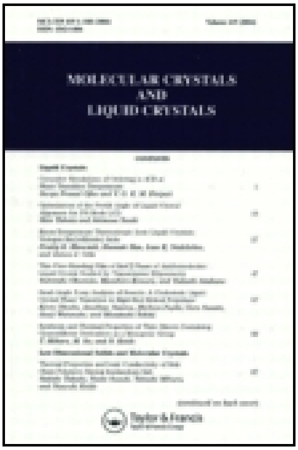

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Novel Adsorption Behavior of Nestled $C_{14}AsF_6$

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Stage-1 nestled $C_{14}AsF_6$ and un-nestled C_xAsF_6 ($x \approx 10$) were prepared by the reaction of graphite with O_2AsF_6 or AsF_5/F_2, and novel adsorption behavior of nestled $C_{14}AsF_{16}$ are discussed.

Keywords: graphite intercalation compounds; hexafluoroarsenate; nestling; adsorption; nano-space; arsenic pentafluoride

INTRODUCTION

Ideal compositions for the nestling of AsF_6^- in the stage–1 C_xAsF_6 graphite intercalation compounds (GICs) have been determined to be $C_{14}AsF_6$ at room temperature[1] and $C_{16}AsF_6$ below 170 K[2], where the fluoride ligands of AsF_6^- are nestled in contiguous three–fold sets of carbon hexagons of the graphite. The exact ratios of C:As:F=14(16):1:6, however, are difficult to attain with graphite/AsF_5/F_2 reaction system owing to its high reactivity. In the course of the study on nestled C_xAsF_6[1], it was found that the direct solid–solid reaction of O_2AsF_6 with graphite yields C_xAsF_6. We have recently found that this reaction is much faster than it had originally been thought; the reaction proceeds essentially within a matter of 10 seconds when an effective mixing of the solids is applied. Adsorption isotherms of nitrogen at 77 K for the nestled $C_{14}AsF_6$ and un–nestled C_xAsF_6 ($x \approx 10$) were measured. The nestled $C_{14}AsF_6$ adsorbs N_2 up to the composition $C_{14}AsF_6 \cdot \frac{1}{2}N_2$, whereas the adsorption capacity of un–nestled C_xAsF_6 is about 1/10 of that of the nestled $C_{14}AsF_6$. This is attributed to the low in–plane density of guest species in the nestled $C_{14}AsF_6$.

EXPERIMENTAL

AsF_5 was prepared by the reaction of fluorine with arsenic at about 200°C. O_2AsF_6 was prepared by exposing a mixture of O_2, F_2 and AsF_5 to UV light[3]. A T-shaped reaction cell, whose branches consisted of a valve and two FEP tubes, was used for the preparation of C_xAsF_6. Reactions were carried out as follows: SP-1 graphite powder (30-100 mg; Union Carbide) and O_2AsF_6 were weighed separately in an FEP tube, and after assembling a T-shaped cell, O_2AsF_6 was transferred onto the graphite, and the mixture was shaken by directly hitting the end of the elastic FEP tube by fins of a small electric fan. Some C_xAsF_6 samples were made by the reaction of graphite with AsF_5/F_2. Sample compositions were checked by gravimetry and tensimetry. Adsorption isotherms of nitrogen at 77 K for the products were measured using a Gemini 2375 (Automatic Surface Area Analyzer; Shimadzu-Micromeritics). Nestling and un-nestling of AsF_6^- in the products were readily determined by XRD[1].

RESULTS AND DISCUSSION

Fig. 1 shows the reaction progress for the formation of nestled $C_{14}AsF_6$ monitored by pressure increase. The pressure rises according to the following equation:

$$14\ C + O_2AsF_6 \rightarrow C_{14}AsF_6 + O_2\uparrow \qquad (1)$$

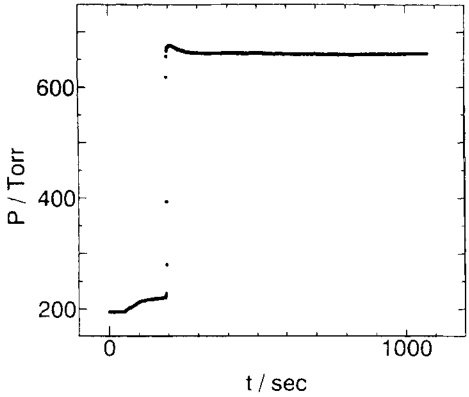

FIGURE 1 Progress of the reaction of graphite with O_2AsF_6 for the formation of nestled $C_{14}AsF_6$ monitored by pressure increase.

