Molecular orbital calculations of hydrogen storage in carbon and boron nitride clusters

Naruhiro Koi*, Takeo Oku

Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

Received 17 December 2003; revised 21 February 2004; accepted 23 February 2004
Available online 2 September 2004

Abstract

Hydrogen gas storage ability in carbon and boron nitride (BN) clusters was investigated by molecular orbital calculations. From single point energy calculations, H₂ molecules would enter from hexagonal rings of C₆₀ and B₃₆N₃₆ clusters and octagonal rings of B₂₄N₂₄ cluster because of lower energy barrier. Chemisorption calculation of hydrogen for BN clusters showed that hydrogen bonding with nitrogen atoms was more stable than that with boron atoms. Stability of H₂ molecules in BN clusters seems to be higher than that of carbon clusters.

Keywords: Hydrogen gas storage; Carbon; Boron nitride; Molecular orbital calculation

1. Introduction

In modern society, required energy is mainly obtained from fossil fuel. However, toxic gas such as carbon dioxide, nitrogen oxide and SOₓ are generated. On the other hand, hydrogen burns to form only water, and there is little influence on environment, and clean hydrogen energy is expected as substitute of fossil fuel in the 21st century. Gas storage ability more than 6.5 wt.% is needed for car application according to the US Department of Energy. Although LaNi₅H₆ is already used as H₂ gas storage materials, the ability is only 1 wt.% because of large atomic number of La and Ni. On the other hand, fullerene-like materials, which consist of light elements such as boron, carbon, nitrogen, would store more H₂ gas compared to the metal hydrides.

Much work has been reported on hydrogen storage ability of carbon (C) nanotubes, fullerenes and nanomaterials, as listed in Table 1 [1–7]. These results indicate the excellent storage ability of carbon nanotubes although the evaluation of hydrogen storage measurements is necessary. Recently, several studies on H₂ gas storage in boron nitride (BN) nanomaterials have been reported, as listed in Table 1 [8–12]. BN nanomaterials are expected in prospective application because BN nanomaterials provide good stability at high temperatures with high electronic insulation in air.

The purpose of the present work is to investigate H₂ gas storage ability of C/BN fullerene-like materials by molecular orbital calculation. Although huge amount of calculation is required to calculate nanotubes, it is considered that H₂ molecules enter from the cap of nanotubes. Barrier energy of ring structures, energy of chemisorption and stable hydrogen position inside the clusters were investigated in the minimum structure of nanotubes.

2. Calculating procedures

B₂₄N₂₄, B₃₆N₃₆ and C₆₀ were selected for cluster calculations. To investigate the optimized structures of C₆₀, B₂₄N₂₄ and B₃₆N₃₆, semi-empirical molecular orbital calculations (PM5) were performed by using MOPAC 2002 (Fujitsu Corp., Chiba, Japan). Energies of C₆₀, B₂₄N₂₄ and B₃₆N₃₆ with H₂ molecules were computed by first principal
single point energy (SPE) calculations using GAUSSIAN 98 (Gaussian, Inc., PA, USA). In the calculation, ‘6-31G(d)’ was used as ground function with Hartree-Fock level. Chemisorption calculations of hydrogen atoms were performed on boron and nitrogen position for BN clusters and carbon clusters by PM5 calculations [13]. For the stability calculations of H\textsubscript{2} molecules in these clusters, 30 H\textsubscript{2} molecules were also introduced in the clusters.

### 3. Results and discussion

C\textsubscript{60}, B\textsubscript{24}N\textsubscript{24} and B\textsubscript{36}N\textsubscript{36} clusters have energy barriers for H\textsubscript{2} molecules to pass through 4-, 5-, 6- and 8-membered rings. Fig. 1 is a structural model of a H\textsubscript{2} molecule passing from the hexagonal rings of C\textsubscript{60}, B\textsubscript{24}N\textsubscript{24} and B\textsubscript{36}N\textsubscript{36} clusters. Single point energies for C\textsubscript{60}, B\textsubscript{24}N\textsubscript{24} and B\textsubscript{36}N\textsubscript{36} clusters are summarized in Table 2. When H\textsubscript{2} molecules are set at the center and outside of the cage, the single point energy is equal. \( \Delta E \) is regarded as the energy barrier for H\textsubscript{2} molecules to pass through 4-, 5-, 6- and 8-membered rings. \( \Delta E \) of B\textsubscript{24}N\textsubscript{24} octagonal rings showed the smallest value in the present calculation. This result was reached because the octagonal rings of B\textsubscript{24}N\textsubscript{24} have a large ring size. Since single point energy is equal when H\textsubscript{2} molecules are set at the center and outside of the cage, the energy for H\textsubscript{2} discharge from fullerene-like materials is similar to that of H\textsubscript{2} storage.

