both reactants and products and calculated the ideal-gas partition function as described in detail in [18]. For the solid states, only vibrational modes were included in the partition function. The standard Gibbs free energy changes ΔG^0 for all reactions were then computed from the molecular partition functions and were then used to obtain the equilibrium constants $K_{eq} = \exp(-\Delta G^0/kT)$ at different temperatures in the ideal-gas limit (Henry's law limit for adsorbed species). These values were used to construct van't Hoff plots ($\ln K_{eq}$ versus $1/T$). In all cases we treated rotations, translations, and vibrations as independent of each other. Rotations were treated quantum mechanically at low temperatures [18, 20][6].

3. Results and discussion

The interaction between a growing surface and a chemically reactive atmosphere, especially at high temperatures and pressures, is a quite complicated problem to study since there are many possible arrangements of the atoms in the advancing edge that could lead to different energetics. Since an exhaustive study of all possible atomic configurations would be well beyond the reach of an *ab initio* study, we decided

to focus on edges of only two different symmetries—zigzag and armchair—interacting with atmospheres containing CO, and later also hydrogen. In order to obtain the relevant configurations of atoms on such edges, we investigated the reactions between gas-phase CO molecules and unsaturated edges of both zigzag and armchair symmetries. After the dangling bonds were saturated by the gas-phase species, we studied the reactions with further gas-phase molecules that would lead to a new layer of benzene rings ready for subsequent reaction. Even though the reactions in a real system would likely proceed through different (and more complex) mechanisms, we can still use the results to estimate the equilibrium energetics of the system, and thus study the conditions under which different reactions would be thermodynamically favored.

Our results regarding the interaction of carbon monoxide with an advancing zigzag edge are summarized in figures 1– 4. Figure 1 shows the energetics for the reactions between CO molecules in the gas phase and a zigzag graphene edge resulting in the deposition of a new layer of aromatic rings. The results in figure 1 correspond to a zigzag edge with seven aromatic rings. No substantial difference in the energetics attributable to model size could be found between four-ring, five-ring, six-ring or seven-ring models. The energetics in figure 1 correspond to five reaction steps: (1) the saturation of the edge by CO molecules yielding oxygenated pentagonal structures ((i)–(ii)); (2) the reaction of these oxygenated structures with further CO from the gas phase to form CO_2 ((ii)–(iii)); (3) the deposition of another layer of CO molecules to form oxygenated 5-7-5 ring structures ((iii)–(iv)); (4) the reaction of these structures with further CO to form CO_2 ((iv)–(v)) and (5) the rearrangement of the atoms on the edge to hexagonal structures. The energetic penalty from this last rearrangement is a consequence of the zigzag symmetry of the edge—as we will see later, this does not appear in the armchair edge. Note that the extra oxygen atom in (iii), which actually completes a furan ring with the carbon on the right of the simulation box due to the periodic boundary conditions, is a consequence of doing the calculation with an odd number of rings. The overall energetics for growth, however, are not significantly different when the calculations are done with an even number of rings.

As expected, both of the steps where dangling bonds are saturated ((i)–(ii) and (iii)–(iv)) are highly exothermic. Of the steps where oxygen is removed from the edge by reaction with further gas-phase CO molecules, one ((ii)–(iii)) is endothermic and the other ((iv)–(v)) is exothermic[7]. This is a consequence of the larger steric hindrance experienced by the oxygen atoms bound to the heptagonal rings in (iv), which makes them less strongly bound to the graphene edge. The rearrangement of the benzene rings ((v)–(vi)) is endothermic but to a lesser extent, and the overall process is exothermic. The energy change for the overall reaction (i) + 26CO → (vi) + 13CO$_2$ i.e. the deposition of a new layer of benzene rings on the graphene edge, is −820.3, or −63.1 kcal mol^{-1} per CO molecule

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[6] The statistical mechanical approach used in this work is strictly valid only at low to moderate temperatures and pressures. We compared the ideal-gas thermodynamic properties of the gaseous species (oxygen, water, carbon monoxide, carbon dioxide, and hydrogen) obtained using our approach with those obtained using the data found in the NIST database [19], and found reasonably good agreement for the temperature range covered in figures 7, 9 and 10. For the other species considered in this work, however, there is no available data for comparison to the best of our knowledge.

[7] We also considered the possibility of desorption of the oxygen atoms as O_2 molecules but, as it would be expected, this reaction is highly endothermic and unlikely to occur at low to moderate temperatures.

