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Recrystallization-Induced Defect Porous Nature of C_{60} Crystals

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Abstract. Defective state of C_{60} crystals was controlled by the recrystallization and annealing. The defective structure was examined by the X-ray diffraction and N_2 adsorption at 77 K. Recrystallized C_{60} crystals without annealing showed broad diffraction peaks and the N_2 adsorption isotherm had marked low pressure uptake and a hysteresis in the high pressure region, indicating presence of both micropores and mesopores. The average micropore width was 8 Å which is closed to the C_{60} molecular size, while the average mesopore one was 50 Å. The mesopores disappeared by annealing up to 393 K. On the other hand micropores of 8 Å remained even by heating up to 673 K.

Keywords: fullerene, micropore filling, N_2 adsorption, point defect

Introduction

The fullerenes have offered exciting research subjects in the worldwide science since 1985 (Kroto et al., 1985). The establishment of the preparation has extended its field (Kratschmer et al., 1990). The fullerenes are representatives of van der Waals solids. The crystalline C_{60} crystal has a face-centered cubic (fcc) lattice at room temperature, which changes into simple cubic (sc) lattice below 249 K (Heiney et al., 1991). As the spherical C_{60} molecule of 10 Å effective diameter occupies 0.16 mLg^{-1} for the fcc lattice and 0.11 mLg^{-1} for the sc lattice from the crystal structure, the C_{60} crystals have great intermolecular interstices (0.05 and 0.08 mLg^{-1} for fcc and sc lattices, respectively). High mobility of C_{60} molecules in the van der Waals solid should lead to the formation of highly concentrated point defects due to the treatment, such as sublimation, recrystallization, heating and cooling. If there are sufficient point defects, the isolated interstices can be connected each other to produce open micropores. Here the pores whose width is less than 20 Å are called micropores; mesopores are in the range of 20 Å to 500 Å (Sing et al., 1985). The micropores can offer the reaction field for atoms and molecules, then defective state is essentially important in the surface chemistry of C_{60} crystals (Mckee, 1991).

In the preceding letter we reported that as-received C_{60} crystals have an N_2 adsorption isotherm of type I, indicating the microporous nature (Kaneko et al., 1993); we could not elucidate clearly the origin of micropores. Also it was observed that a large amount of CO_2 is adsorbed by C_{60} crystals (Nagano et al., 1994). The CO_2 adsorption under supercritical conditions should be associated with presence of micropores. In the present work we controlled the defect concentration of C_{60} crystals by the recrystallization and annealing; the relationship between the defective state and the porous nature was shown.

Experimental

The C_{60} powder of more than 99.5% purity was recrystallized from carbon disulfide (the solubility of C_{60} in CS_2 at room temperature determined by the UV-VIS spectrophotometry was 2.6 mg ml^{-1}), accompanying with evaporation of solvent and fast cooling with liquid nitrogen. Thermogravimetrical analysis (TGA) was carried out with a heating rate of 5 K/min from the room temperature up to 923 K in the flow of nitrogen of 30 ml/min. A gradual weight loss with temperature was observed due to desolvation and partial sublimation; the percents to the initial weight at 393 K and 673 K were 13% and 30%, respectively. On the other hand, the corresponding weight loss percents of the as-received sample was 4% and 10%. We used the recrystallized sample (C-0) without and with preheating up to 393 K (C-13) and 673 K (C-30) under the same conditions as the TGA measurements. The X-ray diffraction (XRD) patterns of these three samples and as-received C_{60} sample were obtained by use of nickel filtered CuKα radiation with an automatic diffractometer at room temperature. The N_2 adsorption isotherms at 77 K were gravimetrically determined using a computer-aided apparatus. The samples C-13 and C-30 were evacuated at 383 K and 10^{-3} Pa prior to the adsorption experiments, while sample C-0 was done at 293 K and 10^{-3} Pa.

