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Received: August 13, 2009; Revised Manuscript Received: March 26, 2010

Interactions between atomic Pt and pristine or Stone–Wales-defective (5,5) single-walled boron nitride nanotubes (BNNTs) were studied using density functional theory (DFT) with truncated nanotube models. The binding energy of Pt on a pristine BNNT is about 20 kcal/mol with little dependency on the binding site. On the other hand, when the Stone–Wales (SW) defect is presented, the atomic Pt is preferentially inserted between the B–B bond in the SW defect region with a large binding energy of 58 kcal/mol. On an SW-defective BNNT, the atomic Pt, even placed away from the defect site, may eventually (thermodynamically) move toward the defect area until being trapped between the B–B bond, and the final adduct has decreased reactivity toward both electrophiles and nucleophiles compared with Pt adsorption to pristine BNNTs. Pt adsorption on pure or SW-defective BNNTs makes the hosting nanotube wide-gap semiconductive by introducing the valence states of the absorbed Pt into the band gap of the nanotube. In comparison, the Pt atom filling into a B or N single vacancy on a BNNT changes the electronic structure of the vacancy-defective BNNT so dramatically that the Pt-doped BNNT becomes semiconducting with improved reactivity.

Introduction

Molecular borazine (B₃N₃H₆), isoelectronic to benzene, has a similar electronic structure to benzene, especially in terms of its aromaticity. At the same time, due to their constitutional difference, borazine and benzene also possess some distinct properties. For instance, borazine is usually more reactive than benzene. When these molecular aromatic rings are extended to form layered hexagonal boron nitride (hBN) and carbon graphite networks, their very different properties, in contrast to their molecular counterparts, can be put into diverse uses accordingly. Because of its extraordinary mechanical hardness and chemical inertness, hBN is mostly used as a supporting material for catalytic reactions. Noble metal catalysts supported by hBN are very efficient for deep oxidation of organic compounds with the virtue of low light-off temperature and short initiation time.1 Carbon graphite, on the other hand, is widely utilized as a lubricant and in electronic devices because of its excellent electric conductivity.

When the two-dimensional graphene and hBN sheets are rolled into nanotubes, further changes take place because of the decreased dimensionality. In zigzag single-walled boron nitride nanotubes (BNNTs), the dipole moment is nonzero due to the alternate layers of B and N atoms, in sharp contrast to the nonpolar cases of hBN and armchair BNNTs.2 Unlike homonuclear carbon systems, boron nitride materials consist of two different elements with distinct electronegativities: N and B atoms are electron donors and acceptors, respectively. Local compositional inhomogeneity distinguishes BNNTs from carbon nanotubes (CNTs) and makes BNNTs more versatile upon any structural transformation and functionalization. However, BNNTs have been much less frequently investigated in comparison with the rich literature on CNTs.

One of the most attractive features is that BNNTs with large diameters have band gaps almost invariant to the tube diameter and chirality. Even with little purification, BNNTs can be readily used in nanoelectronics.3 As metal catalyst supporting materials, BNNTs have the merit of good thermal conductivity compared to traditional metal oxide supports.4 The incombustibility at high temperatures and inertness to various chemicals make BNNTs particularly good substrates for catalysis. Strong binding energies between BNNTs and many transition metals also suggest BNNTs to be good candidates as the stationary phase in catalytic processes.5

Pristine BNNTs were first synthesized by an arc discharge process, followed by a variety of preparation methods, including laser ablation, chemical vapor deposition, and chemical substitution,6,7 in which transition metals or their oxides play significant roles. Intuitively, there must be some constructive interactions between transition metals or their oxides and BNNTs (or the BNNT precursors) during the growth period of the nanotube. Understanding such interactions will definitely be helpful in improving the fabrication of BNNTs and may also lead to new metal–BNNT complex based materials. It is thus interesting to study the interaction between some widely available transition metals (e.g., Pt) and BNNTs.