![Fig. 1. Structural model of H\textsubscript{2} molecule passing from hexagonal rings of C\textsubscript{60}, B\textsubscript{24}N\textsubscript{24} and B\textsubscript{36}N\textsubscript{36}](image)

To investigate stability of H\textsubscript{2} molecules in clusters, energies were calculated for H\textsubscript{2} molecules placed in the center of clusters. Structural models are shown in Fig. 3(a)–(c). Energies of C\textsubscript{60}, B\textsubscript{24}N\textsubscript{24} and B\textsubscript{36}N\textsubscript{36} were calculated to be 0.58, −0.71, −0.93 eV/atom mol. This result indicates that B\textsubscript{24}N\textsubscript{24} and B\textsubscript{36}N\textsubscript{36} with H\textsubscript{2} molecules are more stable than C\textsubscript{60} with H\textsubscript{2} molecule. Energies of H\textsubscript{2} molecules absorption were calculated, and structural models are shown in Fig. 3(d)–(f). When more than 22 H\textsubscript{2} molecules were introduced in C\textsubscript{60}, hydrogen atoms chemisorbed inside the cluster. When more than 26 H\textsubscript{2} molecules were introduced in the C\textsubscript{60} clusters, 22 H\textsubscript{2} molecules were in the cluster and eight

### Table 1

Reported data for hydrogen storage in C/BN nanomaterials

| Structure                     | Hydrogen storage (wt.%) | Ref. |
|-------------------------------|-------------------------|------|
| Multi-walled carbon nanotube  | 2.5–4.6                 | [1,7]|
| Alkali-doped carbon nanotube  | 2.61                    | [2]  |
| Amorphous carbon nanotube     | 1.29–3.98               | [3]  |
| BN nanotube                   | 2.6                     | [8]  |
| BN nanotube and nanocapsule   | ~3                      | [10] |

### Table 2

Single point energy for C\textsubscript{60}, B\textsubscript{24}N\textsubscript{24} and B\textsubscript{36}N\textsubscript{36}

| Ring           | Center of cage | Ring | Outside of cage | \( \Delta E^a \) (eV) |
|----------------|----------------|------|-----------------|----------------------|
| C\textsubscript{60} | Pentagonal     | −61,891 | −61,871      | −61,891          | 20          |
|                 | Hexagonal      | −61,891 | −61,874      | −61,891          | 17          |
| B\textsubscript{24}N\textsubscript{24} | Tetragonal   | −51,806 | −51,780      | −51,806          | 26          |
|                 | Hexagonal      | −51,806 | −51,791      | −51,806          | 15          |
|                 | Octagonal      | −51,806 | −51,801      | −51,806          | 5           |
| B\textsubscript{36}N\textsubscript{36} | Tetragonal   | −77,707 | −77,680      | −77,707          | 26          |
|                 | Hexagonal      | −77,707 | −77,693      | −77,707          | 13          |

\( a \) \( \Delta E(\text{eV})=(\text{single point energy at ring})−(\text{single point energy at outside of cage}) \).
hydrogen atoms chemisorbed inside the clusters and C–C bond was broken. Maximum storages are nine hydrogen atoms for B24N24 and 20 hydrogen atoms for B36N36 as summarized in Table 4. Although hydrogen storage (wt.%) of C60 seems to be better than those of BN clusters in Table 4, increased energy by hydrogen addition per hydrogen atom is higher for C60 (4.6–5.2 eV/H atom) compared to BN clusters (3.0–3.1 eV/H atom), which indicates that needed energy for hydrogen storage is lower for boron nitride clusters.

