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Chemical Reaction of Intercalated Atoms at the Edge of Nano-Graphene Cluster

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The chemical reactions of halogen molecules on a nano-graphite cluster are calculated using a semi-empirical calculational method. A real time calculation of the chemical reaction of halogen molecules up to 200 fs which is performed by the dynamic reaction coordinates (DRC) method of the quantum chemistry library shows that the iodine molecule exhibits a special reaction involving the removal of hydrogen atoms from edge carbon atoms. This result might be relevant to recent experiments on the graphitization of pitch at a low temperature of 400°C. We discuss the deformation of the nano-graphite cluster upon the intercalation of halogen atoms.

Keywords: nano-graphite; halogen atoms; chemical reaction; MOPAC; DRC

INTRODUCTION

Recently, non-crystalline graphite clusters with diameters in the nanometer range have attracted much interest with regard to many possible applications as mesoscopic materials. Low dimensionality and finite size effects of nano-size graphite (hereafter called nano-graphite) show new solid properties which are not observed in the macroscopic properties of graphite intercalation compounds(GICs). In this paper we focus our attention on acceptor-type nano-graphite on which an interesting chemical reaction occurs with an iodine molecule at the edge of the nano-graphite cluster.

Takai et al.[1] have observed unpaired spins in fluorine(F)-doped activated carbon fibers (ACFs) in ESR experiments. Since there are many edges or pores at the ACF surface, we can consider ACFs as a kind of nano-graphite structure. In fact, these authors were able to dope F atoms up to the ratio of F/C = 1.2.[1] They found that the number of unpaired spins observed in their magnetic susceptibility experiment increases from a small value at F/C=0.4 to reach a maximum at F/C=0.8, and then decreases up to the saturated value of F/C=1.2. This result clearly shows that the occurrence of unpaired spins comes not from the dangling bonds of the nano-graphite, but rather from another origin, such as an electron localized at an F site.

In a previous paper we have calculated the electronic structure of an F doped nano-graphite and have found that a local deformation of the σ-bond from the sp^2 to the sp^3 configuration occurs for a carbon atom at the doped site.[2] By adding fluorine atoms one by one, we found that the fluorine atoms first terminate at edge sites of the nano-graphite cluster, and then interior carbon atoms become doped by the added fluorine atoms by breaking the π bonds between a carbon atom and its neighboring carbon atoms. However, we did not discuss the localized properties of electronic states around the halogen atoms, which is now discussed in terms of the local density of states (LDOS) in this paper by making a comparison with other halogen atoms.

Yasuda et al.[3] show in their iodine treatment of coal tar pitch at a low temperature of 100°C and subsequent 0.25°C/min heating process up to 800°C, that hydrogen atoms are removed from the coal tar pitch, and that graphitization occurs, while no such transformation occurs when the coal tar pitch is heated without the iodine treatment. Usually graphitization occurs at more than 2000°C for undoped graphite. Nano-graphite clusters, consisting of several layers of graphitic planes with a small area, are obtained by the heat treatment of various pregraphitic carbons, such as poly-paraphenylene (PPP)[4] and phenol-formaldehyde (polyacenic semiconductors, PAS) [5], at temperatures from 700°C to 900°C, where the hydrogen atoms of the precursor hydrocarbon molecules are dissociated from the carbon atoms,[6] and the nano-graphite is formed by connecting the dangling bonds of the carbon atoms thus generated. However, the detailed mechanism of the reaction of iodine in the coal tar pitch and in other hydrocarbons is not clear. It is, however, clear that iodine atoms play a role in removing the hydrogen atoms at low temperature, and we investigated the corresponding chemical reaction.

In the next section we briefly show the method that we adopted and present the calculated results. Finally a summary is given.

METHOD

For our calculations we mainly adopt a hexagonal $C_{24}H_{12}$ cluster (see Fig. 1) in which 12 carbon atoms are terminated by hydrogen atoms at the edge, and the other 12 carbon atoms are located in the interior region of the cluster. Since the halogen atoms in the nano-graphite are localized around the chemical bonds, we can consider the chemical reaction between halogen molecules and a nano-graphite cluster even for the $C_{24}H_{12}$ cluster. In fact, we get a similar local deformation of the lattice for the $C_{54}H_{18}$ cluster. It is noted that the cluster size of $C_{24}H_{12}$ is not sufficient for donor atoms, since the transferred charge from alkali ions to the nano-graphite are delocalized on the cluster.[7].

The bond lengths and bond angles are optimized by using the semi-empirical quantum chemistry library, MOPAC93, in which the parametric method 3 (PM3) for an inter-atomic potential is adopted for the present calculation.[8] We also checked some geometries by an ab-initio calculation to obtain the same optimized geometry and ionicity within the accuracy discussed in this paper. The chemical reaction is calculated for a halogen molecule (I_2 and F_2) with different initial positions and velocities, in which the dynamic reaction coordinate (DRC) method is adopted in the calculation for times up to 200 fs.

