CHEMISTRY LETTERS, pp. 405-408, 1988.

Intercalation of Tetrathiafulvalene(TTF) into Montmorillonite by Reaction with the Interlayer Cations

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Tetrathiafulvalene(TTF) is intercalated into montmorillonite through oxidation by the interlayer Cu^{2+} ion, in excess of the cation exchange capacity of the clay, forming mixed-valent aggregates. TTF cation can be also intercalated through cation exchange with the interlayer Na^+ ion.

Aromatic compounds have been shown to be oxidized by transition-metal cations to form their cations in the interlayer of smectite clay minerals under dry atmosphere.[1-3] Depending on the substituents, they may undergo successive oligomerization or polymerization.[4-6] Characterization of those cationic compounds has been restricted, because the cations are unstable and reduced back to neutral forms under moist atmosphere. Stability of the cation is larger for a molecule with lower ionization potential. Tetrathiafulvalene(TTF) has ionization potential[7] lower than ordinary aromatic hydrocarbons and forms stable cation salts.[8] Van Damme et al. demonstrated that TTF was intercalated in smectite by electron transfer to Fe^{3+} ion in the clay lattice.[9] In this report, we demonstrate the formation of TTF-montmorillonite intercalation compounds through the oxidation of TTF by interlayer Cu^{2+} ion and also through exchange of TTF cation with interlayer Na^+ ion.

Cu-montmorillonite was prepared from Na-montmorillonite (Kunimine Ind.) by cation exchange as described previously.[6] TTF was obtained from Tokyo Chem. Ind. and used without further purification. TTF-bromide(TTF-Br) was prepared electrochemically.[10] Absorption spectra were recorded on a Hitachi recording spectrophotometer 323. X-Ray photoelectron spectra(XPS) were measured using a Vacuum Generators ESCALAB 5 equipped with Mg- and Al-Kα X-ray sources. ESR spectra were obtained with a JEOL-FE3X spectrometer.

When powder of Cu-montmorillonite(200 mg) was suspended into TTF methanol solution (5 mmol dm^{-3}, 200 cm^3) and stirred, brown color developed on the montmorillonite immediately. The amount of TTF taken up by Cu-montmorillonite was estimated by spectrophotometrically measuring changes in the concentration of TTF in the solution. After the reaction time between 7 h to 5 d, the product was filtrated and washed with methanol. Repeated washing with methanol removed about 10% of TTF sorbed, indicating the maximum amount of TTF physically adsorbed on the outer surface of clay particles. The ratio of sorbed TTF to the cation exchange capacity(CEC) of the clay (twice the amount of Cu^{2+} ions) ranged from 1.9 to 2.0. This was in good agreement with the amount of sorbed TTF estimated from S 2p and Si 2s spectra of the TTF-clay complex obtained by XPS. Taking the surface sensitivity of XPS into the consideration, the result suggests that TTF taken up was not significantly enriched on the surface.

The powder X-ray diffraction pattern of TTF-Cu-montmorillonite complex exhibited well resolved (001) lines as shown in Fig. 1. The interlayer spacing depended on the amount of TTF taken up and ranged from 1.75 to 1.80 nm. The increase in the interlayer spacing by as large as 0.85 nm from that of dehydrated montmorillonite(0.95 nm) clearly demonstrates the intercalation of TTF into the montmorillonite layer. A similar lattice expansion was reported for the reaction of TTF with glauconite.$^{9)}$

The reduction of Cu^{2+} upon the formation of TTF-Cu-montmorillonite complex was confirmed by ESR measurement. Almost complete loss of the Cu^{2+} signal and a line due to organic radical were observed. XPS showed that the satellite structure of Cu 2p spectrum characteristic to Cu^{2+} was lost in the complex. Before the reaction, Cu/Si ratio estimated from the intensity of Cu 2p and Si 2s lines was consistent with the CEC, but it increased upon complexation with TTF up to 6 times as large as the original value. The result suggests that as TTF is intercalated, reduced copper migrates to the outer surface of the clay particle, presumably to form metallic particles.

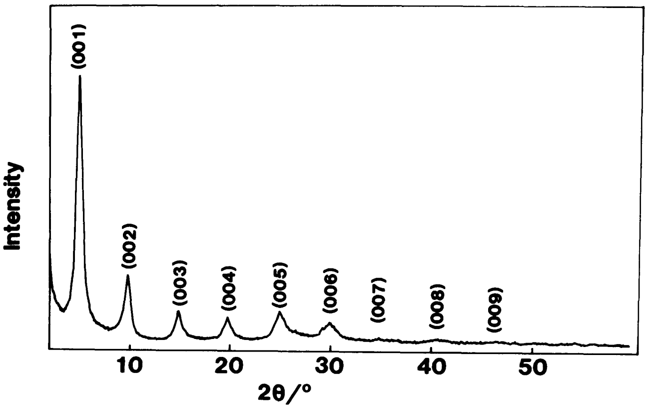

Fig. 1. X-Ray diffraction of TTF-Cu-montmorillonite.

