Photochemical dimerization of acenaphthylene in hydorphobized graphite oxide(II)

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Photochemical dimerization of highly concentrated acenaphthylene molecules was performed in the self-assembled thick film of graphite oxides hydrophobized by alkyltrimethylammonium salt and fluorinated alkylamine. The saturate amount of acenaphthylene molecules in the nanospace available between hydrophobiç molecules became maximum when the hydrophobic molecule/GO ratio was 0.4. Introduction of perfluorinated alkyl chain increased the acenaphthylene content in the samples, which was due to the lower micropolarity of the nanospace in them. Conversion of the acenaphthylene became maximum when the acenaphthylen/hydrophobic molecule ratio reached 2, almost regardless of the host material. In most cases, the *syn-/anti-* ratio of the obtained acenaphthylene dimers were less than 1, when alkyltrimethylammonium salts-intercalated graphite oxide was used. This could be because the distance between acenapthlene molecules was large and the dimers were mostly originated from the triplet excited state. The conversion of acenaphthylene in was high even when the acenaphthyleen content was low, which is ascribed to the high diffusion of excited acenaphthlene molecules between perfluoroamines. This also lowered the syn/anti ratio of acenaphthylene dimer, comparing with that observed in octyleamine-graphite oxide.
Key words:Potochmical dimerization, acenaphthylene, graphite oxide, alkylamine, trimethylalkylammonium ion, perfluoroamine

1. Introduction

Recently, microporous solids such as zeolites, layered materials, etc have been used for reaction media with specific photochemical reactivity [1-8]. By controlling the nature of the nano-space in zeolite, chiral synthesis has been also reported [1-13]. Layered compounds hydrophobized by alkyl amines are expected to be new types of reaction media because the substrates are introduced via hydrophobic interaction and accordingly, various non-ionic substrates are easily introduced. Furthermore, the sizes and properties of the reaction cavity arising between amines can be modified in various ways by changing the contents and sizes of alkyl amines. In our previous letter, we have shown that a large amount of acenaphthylene was intercalated into surfactant-intercalated graphite oxide thin film and photochemical dimerization of acenaphthylene was observed. Spectroscopic and X-ray diffraction data suggested that the space available for the photochemical reaction between the surfactant ions was hydrophobic and flexible [14]. However, the low amount of acenaphthylene in the thin film samples prevented the accurate analyses of the products. In the subsequent paper, we reported photochemical dimerization of acenaphthylene in much thicker film of graphite oxides hydrophobized by n-alkylamine with various alky chain lengths [15]. The conversion of acenaphthylene increased with the increase of its contents in the intercalation compounds and the increase of alkyl chain length. Syn/anti ratio of acenaphthylene dimers increased with the increase of acenaphthylene contents and became larger in intercalation compounds containing alkyl amine with shorter alkyl chain probably because of the

difference in diffusion rate of exited molecules. In this paper, photochemical dimerization of acenaphthylene was performed in various hydrophobized graphite oxides including alkyltrimethylammounium ion and perfluoroalkylamine. When alkyltrimethylammounium ion introduced into GO via ion exchange are used, the hydrophobic molecule contents are very low, therefore, a larger space would be available between alky chain. This would lead high acenaphthylene content and the decrease in the distance between acenaphthylene molecules. On the other hand, fluorinated alkyl chains with low surface energy is expected to facilitate the diffusion of excited molecules. These factors would vary the reactivity of acenaphthylene introduced in the nano-space of hydrophobized graphite oxides.

EXPERIMENTAL

Graphite oxide was prepared from natural graphite powder by Brodie's method at 60℃ [16]. From the elemental analysis data of carbon and hydrogen, $C_8O_{3.2}H_{2.4}$ was obtained for the composition. Lauryltrimethylammonium chloride $(C_{12}H_{25}N(CH_3)_3Cl$, henceforth abbreviated as C12TMA), myristyltrimethylammonium bromide $(C_{14}H_{31}N(CH_3)_3Br$, C14TMA) hexadecylrimethylammonium bromide $(C_{16}H_{33}N(CH_3)_3Br$, C16TMA), stearyltrimethylammonium chloride $(C_{18}H_{37}N(CH_3)_3Cl$, C18TMA), hexadecylamine, $C_{16}H_{33}NH_2$ C16A) and perfluorooctylamine $(C_7F_{15}CH_2NH_2$, C8FA)-intercalated GOs were prepared and the compositions were determined, as previously reported [17-19]. The compositions of the prepared intercalation compounds were $(CnTMA)_xGO$ (n=12-18, x=0.30-0.51) and

(C8FA)$_x$GO (x=0.38 and 0.62) determined from the weight before and after the reaction.