CALCULATED RESULTS

When we put a halogen atom on an interior carbon atom denoted by C_0 of the $C_{24}H_{12}$ cluster as shown in Fig. 1, the optimized position of the halogen atom is not above the center of a hexagonal ring of the carbon atoms, as is commonly observed in alkali-metal doped GICs, but rather above the carbon atom C_0, suggesting that a covalent sp^3 bond forms between the carbon and the halogen atom[2].

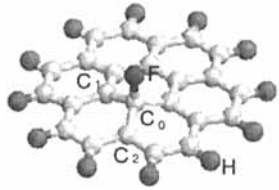

Fig. 1: $C_{24}H_{12}F$ cluster

X	F	Cl	Br
d(X-X) [Å]	1.41	1.99	2.28
Ionicity	−0.15t	−0.07	−0.17
X−C_0 [Å]	1.39	1.87	2.13
$\angle XC_0C_1$ [°]	107	104	98
$\angle C_1C_0C_2$ [°]	112	115	118

Table 1: Optimized geometry of the cluster

The optimized geometry for a halogen atom (X=F, Cl, Br) on the nano-graphite depends on the ionicity and the radius of the halogen atom. In Table 1 we show the inter-atomic distance of a X_2 molecule and the calculated ionicity and geometries for the $C_{24}H_{12}X$ cluster. The inter-atomic distances are relevant to the covalent bonding of the molecules and thus they can be directly compared with the covalent bonding length X−C_0. Since the inter-atomic C−C distance is 1.42 Å or 1.54 Å for sp^2 or sp^3 covalent bonding, respectively, the difference between X−X and C−X depends on the distance of X−X and the hybridization of the carbon atom. The corresponding bond angles of XC_0C_1 and $C_1C_0C_2$ (see Fig. 1) are close to the sp^3 bond angles (109.6°) for a F atom and for sp^2 bond angles (90, 120 degrees for XC_0C_1 and $C_1C_0C_2$ angles, respectively) for a Br atom, which reflect the ionic radius. The optimized C_0−F, C_0−C_1 and C_0−C_2 bond lengths are 1.388, 1.518, 1.520 Å, respectively. The C_0−F bond length is close to the sum of the ionic radius of F (0.68 Å) and half of the C–C distance of graphite (0.71 Å), and the C_0−C_1 and C_0−C_2 bond lengths are slightly smaller than the nearest-neighbor distance of diamond, 1.544 Å, due to the positive ionicity of the carbon atoms.

The one-electron energy states of the $2s$ and $2p$ orbitals of the fluorine atom are coupled with the σ orbitals of carbon. In fact, the local density of states (LDOS) of the C_0 atom shows the disappearance of the π component and an increased width of the σ states upon F doping. The disappearance of the π component in the case of Cl and Br atoms occurs partially, and some π components of the LDOS remain in the energy region of the carbon π orbitals, showing the intermediate hybridization between the sp^2 and sp^3 bonds. It is important to note here that the LDOS at the nearest-neighbor carbon site, C_1, has π character at the original energy region even for F doping. Although the LDOS spectra are different for the different halogen atoms, the absolute values for the LDOS for F, Cl, and Br are similar to each other and that of the undoped cluster. Thus

we can conclude that the deformation of the sp^3 covalent bond is localized only at the bonded carbon sites.

The lack of π bonding at the C_0 site implies the absence of electron spin on the cluster, which can generally be applied to the modulation of the π conjugated system. Thus we expect spin density compensation around the C_0 site. Although the UHF calculation of MOPAC93 is not sufficiently accurate for discussing the spin density quantitatively, we can see a spin density oscillation over the cluster on the A and B sublattices of graphite. In fact, when we put the two F atoms on the cluster, either the spin triplet ($S = 1$) or singlet ($S = 0$) states gives the ground state, depending on whether two F atoms are on the same sublattice or not, respectively. In particular, two F atoms doped on nearest neighbor carbon atoms have an $S = 0$ ground state, while those on the next nearest neighbor sites give a $S = 1$ ground state. Although the energy difference between the spin singlet and spin triplet states decreases with the distance between the two F atoms, it is important to consider this situation to account for the occurrence of unpaired spins in a nano-graphite cluster experimentally.[1]

When we calculate the electronic structure for the iodine doped cluster, we did not get the optimized geometry. This means that there is no possibility for stabilization of an sp^3 covalent bond between C_0 and the iodine atom, since the radius of iodine (I–I distance = 2.67 Å) is large compared with the lattice constant (2.46 Å) of the graphite cluster and since the ionic coupling of iodine atoms with the graphite cluster is preferable. Since the potential barrier for a single iodine atom moving in the direction parallel to the graphene plane is very small compared with the potential perpendicular to the plane, it is difficult to find the optimized position of iodine atoms in the calculation. In the interior region of nano-graphite, only the charge transferred iodine complexes might be observed.[3]

In order to understand the experimental observation of the graphitization of the coal tar pitch at low temperatures, we investigated the chemical reactions of an iodine molecule at the edges of the nano-graphite. Since the dangling bond formation of carbon atoms at the edges is needed for the graphitization, the iodine atoms should play a role for removing hydrogen atoms at the edge sites.