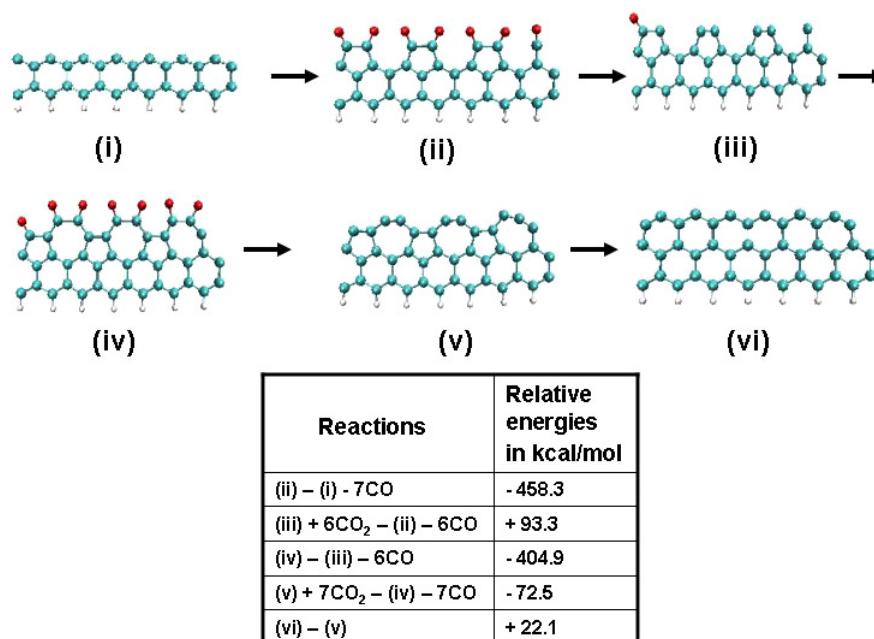| Reactions	Relative energies in kcal/mol
(ii) – (i) - 7CO	- 458.3
(iii) + 6CO_2 – (ii) – 6CO	+ 93.3
(iv) – (iii) – 6CO	- 404.9
(v) + 7CO_2 – (iv) – 7CO	- 72.5
(vi) – (v)	+ 22.1

Figure 1. Equilibrium energetics for a zigzag graphene edge interacting with CO molecules at high CO concentration. Table I (inset): the reactions at different steps and the corresponding reaction energies in kcal mol^{-1}.
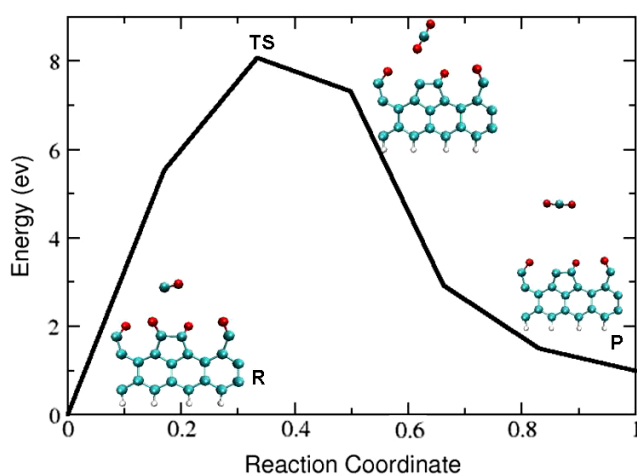

Figure 2. Activation energy barrier for the reaction of an oxygen atom with CO to yield CO_2 at the zigzag graphene edge.
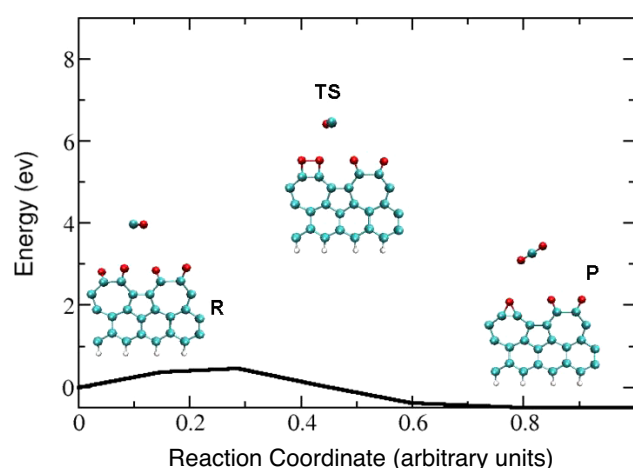

Figure 3. Activation energy barrier for the reaction of an oxygen atom with CO to yield CO_2 when the oxygen atoms are bonded to 7-5-7 carbon rings at the zigzag graphene edge.

deposited, indicating that the deposition is highly favorable thermodynamically at low temperature.