Table 3
Chemisorption energy of hydrogen atoms on C60 and B24N24

|        | Number of hydrogen atoms | Additional position of hydrogen | Heat of formation (eV) Before addition | Heat of formation (eV) After addition | \( \Delta E \) (eV) |
|--------|--------------------------|---------------------------------|----------------------------------------|--------------------------------------|-----------------|
| C60    | 1                        | C                               | 35.21                                  | 35.03                                | −0.18           |
|        | 2                        | C                               | 35.21                                  | 35.81                                | 0.6             |
| B24N24 | 1                        | B                               | −36.12                                 | −34.66                               | 1.46            |
|        | 1                        | N                               | −36.12                                 | −35.67                               | 0.45            |

* \( \Delta E \) = (heat of formation after hydrogen addition) − (heat of formation before hydrogen addition).

hydrogen atoms chemisorbed inside the clusters and C–C bond was broken. Maximum storages are nine hydrogen atoms for B24N24 and 20 hydrogen atoms for B36N36 as summarized in Table 4. Although hydrogen storage (wt.%) of C60 seems to be better than those of BN clusters in Table 4, increased energy by hydrogen addition per hydrogen atom is higher for C60 (4.6–5.2 eV/H atom) compared to BN clusters (3.0–3.1 eV/H atom), which indicates that needed energy for hydrogen storage is lower for boron nitride clusters.

Table 3
Chemisorption energy of hydrogen atoms on C60 and B24N24

|        | Number of hydrogen atoms | Additional position of hydrogen | Heat of formation (eV) Before addition | Heat of formation (eV) After addition | \( \Delta E \) (eV) |
|--------|--------------------------|---------------------------------|----------------------------------------|--------------------------------------|-----------------|
| C60    | 1                        | C                               | 35.21                                  | 35.03                                | −0.18           |
|        | 2                        | C                               | 35.21                                  | 35.81                                | 0.6             |
| B24N24 | 1                        | B                               | −36.12                                 | −34.66                               | 1.46            |
|        | 1                        | N                               | −36.12                                 | −35.67                               | 0.45            |

* \( \Delta E \) = (heat of formation after hydrogen addition) − (heat of formation before hydrogen addition).

Fig. 2. Structural model of H atom chemisorbed on C60 and B24N24.

Fig. 3. Optimized structural model of H2 molecules in the clusters. A H2 molecule in the center of (a) C60; (b) B24N24; (c) B36N36; (d) 22 H2 molecules inside C60 and eight atoms chemisorbed; (e) nine H2 molecules in B24N24; and (f) 20 molecules in B36N36.
storage in BN clusters is lower. From Table 4, stability of H₂ molecules in B₂₄N₂₄ and B₃₆N₃₆ seem to be higher than that of C₆₀.

Carbon and BN fullerenes are sublimated at 600 and 1000 °C, respectively. BN fullerenes have higher thermal and chemical stability than those of carbon fullerenes. BN fullerenes with good thermal and chemical stability can store H₂ molecules with less energy, same chemisorption energy and higher stability, compared to carbon clusters. BN fullerene materials would be better candidates for H₂ storage materials.

4. Conclusion

Hydrogen gas storage ability in fullerene-like materials such as carbon and BN clusters was investigated by molecular orbital calculations. C₆₀, B₂₄N₂₄ and B₃₆N₃₆ clusters were selected as the tip structure of the nanotubes. Hydrogen chemisorptions and stability of H₂ in clusters were calculated, which showed that H₂ molecules enter from hexagonal rings of C₆₀ and B₃₆N₃₆ clusters and octagonal rings of B₂₄N₂₄ cluster because of lower energy barrier. BN clusters could store H₂ molecule easier than carbon clusters, and B₂₄N₂₄ cluster could store H₂ molecule easier than B₃₆N₃₆ cluster. Chemisorption calculation of hydrogen for BN clusters showed that hydrogen bonding with nitrogen atoms was more stable than that with boron atoms. Stability of H₂ molecules in BN clusters might be higher than that of carbon clusters. The present study indicates that the BN cage clusters would be one of the candidates of gas storage materials.

Acknowledgements

The authors would like to thank Mr A. Nishiwaki and I. Narita for many advices on calculations and warm encouragements. This work was partly supported by The Kansai Research Foundation for technology promotion.