Results and Discussion

The crystalline and defective structures were examined by XRD. Figure 1 shows XRD patterns of as-received sample (a), C-0 (b), C-13 (c), and C-30 (d). The XRD pattern of as-received sample shows the well-crystalline fcc lattice. However, the diffraction intensity of the fcc lattice in the XRD patterns of other samples markedly decreases, while four new peaks appear. The peak width of the fcc reflections becomes wider, indicating reduction of crystallite size and presence of stacking order faults. The marked intensity reduction shows presence of point defects such as vacancies, voids and solvent molecules. Two of new four peaks can be assigned to the 110 and 310 reflections of the sc lattice. Then C-13 may be regarded as the mixed crystals of the sc and fcc lattices. Other two peaks denoted by solid arrows whose d-spacings are 4.7 and 9.3 Å come from a superlattice structure. The Miller indices of the superlattice lines are 8/3 1 1 and 4/3 1/2 1/2, suggesting the presence of high density stacking faults or long range ordered point defect structures. In our samples there is no evidence for formation of the orthorhombic structure irrespective of recrystallization from CS_2 solution (Kikuchi et al., 1991).

The heating of C-0 up to 393 K and 673 K leads to desolvation and annealing effect. The peaks due to the fcc lattice grow. C-13 sample almost loses the

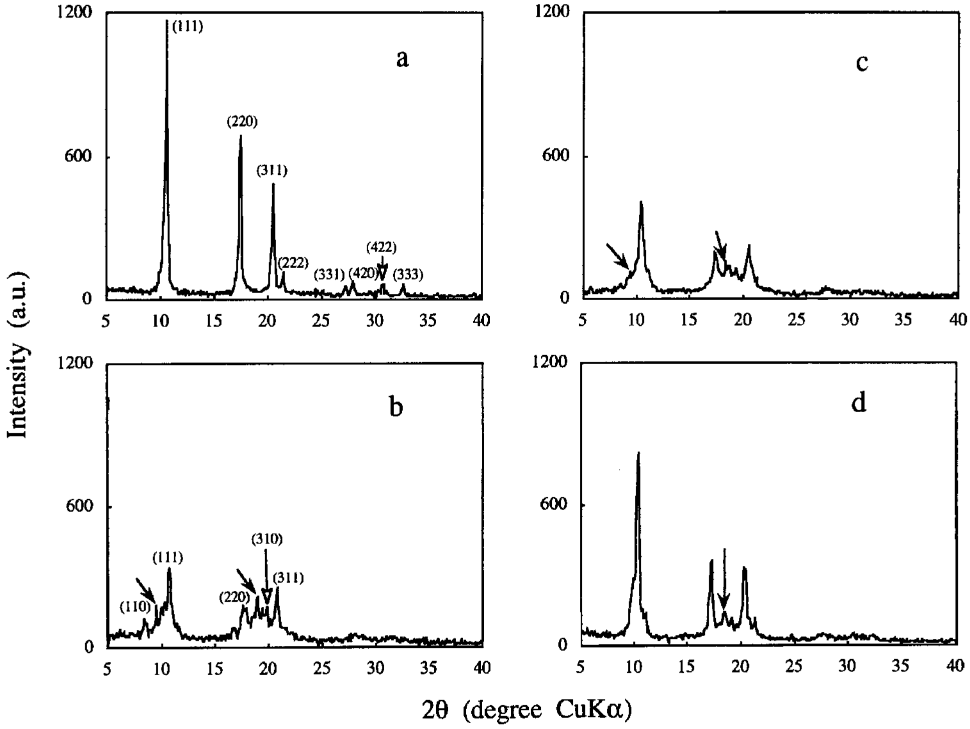

Figure 1. X-ray diffraction patterns: a) As-received C_{60} sample; b) recrystallized without further heating (sample C-0); c) recrystallized and heated up to 393 K (sample C-13); d) recrystallized and heated up to 673 K (sample C-30).