Up to now, most studies have concentrated on zigzag BNNTs, which are energetically more stable than armchair BNNTs of similar diameter. However, because of their structural importance, armchair BNNTs have been frequently identified to play some significant roles in many experiments.8 A high-resolution field emission transmission electron microscopic study showed that BNNTs can interchange between zigzag and armchair conformations upon the presence of structural kinks.9 Besides the stability issues, the electronic structure of BNNTs around the Fermi level is almost invariant to the geometric parameters (tube diameter and chirality) due to the localized ionic B–N bonds. Thus, studies on armchair BNNTs can then be easily transferable to stable zigzag BNNTs.

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Defects were also observed in boron nitride based materials mostly due to mechanical fractures. It was suggested that monovacancies exist in hBN under certain conditions. BNNTs were shown to be more susceptible to bear a monovacancy than hBN. These defects influence the properties of BNNTs in many aspects, including growth behavior and reactivity. Recently, studies on the formation and properties of these defects, especially the Stone-Wales (SW) defects, have aroused the interests of many researchers. This pentagon-heptagon-heptagon-pentagon (5775) SW defect is energetically more stable than the tetragon-octagon defect (aka 4884 defect) and can easily occur to BNNTs with small diameters. A spectroscopic study using a scanning tunneling microscope revealed that the SW defect is localized in terms of its vibration modes and frontier orbitals. In addition to their structural significance, these SW defects have also been utilized as active sites for various processes, where the adsorption strengths and reaction products were found to depend strongly on the nature of orbital interactions.

The SW defect was proposed to be employed to enhance the field emission of BNNTs. To find new molecular storage materials, the adsorption of some diatomic and polyatomic molecules on the SW defects was studied and compared with the adsorption on pristine BNNTs. Out of theoretical studies of molecular hydrogen adsorption on BNNTs, it was found that finetuning the pores (defects) can manipulate the hydrogen adsorption strength of BNNTs. Just recently, much improved reactivity has been suggested based on studies of Ni adsorption on (8,0) BNNTs. Not surprisingly, Pt-doped CNTs have already intrigued research interests after being proven to be good catalysts, potential gas sensors, and hydrogen storage materials. The carbon-doped BNNT was also found to be a better O₃ bearer than pristine BNNTs. Because BNNTs can be both p- and n-type doped, studies of Pt-doped BNNTs may reveal new materials with novel properties, not available to the only n-doping CNTs.

In this paper, we will further the understanding of how the catalytic activity of Pt, a widely used catalyst in the same group of Ni, varies on pristine and defective BNNTs. Pt absorption on pristine and SW-defective (5,5) BNNTs was studied using the spin-unrestricted DFT method. Adsorption strengths and electronic structures were investigated to illustrate the property change of Pt caused by the SW defect in the substrate BNNTs. In comparison, products and properties of doping of atomic Pt into B or N single-vacancies of BNNTs were also studied.

**Computational Details**

All calculations in the current study were carried out using the Gaussian 03 package. The spin-unrestricted Kohn–Sham (KS) equations were solved for the electronic structure. A hybrid functional, B3LYP, was used to approximate the exchange-correlation interactions. Wave functions were expanded in terms of the LanL2DZ atomic centered basis set of double-\(\zeta\) quality with the core electrons represented by the LanL2 effective core potentials.

A truncated (5,5) BNNT with 45 B and 45 N atoms was used to model the (5,5) BNNTs (Figure 1a). Both ends of the truncated BNNT segment were capped with H atoms to saturate dangling bonds. The chemical formula for both pristine and SW-
defective BNNT models is B45N45H20. To study Pt adsorption, a Pt atom was placed at various locations on the pristine BNNT or on top of the SW defect site. Atomic Pt doping into the B and N single vacancies of (5,5) BNNTs was also studied with their empirical formulas of PtB44N45H20 and PtB45N44H20, respectively. Binding energies were calculated by subtracting the electronic energies of the adduct from the sum of individual fractions. A positive binding energy indicates an exothermic adsorption and vice versa. Partial charges and spin densities were calculated based on the natural bond orbital analysis.