In order to get an estimate of the kinetic barriers involved in the key reaction steps for the deposition of carbon on a zigzag graphene edge, we investigated the mechanisms for the reaction of gas-phase CO molecules with oxygen atoms on the edge to yield CO_2 (figures 2 and 3), and the structural rearrangement of the rings at the edge (figure 4), using the nudged elastic band method. We found that the removal of an oxygen atom bound to a pentagonal ring (figure 2) has a very large energy barrier (∼8 eV), which means that this particular reaction is very unfavorable kinetically. In contrast, the removal of an oxygen atom bound to a heptagonal ring

(figure 3) has a much lower energy barrier—not only are the oxygen atoms in the initial state more sterically hindered, but the transition state is a cyclic peroxide structure with no dangling bonds, which makes it much lower in energy.

Finally, the rearrangement of a heptagonal and a pentagonal ring at the graphene edge to form two hexagons, shown in figure 4, has a high energy barrier (∼2 eV). As we discuss later, this step is not necessary when the reaction happens on an armchair edge, which suggests that the growth in the zigzag direction is much less kinetically favorable.

The results in figures 2–4 suggest that the kinetic bottleneck for the growth of a zigzag edge on a CO atmosphere
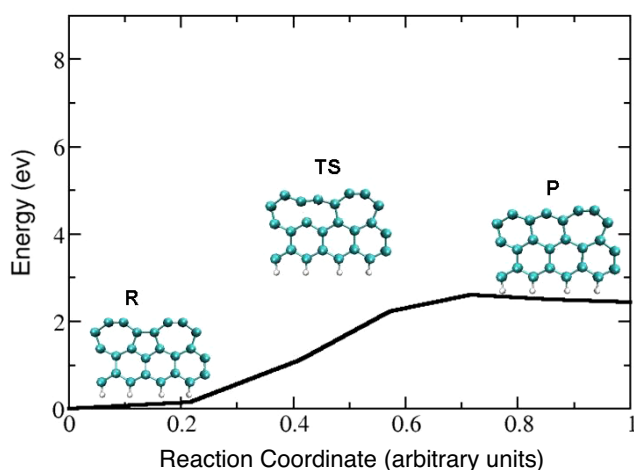
Figure 4. Activation energy barrier for the rearrangement of 7-5-7 carbon rings to 6-6-7 carbon rings at the zigzag graphene edge.

is the removal of oxygen atoms bound to pentagonal rings. Even though we were unable to find a more favorable pathway for this reaction, it is possible that there is a high-pressure concerted mechanism involving more than one CO molecule with a lower activation barrier. An exhaustive search for such a mechanism would require a far larger computational effort. Alternatively, a metal catalyst could be added to promote the deposition of carbon, as has been done experimentally to grow carbon nanotubes [4, 5].

Our results regarding the interaction of gas-phase CO molecules with an armchair graphene edge are presented in figure 5. Because of the symmetry of the armchair edge, it is possible for the CO molecules to directly form hexagonal rings upon deposition. This means that no rearrangement is necessary, and all the steps where oxygen is removed by further reaction with CO are equivalent. As is the case with the zigzag edge, the saturation of the dangling bonds with CO (steps (i) → (ii) and (iii) → (iv) in figure 5) is, as expected, highly exothermic[8]. However, the reaction with further CO to yield CO_2 and a new exposed edge is also exothermic—both of the reactions (ii) → (iii) and (iv) → (v) release approximately 75 kcal mol^{-1} (see footnote 7)[9]. The explanation for this is similar to that for the reaction (iv) → (v) in figure 1: the steric hindrance between the oxygen atoms attached to the hexagonal rings makes them easier to remove. Thus, all the steps from (i) to (v) in figure 5 are exothermic and therefore thermodynamically favorable at low temperature. The overall energy released for the deposition of 12 CO molecules to grow a new row of rings, i.e. (i) + 24CO → (v) + 12CO$_2$ is 684.0, or

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[8] Indirectly, our results suggest that the armchair edge is significantly more stable than the zigzag edge, since the drop in energy per carbon atom added when the edge is saturated with CO is ∼65 kcal mol^{-1} for the zigzag edge versus ∼45 kcal mol^{-1} for the armchair edge. This is so even despite the fact that oxygen atoms on the edge experience higher steric hindrance in the armchair case.