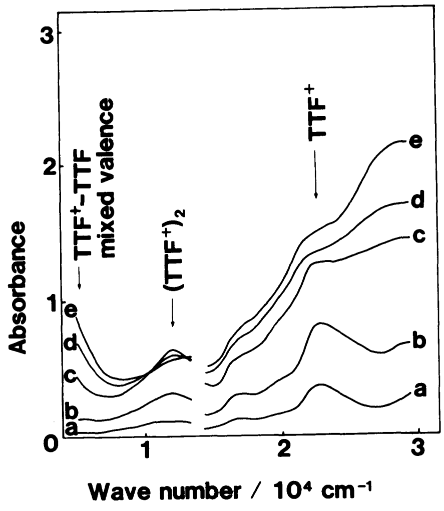

Fig. 2. Absorption spectra of a Cu-montmorillonite film contacted with TTF methanol solution (0.3 mmol dm^{-3}). The film was immersed in methanol during the recording to reduce the effect of scattering. The back-ground due to the film before the reaction was subtracted. (a) after 0.45 h, (b) 1.6 h, (c) 5.4 h, (d) 21 h and (e) 43 h, concn. of TTF increased to 0.9 mmol dm^{-3} after (d).

Figure 2 shows the changes in the absorption spectra of a film of Cu-montmorillonite formed on a quartz plate and contacted with TTF methanol solution. Upon the contact with TTF, the absorption band at about 440 nm (22700 cm^{-1}) due to the formation of TTF cation radical appeared at first(a). The spectrum essentially coincides with the solution spectrum of TTF cation radical generated by the chemical (with Br_2) or electrolytic oxidation and also with that given in literatures.[11,12] As the reaction continued, a new absorption band at 800 nm (12500 cm^{-1}) emerged(b, c). This band is attributed to the formation of the dimer of TTF cation, $(TTF^+)_2$, as was reported for the concentrated solution of TTF cation radical and for the solid chloride salt of TTF (1:1 salt, $TTF\text{-}Cl_{1.0}$).[12] The further contact with the TTF solution caused the band at 800 nm to decrease and simultaneously the absorption in the infrared to increase(d, e). The electronic absorption band in the infrared suggests formation of the aggregate of mixed-valent TTF[12] in which the average charge on a TTF molecule is less than +1. Prolonged contact of the film with TTF also caused the increase in the absorption around 30000 cm^{-1} which was attributable to the aggregated cations and/or the increase in neutral TTF.[11,12] The appearance of absorption band characteristic of the mixed-valent type aggregate is attributed to the sorption of TTF in excess of the CEC of montmorillonite.

A similar compound of TTF which includes TTF molecule in excess of the CEC was obtained by the cation exchange of Na-montmorillonite in contact with the solution containing TTF-Br and TTF. Replacement of Na^+ ion by TTF cation was confirmed with XPS and ESR. The electronic absorption band in the infrared was also observed. As TTF cation can be introduced to the amount of the CEC in the interlayer, Cu^{2+} must be actually reduced to Cu^0 and about a half of total incorporated TTF is neutral, or the average charge on TTF is about +1/2. For both Cu- and Na-montmorillonites, the partial reduction of lattice Fe^{3+} ion (total Fe in the clay was about 1/4 of the CEC) by TTF was observed by the decrease in the intensity of the characteristic ESR line, in accordance with Van Damme et al.. The infrared spectra of the complexes did not show the presence of free neutral TTF.

Preliminary one dimentional Fourier synthesis of electron density in the direction normal to the basal plane was performed on several configurations of intercalated TTF using 7 to 11 (00l) lines, assuming the molecular structure of TTF[13] and the atomic configuration of the aluminosilicate layer unchanged: two TTF layers parallel to the basal plane, and the molecular plane rotated around its perpendicular axis or the short molecular axis kept parallel to the basal plane. The two-parallel-TTF model did not fit the experimental result at all. The best agreement was obtained with the molecular plane perpendicular and the long molecular axis 70° to the basal plane.

To obtain information for the orientation of TTF in the interlayer further, we measured ESR spectra using an oriented film of Cu-montmorillonite built up on teflon substrate, where the silicate layer was oriented parallel to the substrate plane. After the reaction with TTF the film was peeled off and subject to ESR measurement. Anisotropy in g-values for organic radical in the complex was found.

For the magnetic field parallel to the film plane g-value(g_1) was 2.0059 and for the field perpendicular to the film plane it(g_2) was 2.0111. The departure of g-values from that of free electron(g_e = 2.0023) is due to the contribution of S atom to the spin-orbit coupling in TTF radical cation, which should be minimum when the magnetic field is perpendicular to the molecular plane of TTF.14) Thus, the result, $g_2 > g_1 > g_e$, indicates that the plane of TTF radical is highly inclined from the basal plane of silicate layer towards the perpendicular axis, in agreement with the orientation obtained from the X-ray diffraction.

This work was partly supported by Grant-in-Aid for Scientific Research(No. 61540346) from the Ministry of Education, Science and Culture.

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(Received November 11, 1987)