Intercalation of acenaphthylene into hydrophobized GOs was performed as follows. Chloroform solution of acenaphthylene (4.67 mM, 2 mL) were mixed with various amounts of hydrophobized GO solutions (2.0 mg/mL in CHCl$_3$) [14, 15, 20]. The solvent was evaporated in order to obtain film-like sample at the bottom of the vial. The hydrophobic molecule/amine ratios varied between 3/1 and 0.25/1. The saturated amounts of acenaphthylene in the above intercalation compounds were determined from the X-ray diffraction data (Rigaku Rint-2100, CuKα) of the film samples deposited on a glass substrate. This is based on the fact that X-ray diffraction peak derived of crystallized acenaphthylene appears at 2θ=12.5°, when the interlayer spacing is saturated by acenaphthylene. Photochemical dimerization of acenaphthylene in the resulting films of hydrophobized GO with various acenaphthylene/amine ratios was performed at room temperature. UV light (500 W ultra high pressure mercury lamp, Ushio BA-H500) was irradiated to the film sample through optical fiber at room temperature for 2h. The acenaphthylene molecules undergo photochemical dimerization by irradiating UV light, providing syn- and anti-dimers. The use of Corning CS 052 filter (cut off wavelength: 340 nm) prevented the excitation of syn- and anti-dimers at 313 nm. After the reaction, cyclohexane was poured into the vial, which allowed to extract the products from the intercalation compounds. The conversion of acenaphthylene monomer was calculated from the decrease of absorbance at 340 nm in UV-Vis. spectra (Hitachi UV-3010, in cyclohexane solution). Syn/anti ratios of dimers were determined from the ratio of the areas of ^{1}H NMR peaks (CDCl$_3$ solvent) at 4.84 ppm (syn, 4H) and 4.09 ppm (anti, 4H). The micropolarity of the nanospace in intercalation compounds were investigated based on the data of absorption maxima of 4,4-diethylaminoazobenzene with low dipole moment in it. It has been reported that the absorption maxima of this molecule is sensitive to the polarity of the medium. Introduction of 4,4-diethylaminoazobenzene was performed as above.

3. RESULTS AND DISCUSSIONS

3.1 Intercalation of acenaphthylene into various hydrophobized GOs

Fig. 1 shows the typical X-ray diffraction patterns of (C16TMA)$_{0.48}$GOs with various acenaphthylene/C16TMA ratios. The diffraction peaks at 2θ=2.5-2.3° due to acenaphthylene-(C16TMA)$_{0.48}$GOs were observed and their interlayer spacings (I$_c$) were calculated to be 3.37- 3.62 nm. When the acenaphthylene contents increased and reached acenaphthylene/C16TMA ratio of 2.5/1, a diffraction peak at 2θ=12.5° originating

from excess acenaphthylene crystal deposited at the surface of the intercalation compound was observed. This means that the interlayer spacing of amine-intercalated GO was saturated by acenaphthyelene molecules. From these data, the saturated amounts of acenaphthylene intercalated into hydrophobized GOs per GO unit were
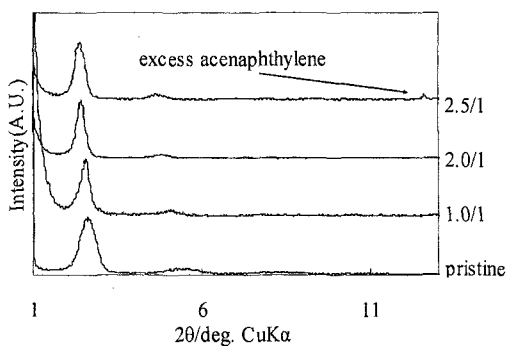

Fig.1 X-ray diffraction patterns of (C16TMA)$_{0.48}$GOs containing acenaphthylene molecules with various acenaphtyhelene/C16TMA ratios

determined. The interlayer spacing of the samples increased almost linearly as the increase of the acenaphthylene content for (C8FA)$_{0.62}$GO and (CnTMA)$_x$GO with n=14, 16 and 18, The slope of the increase of it was very small for (C12TMA)$_x$GOs and (C8FA)$_{0.38}$GO. From their I$_c$ values and the molecular length, it was proved that the hydrophobic molecules took bilayer structure in the gallery of graphite oxide, except for (C8FA)$_{0.38}$GO.