[9] In reality, the energy differences for both of the reactions (ii) → (iii) and (iv) → (v) should be the same for a large surface. The ∼5% difference in the values for (ii) → (iii) (−78.7 kcal mol^{-1}) and (iv)–(v) (−74.7 kcal mol^{-1}) is due to the finite size of our system.

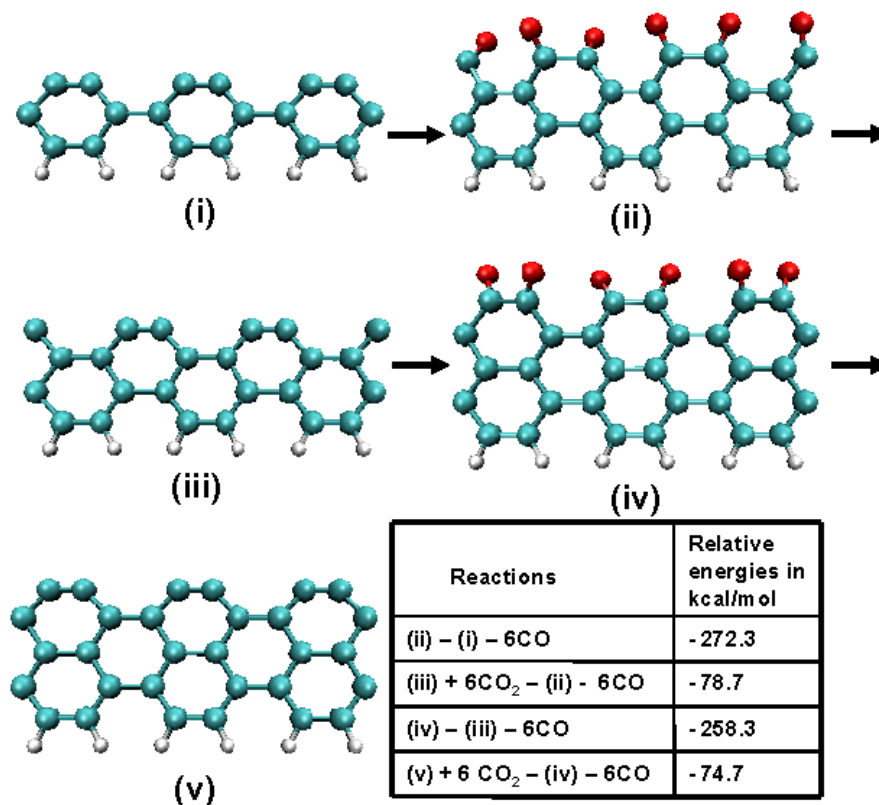| Reactions	Relative energies in kcal/mol
(ii) − (i) − 6CO	-272.3
(iii) + 6CO$_2$ − (ii) - 6CO	-78.7
(iv) − (iii) − 6CO	-258.3
(v) + 6 CO$_2$ − (iv) − 6CO	-74.7

Figure 5. Energetics for the interaction of an armchair graphene edge with gas-phase CO molecules. Table II (inset): the reactions at different steps and the corresponding reaction energies in kcal mol^{-1}.
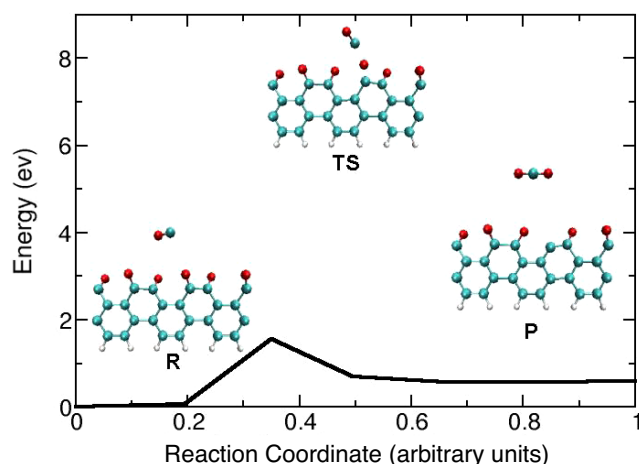
Figure 6. Activation energy barrier for the reaction of an oxygen atom with CO to yield CO_2 at the armchair graphene edge.

