Ni-dispersed fullerenes: Hydrogen storage and desorption properties

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Our study shows that the H_2 storage media using Ni-dispersed fullerenes could be viable alternatives to reversible hydrogen storage. It is demonstrated that a single Ni coated on the fullerene surface can store up to three H_2 molecules. Consequently, at high Ni coverage, Ni-dispersed fullerenes are considered to be the novel hydrogen storage media capable of storing ∼6.8 wt % H_2, thus exceeding the Department of Energy target (6.5 wt %) for automobile applications. Moreover, the H_2 desorption activation barrier of 11.8 kcal/mol H_2 is ideal for many practical hydrogen storage applications. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2168775]

Hydrogen, which can be readily produced from renewable energy sources and mainly produces water as a byproduct, contains much larger chemical energy per mass (142 MJ kg^{-1}) (Ref. 1) than any hydrocarbon fuel. Consequently, it is considered as an ideal fuel to solve energy and environmental problems in the earth that result from using petroleum fuels. Many hydrogen storage methods have been proposed, such as carbon-fiber reinforced high-strength containers,[2] liquid hydrogen,[3] chemical hydrides,[4] and carbon nanotubes (CNTs).[5] In particular, CNT has been suggested as the most promising nanostructure due to its cylindrical structure and high surface-to-volume ratio, which make it ideal for hydrogen storage. However, recent studies[5,6] indicate that the structure of a pristine CNT is not relevant to satisfy the Department of Energy (DOE) target (6.5 wt %) at ambient conditions ideal for many practical applications. This is because the pristine CNT has only the ∼0.8 wt % hydrogen available at ambient conditions.[5] However, we propose the use of nickel-doped fullerenes as the hydrogen storage media capable of exceeding the DOE target (6.5 wt %) at ambient conditions.

The recent experiment[6] proved that Ni-doped multi-walled (MW) CNTs with outer diameters of ∼20 nm could release 2.8 wt % H_2 at ambient conditions. We found that each Ni dispersed on the CNT surfaces has the high affinity for hydrogen by storing up to five H_2 molecules at ambient conditions. On the other hand, it was also determined that the insertion of H_2 into the interlayer of MWCNTs is thermodynamically unstable since it is an endothermic reaction by 24.9 kcal/mol H_2. Consequently, it is considered that Ni-dispersed MWCNTs could release over the 3 wt % if Ni nanoparticles could be dispersed on the surfaces of the CNTs grown in vertical shapes with reduced numbers of interlayers. However, the problem is that not all the techniques to control the growth directions and interlayers are available yet. On the other hand, unlike the CNT, a fullerene has always a single wall and its surface is isotropic; thus there is no need to reduce its interlayer and growth direction. Consequently, the fullerene is considered as a better nanostructure for Ni dispersion to maximize the hydrogen storage capacity than that for the CNT.

A recent study by Barajas-Barraza *et al.*[7] showed that up to 19 H_2 molecules could be stored in a C_{110} fullerene structure. Moreover, Narita *et al.*[8] showed through a molecular dynamic simulation study that H_2 is stable inside the C_{60} cage at ambient conditions. On the other hand, they also found that H_2 could not escape from the cage due to the high activation barrier of 369.1 kcal/mol H_2 for penetration through the cage; thus, using the inside of the cage as a hydrogen storage site is considered as impractical for many applications. On the other hand, the recent study[6] showed that Ni nanoparticles dispersed give the activation barrier of 8.7 kcal/mol relevant for hydrogen desorption at ambient conditions. In addition, a theoretical study[9] by Yildirim *et al.* also found that metals-dispersed nanostructures could be good hydrogen storage materials for practical applications.

To determine electronic wave functions, we use B3LYP (Ref. 10) and KMLYP (Ref. 11) density functional theory (DFT) methods with a split basis set of 6–31 G valence double zeta basis sets[12] for Ni and fullerene carbon atoms and 6–31 G** split valence double zeta basis sets[12] for hydrogen. The B3LYP is shown to accurately predict geometries and thermochemical data compared to generalized gradient approximation[13–17] (GGA) and local density approximation (LDA),[18,19] while the KMLYP has been proven to be more accurate in predicting transition state barriers[11] than other DFT methods. In addition, here our energies include zero point-energy (ZPE) corrections determined at fully optimized geometry with the same basis sets. We have chosen a C_{60} molecule with a diameter of 7.12 Å as the specific system for our study, as shown in Fig. 1. The fullerene has the two distinct bond lengths of 1.46 Å for C−C bonds and 1.40 Å for C=C bonds, which compare to the experimental values of 1.43 Å and 1.39 Å,[20] respectively.