Results and Discussion

Pristine and SW-Defective (5,5) BNNTs. The optimized singlet pristine and SW-defective (5,5) BNNTs are shown in Figure 1. There are two nonequivalent B–N bonds in a pristine (5,5) BNNT: vertical B–N bonds perpendicular to the longitudinal direction of the tube (e.g., the bond between the B1 and N2 atoms in Figure 1a) and slant B–N bonds (e.g., the bond between the B1 and N3 atoms in Figure 1a). Bond lengths obtained in this study are 1.453 Å for the vertical bonds and 1.455 Å for the slant bonds, as shown in Table 1. These bond lengths are in fair agreement with those predicted from an early theoretical study at the PBE1PBE/6-31G(d) level.16 A 90° rotation of these two bonds results in two different SW defects: the type-1 SW defect (SW1) with a slant bond rotation (Figure 1e) and the type-2 SW defect (SW2) with a vertical bond rotation (Figure 1i). The formation of pentagons and heptagons violates the [4n + 2] aromatic rule and makes these defects less stable electronically compared with the perfect hexagonal structure with six π electrons. Moreover, the formation of the homonuclear N–N and B–B bonds “frustrates” the atoms of the SW defect due to the unfavorable electronic interactions in direct donor—donor and withdrawer—withdrawer contacts.8 The electronic energies of SW1 and SW2 were calculated to be 115.9 and 123.8 kcal/mol higher (less stable) than that of the pristine BNNT, respectively. An early study12 showed that the formation energy difference between slant and vertical SW defects decreases as the diameter of the BNNT becomes larger. Together with this early study, our result firmly indicates that the formation energy difference between SW1 and SW2 defects primarily lies in the different rolling-up strain of these two defects.

To investigate the electronic structure of pristine and SW-defective (5,5) BNNTs, the density of states (DOS) of each pristine and SW-defective (5,5) BNNT are shown in Figure 1. The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the pristine BNNT was calculated to be 6.02 eV, in good agreement with the experimentally measured value: 5.8 ± 0.2 eV.28 This brings us confidence in the results of our calculations. The HOMO of the pristine BNNT is composed of delocalized pπ orbitals of the N atoms, and the LUMO consists of the unoccupied pπ* orbitals of the B atoms. The energy difference between these two orbitals makes the pristine BNNT an insulator with a wide band gap. The HOMO–LUMO gaps of the SW-defective BNNTs are narrowed slightly because of the appearance of two island-like electronic states from the defect site. The HOMOs of the SW-defective BNNTs are primarily localized pπ* orbitals of the frustrated N atoms, and the LUMOs are mainly localized pπ orbitals of the frustrated B atoms. This computational result is consistent with the observations made from a scanning tunneling study.14 The orbital-energy-raised HOMO, the orbital-energy-lowered LUMO, and the locality of

<table>
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<tr>
<th>TABLE 1: Bond Lengths (in Å), Binding Energies (in kcal/mol), and Partial Charges on Pt for Pt Absorptions on Pristine (5,5) BNNTs at Different Sites</th>
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</thead>
<tbody>
<tr>
<td><strong>pristine BNNT</strong></td>
</tr>
<tr>
<td>-------------------------------------------------------------</td>
</tr>
<tr>
<td>binding energy</td>
</tr>
<tr>
<td>charge on Pt</td>
</tr>
<tr>
<td>B1–N2 distance</td>
</tr>
<tr>
<td>B1–N3 distance</td>
</tr>
<tr>
<td>N2–B5 distance</td>
</tr>
<tr>
<td>Pt–N2 distance</td>
</tr>
<tr>
<td>Pt–B1 distance</td>
</tr>
</tbody>
</table>

Symmetrically equivalent bonds are only listed once.