Fig.2 shows the saturated acenaphthylene content per GO unit as a function of the hydrophobic molecule content in GO. This increased as the increase of x in (CnTMA)$_x$GO and became maximum when x reached 0.4, then decreased to about 0.6 mol/GO, which was similar to those observed for (CnA)$_x$GO (n=8, 12, 16, x=0.62, 1.24) reported in our previous paper. On the other hand, larger amounts of acenaphthylene molecules were intercalated into (C8FA)$_x$GO. The less polar environment around acenaphthylene molecules in (C8FA)$_x$GO than
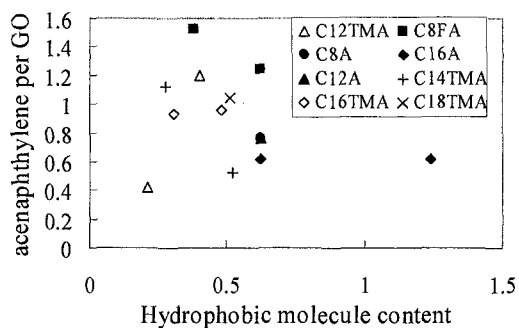

Fig.2 The saturated acenaphthylene content in (CnTMA)$_x$GOs as a function of CnTMA content

that in $(C8A)_xGO$ or $(CnTMA)_xGO$ would be responsible for this change in saturated acenaphthylene content. The absorption maximum of 4,4-diethylaminoazobenzene in $(C8FA)_xGO$ (415 nm) was observed at lower wavelength than that of $(C8A)_xGO$ or $(CnTMA)_xGO$ (423-432 nm) with similar x values, indicating lower polarity of the nano-space in $(C8FA)_xGO$. The micropolarity of the nano-space in hydrophobized GOs was relatively high and was comparable to those of ethanol (417 nm) or dimethylfromamide (425 nm). The low acenaphthylene content in $(CnTMA)_xGOs$ with low CnTMA content could be also due to the high micropolarity due to the oxygen containing groups of graphite oxide layer. This will be discussed in more detail in the subsequent paper.

3.2 Photochemical dimerization of acenaphthylene in trimethylammonium ion-intercalated GOs

Fig.3 shows the conversion of acenaphthylene in $(CnTMA)_xGOs$ as a function of acenaphthylene/CnTMA ratios. It was very low when the acenaphthylene/CnTMA ratio was small, almost regardless of the alkyl chain length and CnTMA content in GO, which would be due to the large distance between intercalated acenaphthylene molecules. As was indicated by the monomer emission from pyrene molecules in $(C16TMA)_{0.48}GO$ in our previous study, most of the acenaphthylene molecules were also located in different sites and, therefore, the distance between adjacent molecules was large. As the
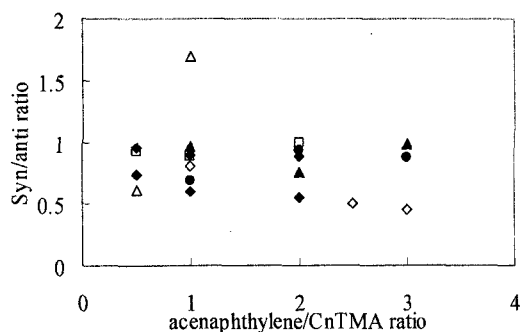
Fig.3 Conversion of acenaphthylene in $(CnTMA)_xGOs$ as a function of acenaphthylene/CnTMA ratios.
(◆ : $(C12TMA)_{0.21}GO$, ◇ : $(C12TMA)_{0.40}GO$, ▲ : $(C14TMA)_{0.28}GO$, △ : $(C14TMA)_{0.52}GO$, ● : $(C16TMA)_{0.31}GO$, ○ : $(C16TMA)_{0.48}GO$, □ : $(C18TMA)_{0.51}GO$)

increase of acenaphthylene/CnTMA ratio, the conversion increased and then decreased after it reached 2. One possible explanation for this phenomenon is that the formed acenaphtylene dimers in the interlayer spacing partly prevented further diffusion and as the result, the reaction of excited acenapthylene molecules.

