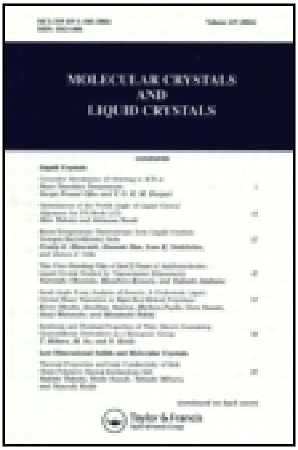

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Rare gas storage and chemical reaction using nanospace in C 60 lattice

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RARE GAS STORAGE AND CHEMICAL REACTION USING NANOSPACE IN C_{60} LATTICE

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We demonstrated that rare gas (RG) occluded in the C_{60} lattice has a chemical interaction with C_{60}. In order to evaluate the interaction between RG and C_{60}, we calculated the electronic state of $C_{60}(RG)_n$ (n = 1,2,3) crystals. RG atoms in $C_{60}(RG)$ (RG = He, Ne, Ar) are neutral, whereas those in $C_{60}Kr$ and $C_{60}Xe$ have positive Mulliken charges of 0.99 and 1.04, respectively. For $C_{60}(RG)_2$ and $C_{60}(RG)_3$, a slightly positive charge of 0.02 appeared on Ar atom in $C_{60}Ar_2$ and $C_{60}Ar_3$. The chemical reaction such as a hydrogenation of CO to CH_4 was found to occur in the nanospace of C_{60}-sodium-hydrogen.

Keywords: fullerene; C_{60}; rare gas; nanospace; first principle calculation; chemical reaction

INTRODUCTION

In the measurement of thermal desorption (TD) for C_{60}-sodium-hydrogen ternary superconductor, we noticed that the samples include a trace of argon because of a handling in a glove box filled with argon gas. Then we detected stoichiometric amounts of RG in C_{60} powders exposed to RG under ambient pressure at 473 K. Interestingly, RG seems to chemically

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interact with C_{60} from the experimental results of gas desorption peak at high temperature by TD, large chemical Shift of $Ar2_P$ band by XPS and weak signal by ESR for the C_{60}-Ar compound [1,2]. On one hand, C_{60}-sodium-hydrogen compound includes catalytic sodium ion and chemically active hydride ion in the octahedral site [3]. We thought that a chemical reaction would occur in this nanospace by introducing various gases.

In this paper, we present the results of the electronic state calculation of $C_{60}(RG)_n$ (n = 1,2,3) crystals to evaluate the interaction between RG and C_{60}. The results of a chemical reaction using C_{60}-sodium-hydrogen system is also presented.

EXPERIMENTAL

C_{60} and C_{60}-RG crystals were built by Crystal Builder in a Cerius2 software. They were geometrically optimized and their electronic states were calculated by CASTEP in the Cerius2 with a first principle theory based on a density functional method within a local density approximation using an ultrasoft pseudopotential.

C_{60}-sodium-hydrogen compound was prepared by direct reaction of C_{60} and sodium hydride (NaH) [4]. C_{60}-Na-H powders were exposed to 0.1 atm CO or N_2 gas at 473 K for three days. The gases after reaction were analyzed by thermal desorption apparatus equipped with mass-spectrometers and pressure gauges.