Figure 2. Optimized geometries, frontier orbitals, and density of states (DOS) of singlet Pt-adsorbed pristine (5,5) BNNTs. Purple, blue, and pink spheres represent Pt, N, and B atoms, respectively. Orbital energies are shown in the parentheses. In the DOS plots, black curves indicate the total DOS, whereas purple, blue, and green curves indicate Pt, N, and B local DOS, respectively. Red vertical lines mark the Fermi levels.
these two frontier orbitals slightly improve the reactivity of the SW-defective BNNTs compared with the pristine BNNT.

Pt Absorption on Pristine and SW-Defective BNNTs. Pt adsorption on pristine BNNTs results in two different singlet local minima, PtBNNTa and PtBNNTb, whose optimized geometries and frontier orbitals are shown in Figure 2. The Pt atom can either locate on top of an N atom (PtBNNTa) or bridge two adjacent B and N atoms (PtBNNTb). The geometric parameters can be found in Table 1. For the convenience of discussion, the N and B absorption sites are designated as N2 and B1 in Figure 1.

The partial charge analysis indicates only a small charge transfer between the Pt atom and the pristine BNNT. The binding energies for PtPBNNTa and PtPBNNTb are about 21.4 kcal/mol, much weaker than that obtained in an early study of Pt adsorption on the sidewall of a zigzag (8,0) BNNT, in which the Pt atom only bridged the two adjacent N–B pair. The weak dependence of the binding energy on the binding site signifies...
TABLE 2: Bond Lengths (in Å), Binding Energies (in kcal/mol), and Partial Charges on Pt for Pt Absorptions on Type-I SW-Defective (5,5) BNNTs at Different Sites

<table>
<thead>
<tr>
<th></th>
<th>SW1</th>
<th>PtSW1a</th>
<th>PtSW1b</th>
<th>PtSW1c</th>
<th>PtSW1d</th>
<th>PtSW1e</th>
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<tr>
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<tr>
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<td>0.174</td>
<td>0.204</td>
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<td>B1—N2 distance</td>
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<td>1.452</td>
<td>1.503</td>
<td>1.451</td>
<td>1.436</td>
<td>1.421</td>
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<td>1.687</td>
<td>1.702</td>
<td>1.691</td>
<td>1.694</td>
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<td>1.666</td>
<td>1.463</td>
<td>1.468</td>
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<tr>
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<td>1.466</td>
<td>1.476</td>
<td>1.460</td>
<td>1.470</td>
<td>1.496</td>
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<tr>
<td>Pt atop X—Y bond</td>
<td>B1—B3</td>
<td>B1—N2</td>
<td>N2—B5</td>
<td>B1—N4</td>
<td>N6—B16</td>
<td></td>
</tr>
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<td>2.033</td>
<td>2.214</td>
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<td>2.210</td>
<td>2.070</td>
<td>2.257</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3: Surrounding Bond Lengths (in Å), Partial Charges, and Spin Densities of Pt in Pt-Doped (5,5) BNNTs

<table>
<thead>
<tr>
<th></th>
<th>B substitution</th>
<th>N substitution</th>
</tr>
</thead>
<tbody>
<tr>
<td>charge on Pt</td>
<td>1.154</td>
<td>0.129</td>
</tr>
<tr>
<td>spin density on Pt</td>
<td>0.508</td>
<td>0.430</td>
</tr>
<tr>
<td>perpendicular bond length</td>
<td>2.080</td>
<td>2.124</td>
</tr>
<tr>
<td>slant bond length</td>
<td>1.969</td>
<td>2.001</td>
</tr>
</tbody>
</table>
achieved through introducing defect sites. Using BNNTs with or without the SW defects can adjust the catalytic ability of the supported Pt atoms to optimize reaction conditions for some reactivity sensitive reactions to satisfy the Sabatier principle.29

