Selective Intercalation of Aromatic Molecules into Alkyltrimethylammonium Ion-Intercalated Graphite Oxide

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Selective intercalation of aromatic molecules into alkyltrimethylammonium-intercalated graphite oxide (GO) was investigated. While pyrene, phenanthrene and azobenzene intercalate into cetyltrimethylammonium-intercalated GO and the repeat distance along c-axis increases drastically, anthracene does not intercalate.

Organoammonium ions-intercalated layered materials are attracting much attention because of their interesting structures, absorption of harmful molecules or photoactive ones and application as catalysts. Recent studies on these materials are well reviewed by Ogawa and Kuroda.[1] In this context, recently, it has been reported that organoammonium ions-intercalated graphite oxides show some interesting functions. We have shown that a large amount of pyrene molecules is adsorbed in the space occurring between the alkyl chains of surfactant. From the fluorescence spectra, pyrene molecules adsorb in separated sites.[2] Dékány et al have reported selective sorption of organic liquids such as ethanol, toluene, n-heptane and cyclohexane. The increase of interlayer spacing depended on the polarity of these organic molecules.[3] In this study, we have investigated the intercalation of various aromatic molecules with different sizes into alkyltrimethylammonium-intercalated GOs with different surfactant contents and found that they possess molecular recognition ability.

Graphite oxide ($C_8O_{3.5}H_{2.8}$) was obtained from natural graphite powder by the modified Staudenmaier method.[4,5] Intercalation of cethyltrimethylammonium ($C_{14}H_{29}(CH_3)_3N^+$; C14N), hexadecyltrimethylammonium ($C_{16}H_{33}(CH_3)_3N^+$; C16N) and octadecyltrimethylammonium ($C_{18}H_{37}(CH_3)_3N^+$; C18N) ions was performed by adding aqueous solution of surfactant into the colloidal solution of GO.[6] In this process, the protons of hydroxyl groups in GO were partially exchanged by surfactant ions.[6] The c-axis repeat distance (I_c value) C14N-, C16N- and C18N-intercalated GOs as hosts of aromatic molecules were 1.72 nm, 2.08 nm and 3.55 nm, respectively. The contents of C14N, C16N and C18N ions in the intercalation compounds were 0.25, 0.38 and 0.56 mol per $C_8O_{3.5}H_{2.8}$ GO unit (0.16, 0.25 and 0.36 mol/100 g GO), respectively, as calculated from weight uptake data. These values were somewhat smaller than those observed for GO prepared by the Brodie method as reported in the previous paper and this indicates that many hydroxyl groups still exist in the layer of GO.[6] However, the samples obtained in this study were well soluble in chloroform. Intercalation of aromatic molecules such as naphthalene ($C_{10}H_8$), fluorene ($C_{13}H_{10}$), anthracene ($C_{14}H_{10}$), phenanthrene ($C_{14}H_{10}$) pyrene ($C_{16}H_{10}$), and azobenzene ($C_{12}H_{10}N_2$) were performed by the cast method[2] from $CHCl_3$ solution (5 ml) of intercalation compound (10 mg) and aromatic molecules (10 mg) on glass substrate. The ratios of aromatic molecule/surfactant were between 2.9 and 6.9, which were much larger than that found for pyrene in C18N-GO (pyrene/C18N ratio was 1) in our previous paper.[2]

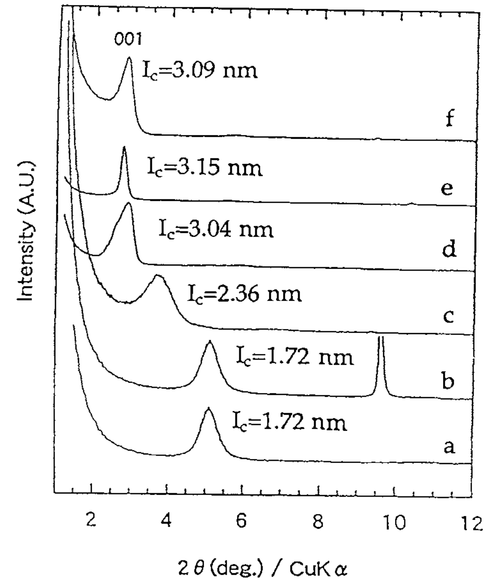

Figure 1. X-Ray diffraction patterns of (a):C14N-GO and C14N-GOs containing (b):anthracene, (c):fluorene, (d):azobenzene, (e):pyrene and (f):phenanthrene.