Figure 7. van't Hoff plot for the two main steps in the deposition of carbon on an armchair graphene edge in a CO atmosphere.

57.0 kcal mol^{-1} per CO molecule deposited. Even though this is lower than the value for the zigzag edge, the fact that every step is endothermic suggests that the growth in the direction of the armchair edge is more favorable than the growth in the direction of the zigzag edge.

In analogy with the zigzag case, we investigated the mechanism for the reaction between an oxygenated armchair edge ((ii) in figure 5) and a gas-phase CO molecule using the nudged elastic band method. The results are shown in figure 6. The reaction barrier, about 1.5 eV, is still quite high[10], but considerably smaller than the barrier for the removal of an oxygen atom from a pentagonal ring in the zigzag edge (~8 eV, figure 2). This indicates that the kinetic bottleneck for the deposition of carbon from CO is much lower on an edge of armchair symmetry, and therefore the growth in this direction is not only more favorable thermodynamically, but also kinetically. This is in agreement with other theoretical studies [21] and experimental results [22–24] for the growth of carbon nanotubes. For this reason, in the rest of the paper we only consider reactions on edges of armchair symmetry. Nevertheless, for the reaction to be practical at low to moderate temperatures and pressures, our results suggest that it would still be necessary to lower the activation barrier by using a catalyst.

In order to study the effect of temperature on the equilibrium distribution of CO and CO_2 over an advancing graphene edge, we estimated the equilibrium constant, K_{eq}, for the first two reaction steps shown in figure 5. Figure 7 shows the results as a van't Hoff plot. As expected, since both reaction steps are highly exothermic, both reactions are very favorable at low to moderate temperatures. From the equilibrium data one would expect, based purely on thermodynamics, that significant deposition of carbon would happen below ~1000 K. However, as mentioned above, in the absence of a catalyst this is a mainly kinetically limited process.

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[10] Note that, as with the zigzag case, we cannot preclude the existence of a more complex high-pressure mechanism involving more than one CO molecule with a lower barrier.
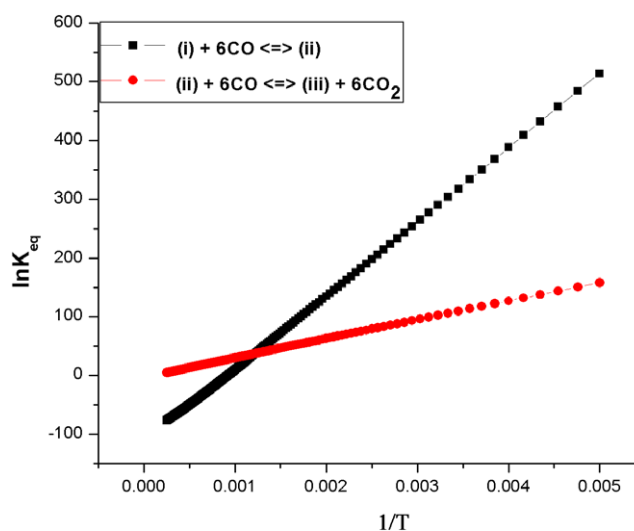
The calculations discussed up to this point involve the interaction of pure CO with a graphene surface. We have also studied the selective oxidation of CO in the presence of hydrogen, which is of interest for the purification of fuel cell feed. For this system we considered two types of reactions: (1) the competition between hydrogen and CO for the active sites on the graphene edge, and (2) the incorporation of hydrogen from the gas phase onto the oxygenated edge to form hydroxyl and carboxyl groups on the edge.

Figure 8 shows the energetics for the adsorption of hydrogen on a graphene edge and subsequent displacement of graphene-bound hydrogen by carbon monoxide. As expected, the adsorption of H_2 on the graphene edge (steps (i)–(ii)) is highly exothermic, as is the adsorption of CO (steps (i)–(ii) and (iii)–(iv) in figure 5). However, the binding of CO with the armchair graphene edge is slightly stronger than that of H_2, and thus the displacement of hydrogen by CO on the edge ((ii)–(iii)) is slightly exothermic. This shows that, at low to moderate temperatures, it is more favorable to deposit CO on the edge than to deposit hydrogen.