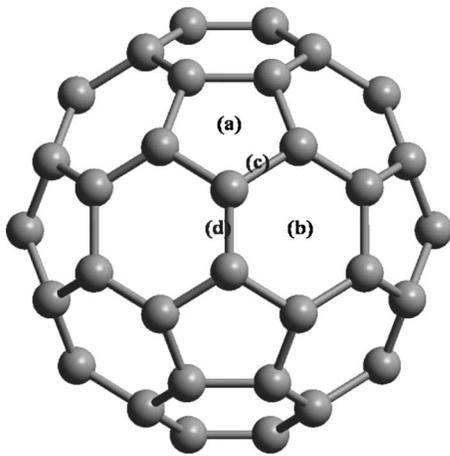[a)]Author to whom correspondence should be addressed; electronic mail: jeungku@kaist.ac.kr

FIG. 1. The optimized geometries for C_{60}. There are four stable positions for Ni dispersion at: (a) the center of pentagonal ring, (b) the center of hexagonal ring, (c) the edge between pentagonal and hexagonal rings, and (d) the edge between two hexagonal rings, where gray colors are for C atoms.

First, we have explored the hydrogen storage capacity on the pristine C_{60}. The physical adsorption reaction by a H_2 molecule on the outside surface of the fullerene was found to be unstable as it is endothermic by 0.7 kcal/mol H_2, while its corresponding chemical adsorption reaction was determined to have the exothermic enthalpy of 15.2 kcal/mol H_2. However, it was determined that chemical adsorption by H_2 molecules on pristine fullerenes has a high activation energy of 83.1 kcal/mol H_2. Consequently, using the computed partition functions for the reactants and the transition state, the reaction rate k of the canonical rate equation[21] is determined by

$$k = \Gamma(T) \frac{k_B T}{h} \frac{Q_{TS}}{Q_A Q_B} \exp\left(\frac{-\Delta E_0}{k_B T}\right), \qquad (1)$$

where $\Gamma(T)$ is the thermal tunneling coefficient,[22] Q_{TS} is the partition functional for the transition state, Q_A and Q_B are the partition functions for the reactants A and B, respectively, and ΔE_0 is the barrier height. The resulting dependence of chemisorption on pristine C_{60} is given by $k = 1.76$

$\times 10^{17} \exp(-83.1 \text{kcal/mol}/RT)(R = 2.0 \text{ kcal/mol K})$. In this respect, chemisorption on a pristine fullerene should occur at a very high temperature instead of at room temperature, which is consistent with the experimental results of Loutfy *et al.*[23]

Contrary to our previous study on the Ni-dispersed CNTs,[6] our theoretical calculations find that each Ni atom dispersed on a fullerene could store up to three H_2 molecules at temperatures up to room temperature, where spin-polarization effects were completely considered. Recently, Zhao *et al.* have also studied hydrogen storage properties on nickel-doped fullerenes.[24] On the other hand, it was assumed that the metal is the most stable on the center of the pentagonal rings of C_{60}. However, our first-principles calculations prove that the most stable sites for metal dispersion are edge sites between hexagonal rings instead of their assumed center of pentagonal sites. In fact, there are the four distinct sites for Ni dispersion in a C_{60}, as shown in Fig. 1: (a) the center of a pentagonal ring, (b) the center of a hexagonal ring, (c) the edge between hexagonal and pentagonal rings, and (d) the edge between two hexagonal rings. The Gibbs energy of ΔG for Ni adsorption is calculated by a following equation:

$$\Delta G_{\text{Ni adsorption}} = \Delta H - T\Delta S, \qquad (2)$$

where ΔH and ΔS are the enthalpy and entropy changes, respectively. The lowest enthalpy structure is found to be for the case (d), with the case (c) 10.4 kcal/mol, the case (a) 15.7 kcal/mol, and the case (b) 16.6 kcal/mol higher. Consequently, this indicates that the case (d) corresponds to the global minimum state. On the other hand, the largest diffusion barrier of Ni diffusion from the local minima in the above to the global minimum state (d) is determined to be very small (6.3 kcal/mol), thus implying that Ni in the local minimum states could easily transform to the global minimum state even at the very low temperatures larger than 109 K. In addition, the entropy difference of 0.03 kcal/mol K between the global minimum (d) and the dissociated state into a fullerene plus Ni atoms finds that the global minimum state for a Ni-dispersed fullerene could be stable up to 1176 K. The exothermic adsorption energy for Ni at the most stable position of (d) is 37.6 kcal/mol, and the distances be-
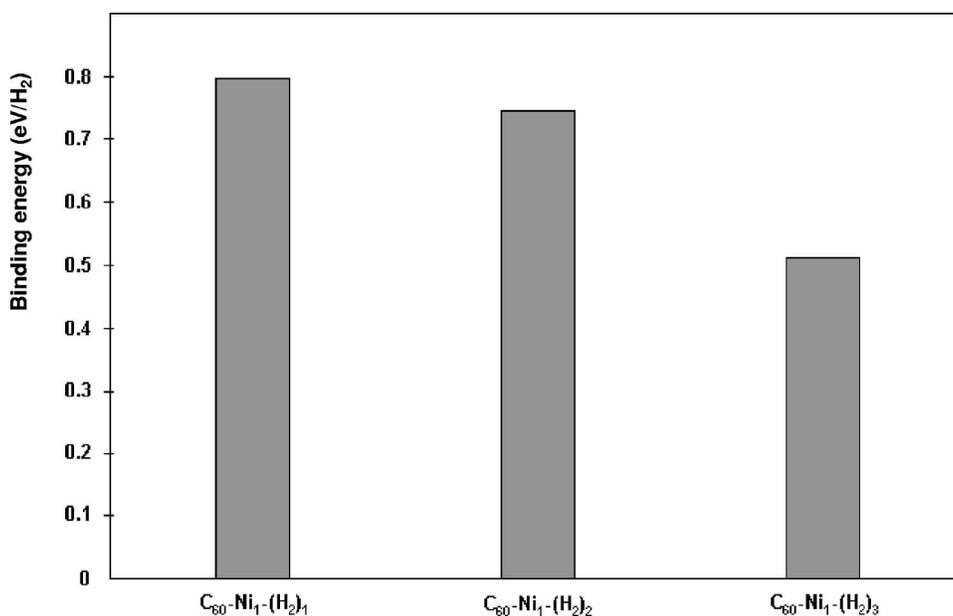

FIG. 2. Hydrogen adsorption energy per H_2 on the C_{60}-Ni_1-$(H_2)_n$ cluster, where n is 1 to 3.
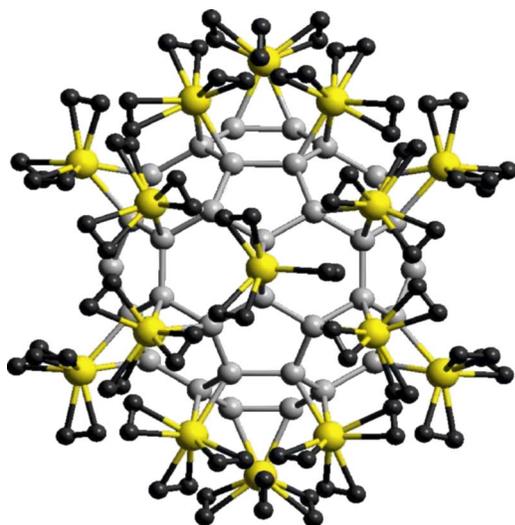
FIG. 3. (Color online) Hydrogenated Ni-dispersed C_{60}. Three hydrogen molecules could be adsorbed to a Ni atom. Carbon, nickel, and hydrogen atoms are shown in silver, yellow, and black, respectively.

tween Ni atoms and their nearest C atom are 1.82 Å. A C_{60} includes two different C—C and C=C bond characters. A C=C bond site in the edge between two hexagonal ring sites is found to be more favorable for metal dispersion.

In addition, we find that the Mulliken charge on Ni is 0.51. Consequently, the resulting dipole moment of 5.15 D from a Ni-C_{60} cluster, compared to the case of 0.002 D for the pristine C_{60}, is sufficient to enhance the van der Waal's interaction between hydrogen and Ni-C_{60}. We also determine the Ni adsorption energies of −47.5 kcal/mol Ni and −54.5 kcal/mol Ni for Ni_2 and Ni_3 nanoparticles, respectively. All Ni atoms in these cases were also found to be most stable at the edges of the same hexagonal ring sites, as in the case of the first Ni. The C-Ni and Ni-Ni bond distances for C_{60}-Ni_2 are determined to be 1.82 and 2.52 Å, while the C—Ni bond and Ni-Ni bond distances for C_{60}-Ni_3 are 1.88 and 2.53 Å, respectively.

Figure 2 shows the hydrogen adsorption behaviors as hydrogen molecules adsorbed in the C_{60}-Ni_1 cluster increase. The physisorption energy is calculated by a following equation:

$$\Delta H_{physi} = H_{tot}(H_2 + fullerene) - H_{tot}(fullerene) - H_{tot}(H_2)$$