Figure 1. shows the X-ray diffraction patterns of C14N-intercalated GO samples after the intercalation of various aromatic molecules. The I_c value of the pristine C14N-intercalated GO (1.72 nm) indicated that the surfactants located as flat bilayer with their alkyl chains almost parallel to the GO sheet.[3,6] When azobenzene, pyrene and phenanthrene were intercalated into this material, the I_c values of the film increased drastically from 1.72 nm to 3.04 - 3.15 nm. This suggests that the orientation of alkyl chains was changed as the result of the adsorption of aromatic molecules in the space occurring between the alkyl chains[2,3]. In case of fluorene, it was adsorbed in the film, however, the increase of the I_c value was 0.6 nm, significantly smaller than those observed for the above three aromatic molecules. This would be because the distribution of surfactant in the layer of GO was not completely uniform and some of the adsorption sites were not accommodate to fluorene.

On the other hand, the I_c value of anthracene-containing film was the same as that of the pristine C14N-GO. The peak at around 2θ=9.5° is due to crystalline anthracene which was not intercalated into C14N-intercalated GO but was deposited on the surface area of the film. Naphthalene molecules with smaller size were also not intercalated into C14N-GO. These results suggest that larger molecules are easily adsorbed in surfactant-intercalated GO probably because of the larger hydrophobic interaction between alkyl chains of surfactant and aromatic molecules. The

Table 1. The increases of I_c values of surfactant-intercalated GOs as the result of the intercaltion of aromatic molecules.

Host	surfactant content / mol / GO unit	guest[a], increase of I_c value / nm					
		NA	AN	FL	PH	PY	AZ
C14N-GO	0.25	0	0	0.64	1.43	1.37	1.32
C16N-GO	0.38	-[b]	0.18	1.07	1.32	1.05	1.26
C18N-GO	0.56	0.12	0.27	0.06	0.24	0.34	0.21

[a] NA:naphtharene, FL:fluorene, AN:anthracene, PH:phenanthrene, PY:pyrene, AZ:azobenzene. [b] amourphous.

sizes of anthracene, phenanthrene and fluorene might be close to the critical one which determines whether intercalation is possible or not.

The changes of I_c values of the various surfactant-intercalated GOs with different surfactant contents as the result of intercalation of aromatic molecules are summarized in Table 1 together with the data obtained for C14N-GO. When the surfactant content increased, the I_c values of the surfactant-intercalated GOs also increased as the result of the intercalation of anthracene and naphthalene that were not intercalated into C14N-GO. The small increases of the I_c values (0.06 nm - 0.34 nm) for C18N-GO is likely because the I_c value was so large that intercalation of aromatic molecules caused no major change in the orientation of alkyl chains of surfactant. The change in the intercalation behavior depending on the host materials would be because the distance between the adjacent alkyl groups of surfactants becomes smaller and accordingly even smaller molecules can be surrounded by a larger number of the alkyl chains of surfactants. The increase of hydrophobic interactions between aromatic molecules and alkyl chains would allow them to stay between the layer of the intercalation compounds, in other words, the critical molecular size for intercalation became smaller. Therefore, even the smaller molecules of naphthalene were intercalated into C18N-GO with a high surfactant content.

The selectivity observed in the present system is completely different form that reported in the other organically modified layered materials such as clay minerals[7-10] and transition metal phosphonates,[11,12] though in these cases adsorption was also controlled by changing the distance between adjacent organic groups. In these organically modified materials, smaller and/or less bulky organic molecules were preferably adsorbed. This difference of the selectivity is likely due to the existence of the residual hydroxyl groups on the surface of surfactant-intercalated GO. They could make the surface of the layer hydrophilic enough to prevent the adsorption of smaller molecules. These results obtained in this study indicate that surfactant-intercalated GOs showing interesting selectivity for aromatic molecules are one of the promising host materials for molecular recognition.

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