As in the case of a pure CO atmosphere, oxygen atoms can be removed from the edge by further reaction with either gas-phase CO molecules to yield CO_2 (steps (ii)–(iii) and (iv)–(v) in figure 5) or with gas-phase hydrogen molecules to yield water. However, the latter reaction is less exothermic by 16.7 kcal mol^{-1} and thus, at low to moderate temperatures, the majority of the edge-bound oxygen will react with CO instead of hydrogen. We also considered a few other pathways by which water could be formed in the system, as shown in steps (ii)–(ii-a) and (ii)–(ii-b) in figure 8. To detach one H_2 molecule from the edge as H_2O ((ii)–(ii-a)), the energy needed for the reaction is +112.6 kcal mol^{-1}. Even if the unsaturated bond is saturated with CO, as in (ii-b), the reaction is still quite endothermic (+17.7 kcal mol^{-1}), and thus thermodynamically unfavorable at low to moderate temperatures.

Figure 9 shows a van't Hoff plot for the relevant reactions in figure 8 between an armchair graphene edge and a mixture
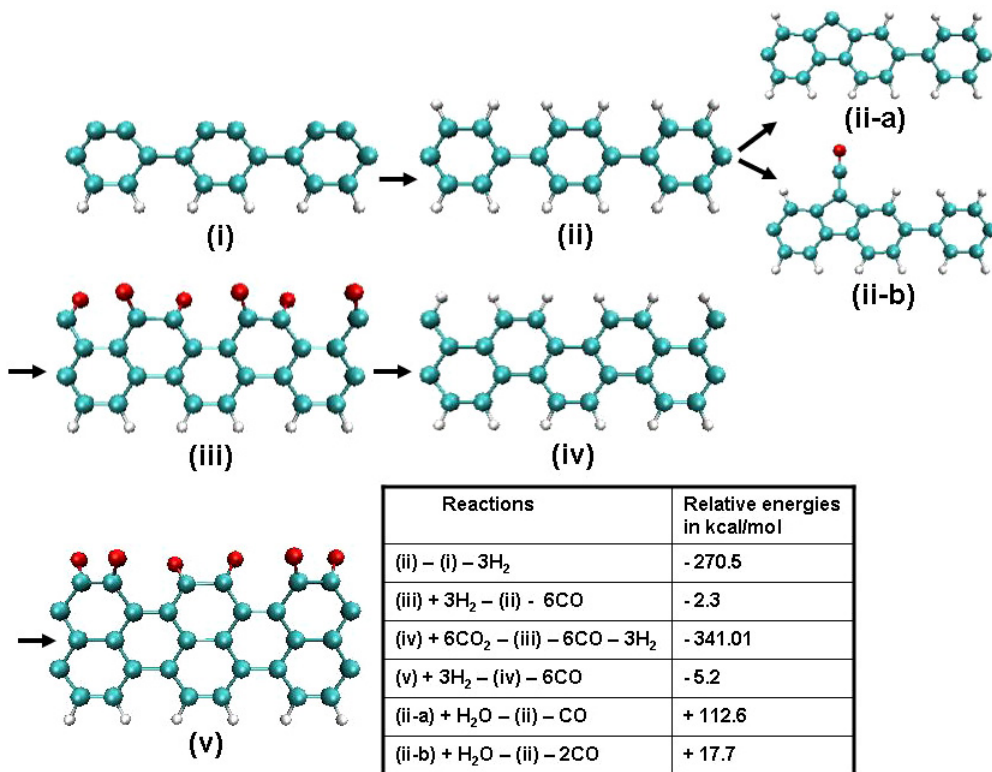
Figure 8. Energetics for the competition between CO and hydrogen for the active sites on the advancing graphene edge. Table III (inset): relative energies in kcal mol^{-1} for each of the reaction steps.