Pt-Doped (5,5) BNNTs. The doublet Pt-doped (5,5) BNNTs were also studied with their optimized structures shown in Figure 4. Some geometric parameters, partial charge, and partial spin density on the Pt atom are shown in Table 3, in good agreement with a recent theoretical study.21 The Pt atom can replace either a N atom (N substitution) or a B atom (B substitution). The N-substitution doping leads to a slightly positive partial charge accumulation on the Pt atom. The Pt–B bond lengths are comparable to those in PtSW1a. The spin density is primarily located on the Pt atom and its three surrounding B atoms. The Pt LDOS contributes greatly to the total DOS in the region from −12.0 to −3.0 eV, which indicates strong interactions between

Figure 4. Optimized geometries, frontier orbitals, and density of states (DOS) of doublet Pt-doped (5,5) BNNTs. Purple, blue, and pink spheres represent Pt, N, and B atoms, respectively. Orbital energies are shown in the parentheses. In the DOS plots, black curves indicate the total DOS, whereas purple, blue, and green curves indicate Pt, N, and B local DOS, respectively. Red vertical lines mark the Fermi levels. The curves above the x axis indicate α-spin DOS and those below, β-spin components.
the Pt atom and the N-vacant BNNT (Figure 4d). The α-spin HOMO comprises Pt 5d6s and 6p orbitals, which move the α-spin HOMO energy upward to −3.67 eV and make the Pt-doped BNNT a good electron donor. Ascribed to the constituent α-spin LDOS of the B atoms around the vacancy site and from the Pt 6s and 6p orbitals, the α-spin LUMO is also shifted upward to −1.74 eV and becomes less reactive toward nucleophiles. The β-spin HOMO is composed of the N pπ orbitals, similar to that of a pristine (5,5) BNNT. The β-spin LUMO is similar to the α-spin LUMO, but with more contributions from remote B atoms. The band gap is only about 1.9 eV, turning Pt-doped BNNTs semiconducting.

Replacing a B atom with a Pt atom also makes the Pt-doped BNNT semiconductor by lowering the energy of the α-spin LUMO. The α-spin HOMO is now composed of Pt 5d orbitals. The α-spin LUMO is made of Pt 5d orbitals and N pπ orbitals, which lowers its energy to −5.6 eV. On the other hand, the N contribution to the α-spin LUMO makes this Pt-doped BNNT a good electron acceptor. The β-spin HOMO is mainly from p orbitals of the N atoms around the vacancy site and Pt 5d orbitals. The β-spin LUMO energy is lowered by the participation of Pt 5d orbitals. In contrast to the small amount of charge transfer in the N-substitution doping, the Pt atom that substitutes for a B atom donates 1.15 electrons toward its bonding N atoms and the charge flow is also accompanied by the spreading of the spin density over the Pt and its three surrounding N atoms. The (positive) charge difference on the dopant Pt atom between the B-substitution and N-substitution doping cases can be well explained by the electronegativity disparity between boron and nitrogen. The more electronegative nitrogen atom withdraws more electrons from the Pt atom in the case of the B-substitution than the N-substitution doping. Both orbitals and electrostatic character favor nucleophilic attack: electron-rich molecules, such as N2 or CO, shall absorb strongly on the dopant Pt atom. In fact, Li et al. have found that Pt-doped BNNTs are good hydrogen storage materials because of the optimal binding energy for dihydrogen on these nanotubes.21

Conclusion

Spin-unrestricted hybrid DFT calculations were carried out to investigate the interactions between atomic Pt and the pristine, SW-defective, and vacancy-defective (5,5) BNNTs. By comparing the binding strengths, we conclude that Pt can move freely on the surface of a pristine BNNT or be trapped between the B–B bond at the defect site of an SW-defective BNNT with decreased reactivity. Electronic structures were studied by analyzing the DOS and frontier orbitals of these systems. The Pt atom can modify the electronic structures of the pristine and SW-defective BNNTs by introducing Pt states into the nanotube band gaps and can thus make these nanotubes more reactive.

Acknowledgment. Financial support for this project was provided by a grant from the Natural Sciences and Engineer Research Council (NSERC) of Canada.

References and Notes