References

[1] P.X. Hou, S.T. Xu, Z. Ying, Q.H. Yang, C. Liu, H.M. Cheng, Hydrogen adsorption/desorption behavior of multi-walled carbon nanotubes with different diameters, Carbon 41 (2003) 2471–2476.
[2] S. Challet, P. Azais, R.I.M. Pelleng, O. Isnard, J.-L. Soube roux, L. Duclau, Hydrogen adsorption in microporous alkali-doped carbons (activated carbon and single wall nanotube), in press J. Phys. Chem. Solids 65 (2004) 541–544.
[3] L. Ci, H. Zhu, B. Wei, C. Xu, D. Wu, Annealing amorphous carbon nanotubes for their application in hydrogen storage, Appl. Surf. Sci. 205 (2003) 39–43.
[4] G. Seifert, Hydrogen on and in carbon nanostructures, in press Solid State Ionics 168 (3–4) (2004) 265–269.
[5] M. Becher, M. Haluska, M. Hirscher, A. Quintel, V. Skakalov, U. Dettlaff-Weglikowska, X. Chen, M. Hulman, Y. Choi, S. Roth, V. Meregalli, M. Parrinello, R. Stro¨ bel, L. Jo¨ rissen, M.M. Kappes, J. Fink, A. Zettel, I. Stepneck, P. Bernier, Hydrogen storage in carbon nanotubes, C.R. Physique 4 (2003) 1055–1062.
[6] X. Li, H. Zhu, C. Xu, Z. Mao, D. Wu, Measuring hydrogen storage capacity of carbon nanotubes by tangent-mass method, Int. J. Hydrogen Energy 28 (2003) 1251–1253.
[7] W.Z. Huang, X.B. Zhang, J.P. Tu, F.Z. Kong, J.X. Ma, F. Liu, H.M. Lu, C.P. Chen, The effect of pretreatments on hydrogen adsorption of multi-walled carbon nanotubes, Mater. Chem. Phys. 78 (2002) 144–148.
[8] R. Ma, Y. Bando, H. Zhu, T. Sato, C. Xu, D. Wu, Hydrogen uptake in boron nitride nanotubes at room temperature, J. Am. Chem. Soc. 124 (2002) 7672–7673.
[9] T. Oku, M. Kuno, Synthesis, argon/hydrogen storage and magnetic properties of boron nitride nanotubes and nanocapsules, Diam. Relat. Mater. 12 (2003) 840–845.
[10] T. Oku, M. Kuno, I. Narita, Hydrogen storage in boron nitride nanomaterials studied by TG/DTA and cluster calculation, in press J. Phys. Chem. Solids 65 (2004) 549–552.
[11] I. Narita, T. Oku, Molecular dynamics calculation of H₂ gas storage in C₆₀ and B₂₄N₂₄, Diam. Relat. Mater. 11 (2002) 945–948.
[12] T. Oku, I. Narita, Calculation of H₂ gas storage for boron nitride and carbon nanotubes studied from the cluster calculation, Physica B 323 (2002) 216–218.
[13] J.J.P. Stewart, MOPAC 2002, Fujitsu Ltd, Tokyo, Japan, 2002.

Table 4

| Introduced H₂ | Optimized H₂ | Heat of formation (eV) | Hydrogen atoms chemisorbed inside cluster | Hydrogen storage (wt.%) | Heat of formation per added H atom (eV/H atom) |
|---------------|-------------|-----------------------|-------------------------------------------|------------------------|---------------------------------------------|
| C₆₀           | 0           | 35.21                 | 0                                         | 5.8–6.5                | 4.6–5.2                                      |
|               | 20          | 127.54                | 0                                         |                         |                                             |
|               | 22          | 143.01                | 0                                         |                         |                                             |
|               | 25          | 164.87                | 4                                         |                         |                                             |
|               | 26          | 169.63                | 8a                                        |                         |                                             |
|               | 30          | 165.59                | 4                                         |                         |                                             |
| B₂₄N₂₄        | 0           | 36.12                 | 0                                         | 2.9                    | 3.0                                         |
|               | 9           | −9.44                 | 0                                         |                         |                                             |
|               | 0           | −69.33                | 0                                         |                         |                                             |
| B₃₆N₃₆        | 20          | −6.66                 | 0                                         | 4.3                    | 3.1                                         |

* A C–C bond was broken.