RESULTS AND DISCUSSION

1. Interaction Between RG and C_{60}

C_{60} crystal with a lattice constant $a = 14.16$ Å and a space group $Fm\bar{3}$ was built using three atomic coordinates of C1 (0, 0.049, 0.245), C2 (0.217, 0.080, 0.094) and C3 (0.184, 0.151, 0.052) which were refined by Reitveld analysis for $C_{60}Na_{3.6}H$ superconductor [5]. a of the optimized C_{60} crystal was 14.207 Å. In the same way, we built $C_{60}(RG)_n$ (n = 1,2,3) crystals. They are C_{60}(RG) in which one RG atom is placed at an octahedral (O) site, $C_{60}(RG)_2$ with one RG atom at a tetrahedral (T) site and $C_{60}(RG)_3$ with each one RG atom at both sites. Table 1 listed total energy (TE), a and charge (ρ) on RG atom obtained by Mulliken population analysis for the geometrically optimized $C_{60}(RG)_n$ (n = 1,2,3) crsytals. As for C_{60}(RG), RG atoms in C_{60}He, C_{60}Ne and C_{60}Ar are neutral, whereas those in C_{60}Kr and C_{60}Xe have positive Mulliken charges of 0.99 and 1.04, respectively. As for $C_{60}(RG)_2$, a slightly positive charge of 0.02 in $C_{60}Ar_2$ appears and positive

TABLE 1 Calculated Values of Total Energy (TE), Lattice Constant (a) and Mulliken Charge (ρ) on RG Atom for C_{60}(RG), $C_{60}(RG)_2$ and $C_{60}(RG)_3$

Compounds	TE (eV)	a (Å)	ρ
$C_{60}He$	−9383	14.208	0.00
$C_{60}Ne$	−10261	14.207	0.00
$C_{60}Ar$	−9881	14.207	0.00
$C_{60}Kr$	−9810	14.214	0.99
$C_{60}Xe$	−9734	14.221	1.04
$C_{60}He_2$	−9459	14.210	0.00
$C_{60}Ne_2$	−11214	14.278	0.00
$C_{60}Ar_2$	−10456	14.386	0.02
$C_{60}Kr_2$	−10313	14.521	1.24
$C_{60}Xe_2$	−10159	14.575	1.28
$C_{60}He_3$	−9535	14.234	0.00[a)], 0.00[b)]
$C_{60}Ne_3$	−12167	14.298	0.00[a)], 0.00[b)]
$C_{60}Ar_3$	−11029	14.305	0.00[a)], 0.02[b)]
$C_{60}Kr_3$	−10815	14.484	0.95[a)], 1.50[b)]

[a] charge on RG atom in the O-site.
[b] charge on RG atom in the T-site.

charges in $C_{60}Kr_2$ and $C_{60}Xe_2$ increase to 1.24 and 1.28. As for $C_{60}(RG)_3$, the charges on RG atoms in the O-site and the T-site correspond to those of C_{60}(RG) and $C_{60}(RG)_2$.

Although we must consider the ambiguity in ultrasoft pseudopotential method and Mulliken population analysis, the positive charge on RG atom increases in the sequence He, Ne $<$ Ar $<$ Kr $<$ Xe. The positive charge on RG atom and the negative charge on C_{60} molecule indicate the charge-transfer (CT) state between RG and C_{60}. According to the theory of CT between a donor and an acceptor [6], the degree of CT depends on the difference (I_P-E_A) between an inonization potential (I_P) of RG and an electron affinity (E_A) of C_{60}. A smaller value of (I_P-E_A) gives a larger degree of CT. In the present system, E_A is constant and I_P decreases in the sequence He $>$ Ne $>$ Ar $>$ Kr $>$ Xe. The magnitude of Mulliken charge on RG atom in $C_{60}(RG)_n$ ($n = 1,2,3$) is qualitatively explained with (I_P-E_A).

The calcualtion predicts the observation of strong ESR signal in $C_{60}Kr_n$ and $C_{60}Xe_n$. We are now in progress to prepare these compounds under high temperature and high pressure to enhance the content of RG.