Initially the cell was filled with nitrogen and the pressure was measured every second. At $t\sim40$ s O_2AsF_6 was transferred onto graphite (*ca.* 100 mg). The reaction immediately started as the mixture was perturbed in an effort to transfer O_2AsF_6 thoroughly. When a violent shaking started at $t\sim200$ s, the pressure increased drastically but stopped increasing within 10 s, indicating a very fast solid phase reaction.

Adsorption isotherms of nitrogen at 77 K for (a) graphite, (b) un-nestled $C_{9.8}AsF_6$, (c) un-nestled $C_{11.9}AsF_6$, (d) nested $C_{13.6}AsF_6$, and (e) nestled

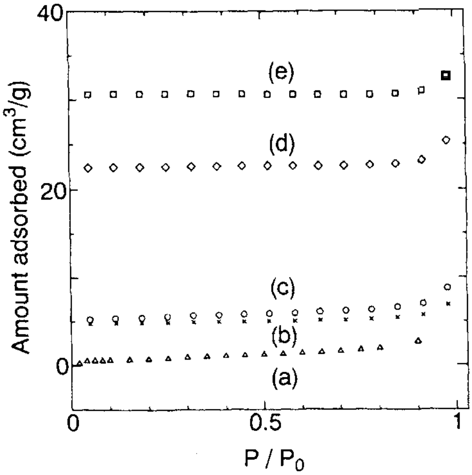

FIGURE 2 Adsorption isotherms of nitrogen at 77 K for (a) graphite, (b) $C_{9.8}AsF_6$, (c) $C_{11.9}AsF_6$, (d) nestled $C_{13.6}AsF_6$, and (e) nestled $C_{15.1}AsF_6$.

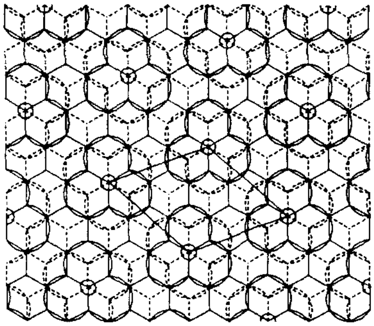

FIGURE 3 In-plane √7×√7 arrangement of AsF_6^- for the nestled $C_{14}AsF_6$.

$C_{15.1}AsF_6$ are shown Fig. 2. Their BET surface areas were 2, 17, 19, 80 and 109 m^2/g, respectively. Sample (b) was made with AsF_5/F_2, and the others with O_2AsF_6. As can be seen from the figure, the amounts of N_2 adsorbed by the nestled C_xAsF_6 are significantly larger than those by the un-nestled C_xAsF_6. For the nestled $C_{15.1}AsF_6$, the amount of adsorbed N_2 corresponds approximately to the formula $C_{15.1}AsF_6 \cdot \frac{1}{2}N_2$. This is because that, in the nestled $C_{14}AsF_6$, the in-plane density of AsF_6^- is low as shown in Fig. 3[1]. The value of 14 in the stage-1 $C_{14}AsF_6$ is to be compared with 8 in the stage-1 C_8AsF_5[4]. Without nestling, $C_{14}AsF_6$ would be a mixture of stages-1 and -2 with a higher in-plane density of guest species, which would hinder the incorporation of N_2. The composition $C_{14}AsF_6$ corresponds to the highest density of *nestled* AsF_6^-. This is because that two F-ligands belonging to two different AsF_6^- cannot nestle in two edge-sharing hexagons of graphite network owing to the "large" size of the F-ligands. For un-nestled C_xAsF_6, *ca.* $C_{10}AsF_6$ has the highest density of AsF_6^-. This allows us to estimate the space available for N_2 adsorption in the nestled $C_{14}AsF_6$ as follows. $C_{14}AsF_6$ can be formulated as $C_4C_{10}AsF_6$. The size of AsF_6^- in the *ab*-projection is larger than 3 F-ligands which roughly corresponds to the size of $(3/2) \times N_2$. As a result, the formula $C_4(N_2)_{0.6}C_{10}AsF_6$ is obtained for N_2 adsorption. This can further be approximately reformulated to $C_{14}AsF_6 \cdot \frac{1}{2}N_2$.

In the present study it is not unambiguously clear whether N_2 molecules are adsorbed in the graphite gallery. The high specific surface area for the nestled $C_{14}AsF_6$ might have been caused *via* the reaction of graphite with O_2AsF_6, which served as surface activation of the graphite, and it may not be associated with the interlayer gallery. However, the difference in adsorption capacity for nestled $C_{14}AsF_6$ and un-nestled C_xAsF_6, both of which have experienced the possible surface-activating reaction, support the idea of the interlayer gallery of the nestled $C_{14}AsF_6$ being an active site for N_2 incorporation.

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