DFT Study of the Effect of the Li$_{20}$ Coating Pattern on the Volume and Band Gap of C$_{60}$ Fullerene Cages

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Received November 21, 2012, Accepted December 18, 2012

Key Words : Li$_{20}$C$_{60}$ isomers, DFT calculations, Cage volume change

Hydrogen is a promising green energy source because of its abundance in nature. Hydrogen storage materials (HSM) have thus received much attention from researchers. The most remarkable theoretical reports of the HSM involve metal atoms coated on carbon fullerenes and nanotubes.$^{1-5}$ Alkali-metal-doped C$_{60}$ has received much attention as an HSM. Recently, the structure and electronic properties of Na$_8$C$_{60}$ and Li$_8$C$_{60}$ (n ≤ 12) nanoclusters in the framework of density-functional theory were reported.$^6$ Carbon-based nanomaterials are promising novel materials for hydrogen storage because of their surface-to-volume ratio and porosity along with other unique properties. Li$_{12}$C$_{60}$ and Na$_{12}$C$_{60}$ remarkably enhance hydrogen adsorption with a gravimetric density of approximately 9 wt %.$^7,8$ Previous studies on alkali-metal-doped C$_{60}$ nanoclusters suggested that, depending on their concentration, alkali metal atoms either homogeneously cover the surface of C$_{60}$ or form one or more metal islets in contact with the fullerene. A characteristic example of homogeneous contact is provided by Li$_{12}$C$_{60}$. Li-decorated C$_{60}$ is a candidate for hydrogen storage and has an icosahedral symmetry with each Li atom capping the 12 pentagonal sites of C$_{60}$. In Na$_{12}$C$_{60}$, the isomer with the lowest energy was reported to be made of 3 islands of 4 atoms, which implies that for each tetramer, 3 atoms are in contact with C$_{60}$, 2 via a pentagonal ring and 1 via a hexagonal ring, whereas the fourth atom is capped over the other metal atoms.

Thus, we have investigated C$_{20}$Li$_{20}$ cage regioisomers to determine the effect of the coating pattern of alkali metals on the volume and energy band gap of the C$_{20}$ cage. In this study, we obtained 2 cage regioisomers, C$_{20}$Li$_{20}$ and Li$_{12}$Li$_8$C$_{20}$, which could be interesting candidates for HSM. To our knowledge, previous studies have not analyzed the effect of the coating pattern of alkali metals on the cage volume and HOMO-LUMO energy gap of the fullerene cage. Here, we study these effects for Li$_{12}$C$_{20}$ and Li$_{12}$Li$_8$C$_{20}$ fullerene cages. We used the hybrid density-functional theory (DFT) with Becke’s 3-parameter hybrid method and the Lee-Yang-Parr exchange-correlation functional theory (B3LYP)$^9,10$ to optimize the geometries of the Li$_{12}$C$_{20}$ regioisomers. The electron basis set 6-311G(d,p) was used in this study.$^{11}$ We fully optimized the geometries of C$_{20}$Li$_{20}$ without constraints, using the Gaussian 03 B.04 package suite.$^{12}$ To obtain highly accurate geometries, we used the convergence criterion with tight optimization and an ultrafine pruned (99,590) grid (using the keywords Opt = Tight, Grid = ultrafine). We analyzed the relative energies, charge transfer and the HOMO and LUMO orbitals of the regioisomers.$^{13}$

Here, we obtained 2 optimized cluster geometries and relative energies, which are shown in Figure 1. One geometry is a homogeneous coating of Li atoms on C$_{20}$, which is represented by Li$_{12}$C$_{20}$, and the other geometry is the formation of Li tetrahedral droplets on the surface of the cage, which is represented Li$_{12}$Li$_8$C$_{20}$. Both the clusters are in the T$_h$ point group. The total energy of the Li$_{12}$Li$_8$C$_{20}$ cage isomer is 3.61eV lower than that of Li$_{12}$C$_{20}$. As shown in Table 1(a), the volume of the C$_{20}$ cage fragment in C$_{20}$H$_{20}$, Li$_{12}$Li$_8$C$_{20}$, and Li$_{12}$C$_{20}$ cages is 23.9, 9.8, and 3.9%, respectively, which is higher than the corresponding volume of C$_{20}$. As shown in Figure 1, the bond lengths of C-Li and

![Figure 1. Local minimum energy structures of C$_{20}$Li$_{12}$Li$_8$ and C$_{20}$Li$_{12}$](http://dx.doi.org/10.5012/bkcs.2013.34.2.365)
C-C in the C_{20}Li_{2}C_{20} cage are 1.49 and 2.16 Å, respectively, whereas those in Li_{12}Li_{4}C_{20} are 2.11 Å for C-Li of Li_{4}, 1.46 Å for 2 C-C, and 1.54 Å for 1 C-C among the 3 C-C bonds around C-Li of Li_{4}.

As shown in Table 1(b), the HOMO-LUMO energy gap in C_{20}, C_{20}H_{20}, Li_{12}Li_{4}C_{20}, and Li_{12}C_{20} cages was 1.67, 7.99, 0.47, and 1.53 eV, respectively. Hydrogen adducts on C_{20} increase the HOMO-LUMO gap, whereas Li adducts on C_{20} decrease the gap, which implies that the coating of both Li atoms on the C_{20} cage induces kinetic instability. Although the homogeneously coated Li_{12}C_{20} is seriously and kinetically unstable, C_{20} coated with tetrahedral Li droplets is slightly unstable when compared with C_{20}. In C_{20}H_{20} and Li_{12}C_{20} cages, the Mulliken charges of all the H and Li atoms are the same, i.e., 0.08 per atom, and those of all C atoms are -0.08 per atom, which implies that all H and Li atoms are electron donors and that the C_{20} cage is an electron acceptor. However, in Li_{12}Li_{4}C_{20}, the C_{20} cage fragment accepts -0.03 electrons per atom, whereas the Li atoms of Li_{12} and Li_{4} accept -0.21 electrons per atom and donate 0.23 electrons per atom, respectively. Thus, the environment of the Li atoms in the Li_{12}Li_{4}C_{20} cage cluster affects the electronic properties of the Li atoms, which show electron acceptor and donor properties depending on where they exist. This charge pattern is topologically identical to that of C_{60} in contact with alkali metal clusters. Therefore, owing to the particular electronic structure of Li_{12}C_{20} cage isomers, it is expected that the investigation of hydrogen adsorption on these Li_{12}Li_{4}C_{20} and Li_{12}C_{20} cage isomers will be of particular interest.

In summary, we investigated the atomic structure and electronic properties of C_{20}Li_{12}C_{20} cage isomers. Two isomers were used: C_{20} homogeneously coated with Li and C_{20} coated with tetrahedral clusters of Li. Greater volume change was observed for C_{20} homogeneously coated with Li. The volume of both the isomers increased when they were compared with that of C_{20} but decreased when compared with that of C_{20}H_{20}. Although the HOMO-LUMO energy gap of C_{20} increased in C_{20}H_{20}, it decreased in both Li_{12}C_{20} and Li_{12}Li_{4}C_{20}. The HOMO-LUMO gap of Li_{12}Li_{4}C_{20} was slightly larger than that of Li_{12}C_{20}. The Mulliken charge of carbon atoms directly connected to Li atoms was positive in Li_{12}Li_{4}C_{20} but negative in C_{20}H_{20} and Li_{12}C_{20}.

Acknowledgments. This work was supported by Wonkwang University in 2010.

References