2. Chemical Reaction

Figure 1(a) shows the mass spectrum at 650 K of the desorbed gases from the sample of C_{60}-Na-H exposed to CO. The species corresponding to

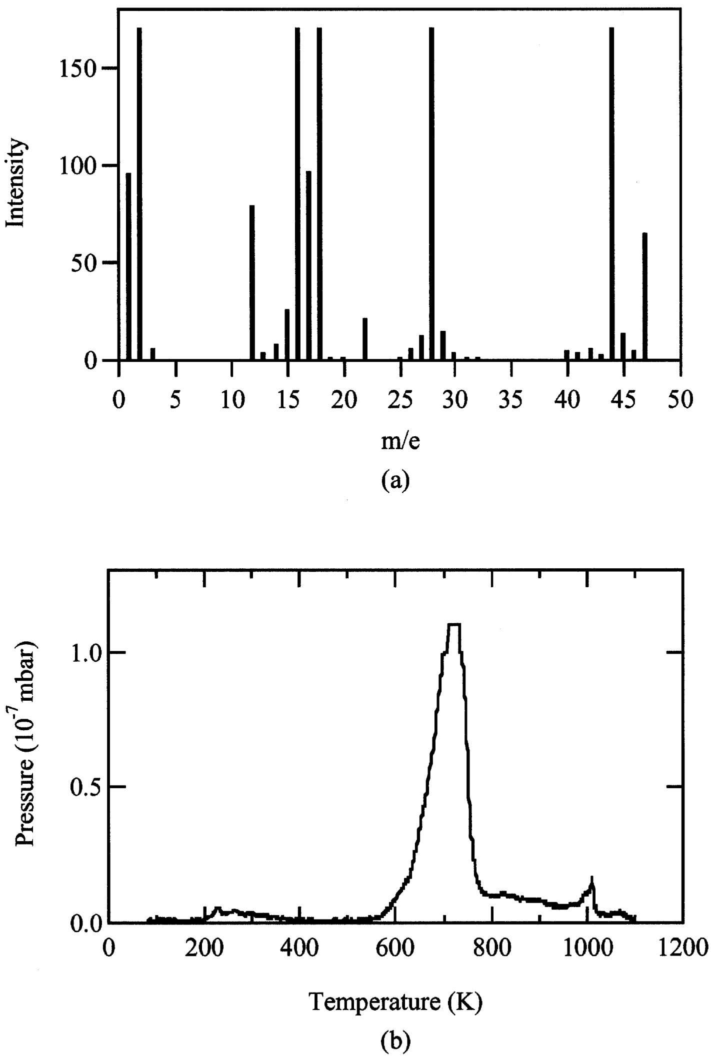

FIGURE 1 Analyses of the desorbed gases from the sample of CO/Na-H-C_{60} ((a): mass spectrum at 650 K, (b): thermal desorption spectrum).

m/e = 2, 16, 28 and 44 can be assigned to H_2, CH_4, H_2O, CO and CO_2. The species of m/e = 1, 12 and 15 are H, C and CH_3 as fragments of CH_4. Considering the products of CH_4, H_2O and CO_2, the following hydrogenation occurs:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2.$$

Figure 1(b) shows the TD spectrum of CH_3 (m/e = 15) as a fragment of CH_4. The peak temperature (T_P) of desorption is observed around 720 K. The desorption at high temperature suggests that the hydrogenation reaction of CO to CH_4 occurs not on the surface but in the octahedral nanospace including hydrogen in the C_{60} lattice, because for the surface reaction, T_P should be low due to the desorption of physically adsorbed CH_4.

Next we prepared the sample of C_{60}-Na-H exposed to N_2 and analyzed the desorbed gases upon heating. The parent peak of m/e = 17 corresponding to NH_3 and its fragmentation from m/e = 14 to m/e = 16 were observed in the mass spectrum at 650 K, Thus, in the N_2/C_{60}-Na-H system, the following NH_3 synthetic reaction occurs:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

T_P of NH (m/e = 15) as a fragment of NH_3 in the TD spectrum was observed around 650 K. Since this temperature is also high, NH_3 will be synthesized in the nanospace.

The nanospace in C_{60}-Na-H gives a chemical reaction field. One can apply this method to other various reactions such as the reduction of CO_2, NO, NO_2 *etc.* and the synthesis of CH_3OH, CH_3CHO, CH_3COOH *etc.*

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