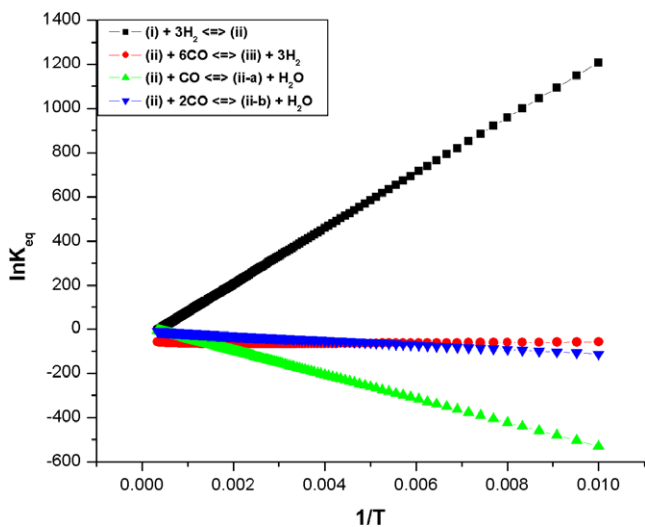| Reactions	Relative energies in kcal/mol
(ii) − (i) − 3H$_2$	− 270.5
(iii) + 3H$_2$ − (ii) − 6CO	− 2.3
(iv) + 6CO$_2$ − (iii) − 6CO − 3H$_2$	− 341.01
(v) + 3H$_2$ − (iv) − 6CO	− 5.2
(ii-a) + H$_2$O − (ii) − CO	+ 112.6
(ii-b) + H$_2$O − (ii) − 2CO	+ 17.7

Figure 9. Plots of equilibrium constants versus temperature for the main reactions in figure 8.

of CO and H$_2$. From this plot it is clear that at low to moderate temperatures, carbon monoxide is preferentially bound to the active sites on the advancing edge, and the reactions that would lead to significant oxidation of hydrogen to yield water are unfavorable.

As mentioned above, we also considered some of the reactions that could occur between gas-phase hydrogen and graphene-bound oxygen atoms. The simplest and most likely of these are the formation of hydroxyl (OH) and carboxyl groups (COOH). Figure 10 shows the energetics of a representative set of reactions involving these functional groups. The formation of hydroxyl groups ((i)–(ii) in figure 10) and the addition of CO to these hydroxyl groups to form carboxyl groups ((ii)–(iii)) are both exothermic, and therefore favorable at low to moderate temperatures. Carboxyl groups formed in this way can further react with gas-phase CO to yield CO$_2$, or with gas-phase hydrogen to form water—both processes would result in a net deposition of carbon on the graphene edge. Both of these reactions are quite exothermic but, as was the case with carbonyl oxygens (figure 9), the reaction of the carboxyl oxygens with CO to yield CO$_2$ is considerably more exothermic than the reaction with hydrogen to yield water. Thus at low and moderate temperatures, we would expect both hydroxyl and carboxyl groups to be formed on the advancing graphene edge. However, the presence of these groups does not hinder the deposition of carbon, and thus deposition is still thermodynamically favorable. Furthermore, carbon deposition is more favorable than the oxidation of hydrogen at low to moderate temperatures.

The temperature dependence of the equilibrium constant for the reactions in figure 10 is shown in figure 11 as a van't Hoff plot. From this plot it is clear that, at temperatures below ∼300 K, the deposition of both hydrogen and carbon monoxide on the edge to form hydroxyl and carboxyl groups is thermodynamically favorable, as is the oxidation of gas-phase CO by reaction with carboxyl groups. The least favorable reaction is the formation of water at the expense of gas-
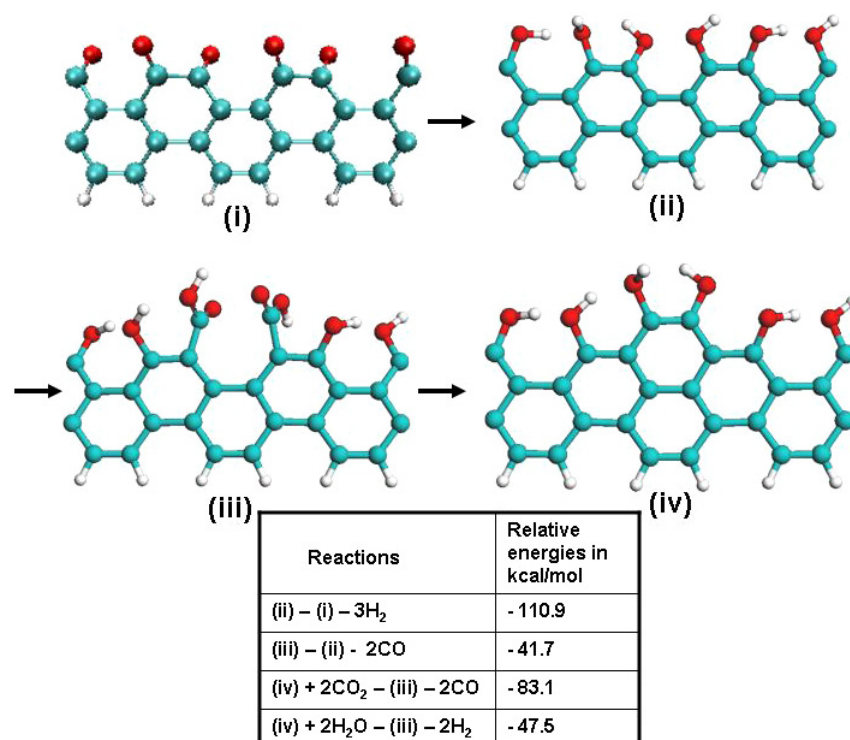
Reactions	Relative energies in kcal/mol
(ii) – (i) – 3H$_2$	- 110.9
(iii) – (ii) - 2CO	- 41.7
(iv) + 2CO$_2$ – (iii) – 2CO	- 83.1
(iv) + 2H$_2$O – (iii) – 2H$_2$	- 47.5