Fig.4 shows the syn/anti ratios of the acenaphthylene dimers formed in $(CnTMA)_xGOs$ as a function of acenaphthylene contents. No apparent dependence of them on the chain length of CnTMA,

acenaphthylene/CnTMA ratio nor CnTMA content in GO. They were between 0.5 and 1, except for $(C14TMA)_{0.52}GO$. The mechanism of the photochemical dimerization of acenaphtylene has been already investigated in detail and it is proved that the anti-dimer is formed only from triplet excited state, while syn-dimer from both singlet and triplet states. In the present study, therefore, the low syn/anti ratio of the acenaphthylene dimers indicates that these are mostly originated from the triplet excited state of acenaphthylene, though further confirmation by spectroscopic information should be needed. One possible explanation for these low syn/anti ratios is the large distance between acenaphthylene molecules introduced in the nanospace available between CnTMA ions even when the acenaphthylene content is high. The relatively high syn/anti ratio observed for $(C14TMA)_{0.52}GO$ would be due to smaller nanospace as expected from the high C14TMA content and shorter alkyl chain length. This reduced the distance between acenaphthylene molecules and prevented the diffusion of excited molecules. This would lead the decrease of conversion and increase of the ratio of syn-dimer from singlet excited state as was observed for octylamine-intercalated GO in our previous study [15].
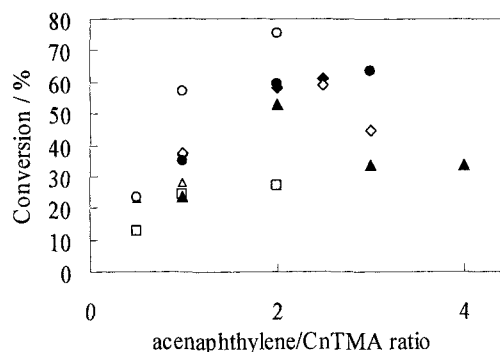
Fig.4 Syn/anti ratios of acenaphthylene dimer formed in $(CnTMA)_xGOs$ as a function of acenaphthylene/CnTMA ratios.
(◆ : $(C12TMA)_{0.21}GO$, ◇ : $(C12TMA)_{0.40}GO$, ▲ : $(C14TMA)_{0.28}GO$, △ : $(C14TMA)_{0.52}GO$, ● : $(C16TMA)_{0.31}GO$, ○ : $(C16TMA)_{0.48}GO$, □ : $(C18TMA)_{0.51}GO$)

3.3 Photochemical dimerization of acenaphthylene in perfluorooctylamine-intercalated GOs

Fig.5 shows the conversion of acenaphtylene in $(C8FA)_{0.38}GO$ and $(C8FA)_{0.62}GO$ with various acenaphthylene content. It was relatively high, even when the acenapthylene content was very low and was almost constant. This could be ascribed to the lower micropolarity of the nanospace in $(C8FA)_xGOs$, which facilitated the diffusion of excited molecules between fluorinated alkyl chains. The diffusion of the formed acenaphthylene dimers might be relatively low, which

prevented further diffusion of excited molecules as was observed for $(CnTMA)_xGO$ samples in the previous section. This is an explanation for the lower conversion observed for $(C8FA)_{0.38}GO$ with acenaphthylene/C8FA ratio of 4.
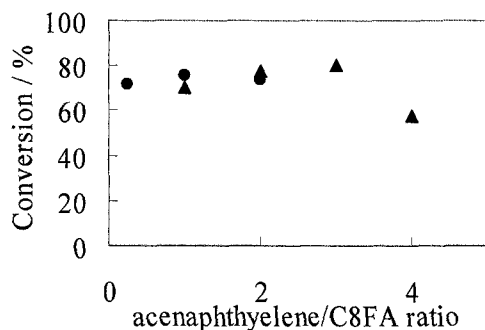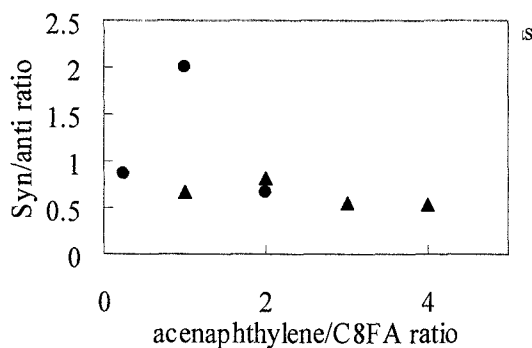

Fig.6 shows the syn/anti ratio of acenaphthylene dimers formed in $(C8FA)_xGOs$. As expected from high conversion, syn/anti ratio was low, however, that of $(C8FA)_{0.62}GO$ with acenephthylene/C8FA ratio of 1 reached 2, which was larger than those obtained in $(CnTMA)_xGOs$. One possible explanation for this fact

would be the shorter distance between acenaphthylene molecules derived of short alkyl chain.