(3)

where $H_{tot}(H_2 + fullerene)$ is the enthalpy of the fullerene-H_2 system at 298 K, H_{tot} (fullerene) is the enthalpy for the fullerene, and $H_{tot}(H_2)$ is the enthalpy for an optimized H_2 molecule. The binding enthalpy change of the first hydrogen molecule adsorbed by the nickel atom is determined to be 18.5 kcal/mol, which is lower than the result of Zhao *et al.*[24] by 31.8 kcal/mol. Zhao *et al.* have reported that Ni could store only one hydrogen molecule. However, our calculations show that Ni is more likely to store up to three hydrogen molecules rather than only one. This discrepancy appears to be reasonable. Zhao *et al.* assumed that Ni is the most stable at the center of a pentagonal ring in the fullerene, while our results show the edge between two hexagonal rings for the most stable site of the Ni atom, as mentioned above. Moreover, we find that three hydrogen molecules could be adsorbed around each Ni with its exothermic enthalpy of

11.8 kcal/mol H_2. It should be noted that this H_2-dispersed fullerene is in a global minimum state. The bond distance between hydrogen and Ni atoms ranges from 1.62 to 1.73 Å, while H—H bonds slightly elongate with bond distances ranging from 0.79 to 0.81 Å compared to the original H-H bond distance of 0.73 Å, which indicates that the bonds between hydrogen and Ni have both physical and chemical bond characters. In C_{60}-Ni_1, the dipole moment is calculated to be 4.40 D. In the case of C_{60}-Ni_2, it is also determined that three hydrogen molecules could be adsorbed around each Ni atom. The adsorption energy for this case is determined to be −9.7 kcal/mol H_2, and the bond lengths between hydrogen and Ni atoms range from 1.61 to 1.76 Å. In the C_{60}-Ni_3 cluster, each Ni atom also stores three hydrogen molecules with the enthalpy change of −7.6 kcal/mol H_2 and the bond distances ranging from 1.60 to 1.77 Å. Consequently, these results indicate that the Ni-dispersed C_{60} could store 90 hydrogen molecules attached to 30 Ni atoms, as shown in Fig. 3. Thus, this results in the hydrogen storage capacity is up to 6.8 wt %.

In conclusion, it was found that each Ni atom adsorbed three hydrogen molecules. These results indicate that a Ni-dispersed fullerene could have 6.8 wt % for its hydrogen storage capacity, which exceeds the DOE target. This enhanced hydrogen storage capacity is attributed to the fact that three H_2 could be adsorbed around each polarized Ni involving the charge transfer from fullerenes.

[1]L. Schlapbach and A. Züttel, Nature (London) **414**, 353 (2001).
[2]N. Takeichi, H. Senoh, T. Yokota, H. Tsuruta, K. Hamada, H. T. Takeshita, H. Tanaka, T. Kiyobayashi, T. Takano, and N. Kuriyama, Int. J. Hydrogen Energy **28**, 1121 (2003).
[3]S. M. Aceves, J. Martinez-Frias, and O. Garcia-Villazana, Int. J. Hydrogen Energy **25**, 1075 (2000).
[4]G. Sandrock and G. Thomas, Appl. Phys. A **72**, 153 (2001).
[5]Q. Wang and J. K. Johnson, J. Chem. Phys. **110**, 577 (1999).
[6]H. S. Kim, H. Lee, K. S. Han, J. H. Kim, M. S. Song, M. S. Park, J. Y. Lee, and J. K. Kang, J. Phys. Chem. B **109**, 8983 (2005).
[7]R. E. Barajas-Barraza and R. A. Guirado, Phys. Rev. B **66**, 155426 (2002).
[8]I. Narita and T. Oku, Diamond Relat. Mater. **11**, 945 (2002).
[9]T. Yildirim and S. Ciraci, Phys. Rev. Lett. **94**, 175501 (2005).
[10]A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[11]J. K. Kang and C. B. Musgrave, J. Chem. Phys. **115**, 11040 (2001).
[12]A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980); R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid*. **54**, 724 (1971); M. J. Frisch, J. A. Pople, and J. S. Binkley, *ibid*. **80**, 3265 (1984).
[13]A. D. Becke, J. Chem. Phys. **85**, 7184 (1986).
[14]J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[15]A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[16]P. M. W. Gill, Mol. Phys. **89**, 433 (1996).
[17]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[18]J. C. Slater, *Quantum Theory of Molecular and Solids: The Self-Consistent Field for Molecular and Solids* (McGraw-Hill, New York, 1974), Vol. 4.
[19]S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[20]J. M. Hawkins, Acc. Chem. Res. **25**, 150 (1992).
[21]K. J. Laidler, *Chemical Kinetics* (McGraw-Hill, New York, 1950), Chap. 3.
[22]J. K. Kang and C. B. Musgrave, J. Chem. Phys. **115**, 11040 (2001).
[23]R. O. Loutfy and E. M. Wexler, IEA Task 12 report, 2001 (unpublished), http://www.ieahia.org/pdfs/NN0094u.pdf.
[24]Y. Zhao, Y. H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. **94**, 155504 (2005).