Figure 10. Representative chemical reactions of CO and H$_2$ at the armchair graphene edge involving hydroxyl and carboxyl groups. Table IV (inset): relative energies for the respective reaction steps in kcal mol^{-1}.
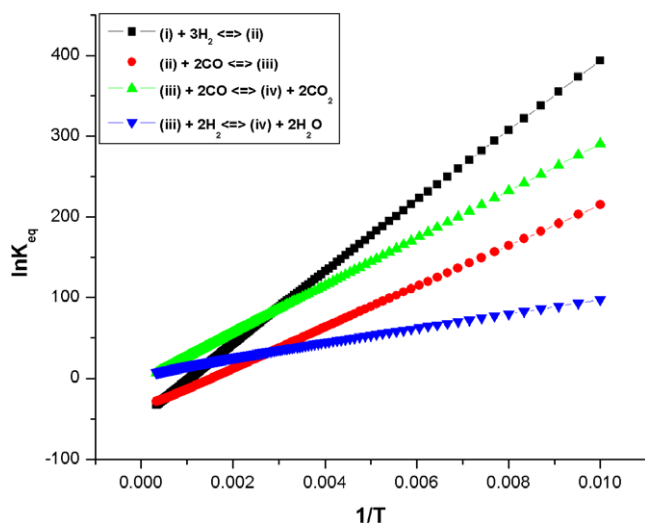

Figure 11. van't Hoff plot for the reactions involving hydroxyl and carboxyl groups at the armchair graphene edge.

phase hydrogen. At moderate temperatures the formation of carboxyl groups is less favorable, but the formation of water from surface oxygen is still less favorable than the formation of carbon dioxide. Only at high temperatures (above 1500 K) is the formation of water thermodynamically favored. We carried out equilibrium calculations with the equilibrium constant data from figure 11[11] at different initial compositions, temperatures

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[11] Our equilibrium calculations also included the constraint of chemical equilibrium in the gas phase, i.e. the water gas shift reaction CO + H$_2$O → CO$_2$ + H$_2$.

and pressures, and found that at most reasonable temperatures and pressures the equilibrium concentration of water in the gas phase is negligible. This shows that, on the basis of a thermodynamic analysis (i.e. in the presence of a suitable catalyst to overcome kinetic barriers) the removal of CO from a hydrogen stream is possible by sequestration and partial oxidation to CO$_2$.

4. Concluding remarks

Using a combination of statistical thermodynamics and density functional theory, we have shown that the adsorption of CO on a graphene edge is a thermodynamically favorable process at low to moderate temperatures. According to our calculations, the growth of graphene edges of armchair symmetry from gas-phase CO is both kinetically and thermodynamically more favorable than the growth of edges of zigzag symmetry, in agreement with similar observations for carbon nanotubes [21–24].

We have also studied the interaction between an advancing graphene edge of armchair symmetry and an atmosphere containing a mixture of carbon monoxide and hydrogen. Our calculations show that, in such a system, the deposition of carbon monoxide on the edge is slightly more favorable than the deposition of hydrogen at low and moderate temperatures. We have shown that the reaction of oxygens bound to the edge with gas-phase CO to yield CO$_2$ is also more favorable thermodynamically than the reaction with gas-phase hydrogen to form water. When including in our model the possibility of forming hydroxyl and carboxyl groups at the edge, we

find that the deposition of carbon and oxidation of carbon monoxide is still thermodynamically favorable without any loss of hydrogen due to oxidation at low and intermediate temperatures. This shows that such a setup could in principle be used to remove carbon monoxide from a stream of hydrogen.

Acknowledgments

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