In summary, the above results indicate that the distance between adjacent acenaphthylene molecules was still large even when the acenaphthylene was saturated in the interlayer spacing of hydrophobized GOs. This means that the formed acenaphthylene dimers were mostly originated from triplet excited state, providing low syn/anti ratio. It is interesting to compare the present results with those obtained in zeolite supercage. Ramamurthy, et al have reported that syn acenaphthylene dimer exclusively formed in Li^+ or Na^+ exchanged Y-type zeolites supercage with comparable micropolariy to that in the interlayer spacing of $(CnTMA)_xGOs$. They suggested that syn-dimer forms when the supercage of zeolite is occupied by two acenaphtyhlene molecues. This difference in the reactivity should be due to the position of acenaphthylene molecules in the hydrophobized GOs which should be clarified in the future. Another

characteristic of this system is that the diffusion of the excited acenaphthylene molecules could be controlled by the introduction of amine containing fluorinated alkyl group. This might be attributed to the lower micropolarity of the space in the intercalation compound. In addition, the low micropolarity in GO hydrophobized by perfluorooctylamine served to increase the saturated acenaphthylene content in the intercalation compound. Finally, it is note worthy to point out that the series of hydrophobized GOs provide unique photochemical reaction media by changing the micropolarity of the nanospace, and controlling the position and amount of molecules introduces in them.

References
1. V. Ramamurthy, J. Photochem. Photobio. C, 1, 145 (2000)
2. M. Ogawa, and K. Kuroda, Bull. Chem. Soc. Jpn., 70, 2593 (1997)
3. K. Takagi, T. Shich, H. Usami, and Y. Sawaki, J. Am. Chem. Soc., 115, 4339 (1993)
4. K. Takagi, H. Usami, H. Fukaya, and Y. Sawaki, J. Chem. Soc. Chem. Commun., 1174 (1989)
5. T. Shichi, K. Takagi and Y. Sawaki, Clay Sci. 10, 503 (1999)
6. R. Sasaki, H. Ogiso, I. Shindaichi, T. Shichi and K. Takagi, Tetrahedron Lett., 56, 6979 (2000)
7. M. Ogawa, H. Kimura, K. Kuroda, and C. Kato, Clay Sci. 10, 57 (1996)
8. M. Ogawa, M. Hama, and K. Kuroda, Clay Miner., 34, 213 (1999)
9. T. Fujita, N. Iyi, and Z. Klapyta, Mater. Res. Bull., 33, 1693 (1998)
10. T. Fujita, N. Iyi, and Z. Klapyta, Mater. Res. Bull., 36, 557 (2001)
10. V. Ramamurthy,et al., Chem. Eur. J. , 8 (2001) 1287
11. V. Ramamurthy, D. R. Corbin, N. J. Turro,Z. Zhang, and M. A. Garcia-Garibay, J. Org. Chem., 56, 255 (1991)
12. V. Ramamurthy, D. R. Corbin, C. V. Kumar and N. J. Turro, Tetrahedron Lett., 31, 47 (1990)
13. J. M. Nerbonne, and R. G. Weiss, J. Am. Chem. Soc., 101, 402 (1979)
14. Y. Matsuo, T. Fukutsuka, and Y. Sugie, Carbon,
15. Y. Matsuo, T. Fukunaga, T. Fukutsuka and Y. Sugie , Mol. Cryst. Liq. Cryst.in press
16. B.-C. Brodie, Ann. Chim. Phys., 59, 466 (1860)
17. F. Aragón J. Cano Ruiz, and D. M. C. MacEwan, Nature, 1959, 183, 740.
18. Y. Matsuo, T. Niwa and Y. Sugie, Carbon, (1999)
19. I Dékány, R. Krüger&Grasser and A. Weiss, Colloid. Polym.. Sci., 276, 570 (1998)
20. Y. Matsuo, K. Hatase, and Y. Sugie, Chem. Commun., 43 (1999)