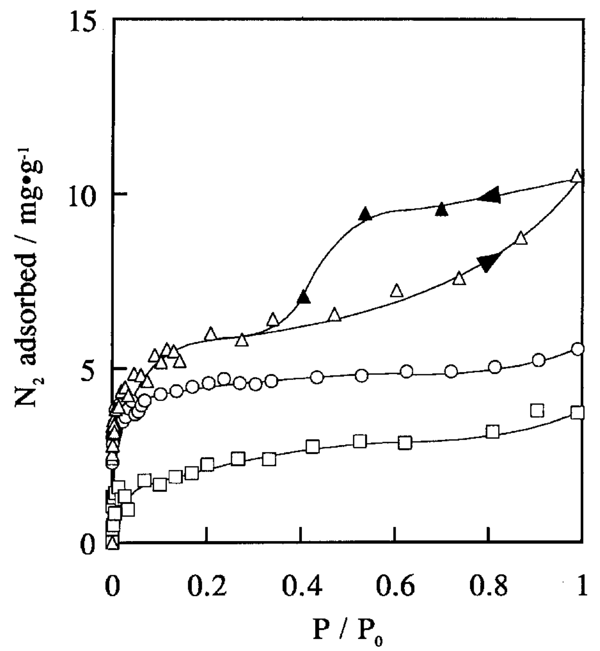

Figure 2. Adsorption isotherms of N_2 on C_{60} crystals at 77 K: a) △ adsorption, ▲ desorption sample C-0; b) ○ sample C-13 c) □ sample C-30.

diffraction peaks due to the sc lattice. On the contrary, C-13 has still the peaks from the superlattice structure. The XRD pattern of C-30 is close to that of as-received sample, although it remains the defective nature.

The defective structures are strongly associated with the pore structures evaluated by the N_2 adsorption. The whole range adsorption isotherms are shown in figure 2. The amount of adsorption sensitively depends on the defective structure. The amount of N_2 adsorption by the highly defective C-0 sample is the greatest. It was difficult to determine the adsorption isotherm of as-received sample. All adsorption isotherms have type I nature, indicating the presence of micropores. Only C-0 has characteristics of both types I and IV and shows a clear hysteresis; C-0 should have both micropores and mesopores. The micropore volume, the total surface area and the external surface area were determined using the high resolution α_s-analysis for the N_2 adsorption isotherms, as shown in Table 1. The more defective sample, the greater the surface area and micropore volume.

The micropore and mesopore size distributions for C-0 were calculated from the Dubinin-Stoeckli relation (Setoyama et al., 1993) with the aid of Gaussian distribution analysis and from the Dollimore-Heal analysis, respectively. Both pore size distributions are shown in figure 3. The average micropore width is 8 Å which is close to the effective size of the C_{60} molecule (10 Å). The peak position of the mesopore size distribution is 50 Å. Thus, C-0 has both micropores of 8 Å width and mesopores. The origin of the micropores should be connected with the structure of molecular defects and the octahedral vacancy sites. On the other hand, aggregation of point defects and stacking faults causes the mesopores. Heating of C-0 at 393 K and 673 K anneals the defective structure, decreasing the mesoporosity at first and then microporosity. In the case of the N_2 adsorption measurement at 77 K, the crystal form should be the sc lattice which has the intermolecular interstices of 0.08 mLg^{-1}. The observed micropore volumes of 0.002 to 0.006 mLg^{-1} is less than one tenth of the possible volume. Almost intermolecular interstices are still isolated and even open channeled micropores are often blocked due to the strong interaction by the quadrupole moment of the N_2 molecules. This work can show the porous nature of C_{60} crystals. The defective nature and the presence of micropores should be strongly associated with chemical reactivities of fullerenes such as alkali metal doping (Haddon et al., 1991).

Table 1. Adsorption parameters of C_{60} samples.

Samples	Surface area (m^2/g) total	external	Micropore volume (ml/g)
C-0	14	4	0.006
C-13	10	1	0.005
C-30	5	1	0.002

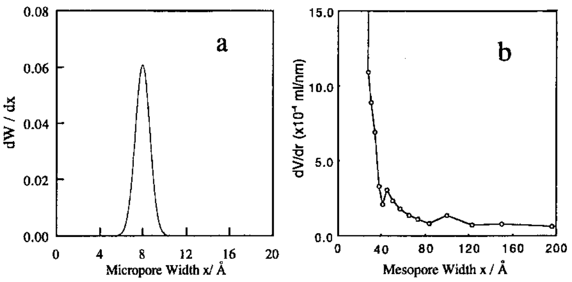

Figure 3. Pore size distributions of C_{60} crystals (sample C-0): a) micropore size disrtribution; b) mesopore size distribution.

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