We consider the following two models for removing the hydrogen atoms upon iodine doping. One is the charge transfer model and the other is the chemical reaction model. In the charge transfer model, when the iodine molecules accept electrons from the nano-graphite cluster, the nano-graphite has a positive charge, which weakens the C–H covalent bonding. However it is not always true that the transferred positive charge to nano-graphite appears at the edges, although the edge states of the non-doped graphene zigzag edges appear at the Fermi energy[9]. This is because the negative I_2^- molecules attract positive charges. Since we did not get the optimized geometry of the iodine molecule for the $C_{24}H_{12}X$ cluster, we cannot estimate the charge transfer effect for such a small cluster. However, we do believe that the charge transfer effect cannot be consistent with the two heating processes in the experiment[3].

On the other hand, according to the chemical reaction model, the iodine atom directly reacts with the hydrogen atom. Although the C–H covalent bond is stronger than the C–I bond, the mass of the iodine atom is sufficiently large that

the iodine atom may be expected to knock the hydrogen atom off by an interatomic scattering process. We now try to model this reaction by a computer experiment.

In Fig. 2 we show results for the chemical reaction between an I_2 molecule and a $C_{24}H_{12}$ cluster. The result is given for an initial kinetic energy of the I_2 molecule of 120 kcal/mol and assuming for simplicity that the iodine molecule moves along the graphite plane without rotation. Further we assume that initially there is no atomic vibration of the $C_{24}H_{12}$ cluster. These assumptions are not realistic for chemical reactions at finite temperatures. However, the chemical reaction does not always occur within the limited computational time, and for most cases, the iodine molecule moved away from the cluster without any chemical reaction. Further, the chemical reaction itself has many reaction paths around the saddle point of the potential barrier (minimum energy required for the reaction), and the chemical reaction occurs as a rare process among the many scattering processes. In this sense the initial kinetic energy of the I_2 molecule is taken to be one-order of magnitude higher (about 10,000 K) than the expected reaction temperature.

In Fig. 2 the chemical reaction proceeds as follows: (1) the iodine molecule approaches the cluster, (2) one iodine atom pushes the hydrogen atom away and makes a chemical bond with the adjacent carbon atom, (3) the hydrogen atom changes its bond from the carbon atom to the iodine atom, and (4) the covalent bond between the two iodine atoms is broken. In the cluster of (4), the ionicity of the carbon, iodine and hydrogen atoms are -0.33,$+0.49$ and -0.22, respectively. Thus we can say that the bonding between carbon and iodine atoms is rather ionic and that a charge transfer complex is formed.

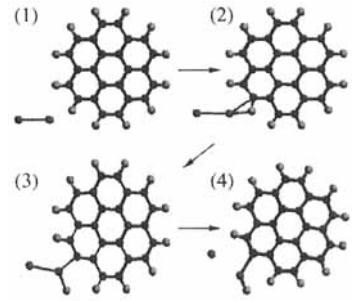

Fig.2 A chemical reaction of an I_2 molecule (left bottom of each figure).

Then we restart from the cluster of (4) of Fig. 2 by specifying the kinetic energy, and we found that the H–I bond is first dissociated, and then the C–I bond is dissociated. In this computer experiment, we started with a very large initial kinetic energy, so that we can observe the dissociation during the first few vibrations. The temperatures corresponding to the initial kinetic energies necessary to dissociate the I–H, C–I, and C-H (or C–C) bonds are 900-1500, 2500-3000, and 9000-11000 K, respectively. Although the initial kinetic energy is not realistic for simulating the experiment, the relative strengths of the chemical bonds are consistent with the experimental values. It is clear that the hydrogen atom of the I–H bond can be dissociated much easier than in the C–H bond. The atomic hydrogen can thus quickly form a H_2 or a HI molecule by the first process or at a lower temperature by the second process. In the subsequent heat-up, the C–I bond is broken and the graphitization process may occur. In this way, this chemical reaction seems to be consistent with the experimental processes.

This hydrogen removal process can occur through the chemical reaction with

a F_2 molecule. When we put a F_2 molecule with the same kinetic energy of 120 kcal/mol at the edge of the nano-graphite cluster, the F_2 molecule does not make a chemical bond with the carbon atom, but instead two HF molecules form. Although this process can make dangling bonds, once the dangling bonds are formed, they are quickly terminated by the other fluorine atoms, which can not contribute to the graphitization. Thus the weak interaction of iodine with the carbon atom seems to be essential for the graphitization at low temperature.

SUMMARY

In summary we considered the chemical bond between halogen atoms and other species on the nano-graphite cluster. The chemical bond made by the halogen atom depends on its ionic properties. In particular, the iodine has a special chemical reaction at the edge sites of nano-graphite. Although our investigation of the chemical reaction is only an example of the large number of chemical reaction paths, the findings that C–I ionic bonds form, and that subsequently the process of removing hydrogen atoms, both seem to be essential steps for the low temperature graphitization process. It would be desirable to seek further experimental evidence in the future for the formation of C–I ionic bonds in the first very low temperature graphitization process.

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