

REACTIONS OF THIOPHENE AND METHYLTHIOPHENES IN THE INTERLAYER OF TRANSITION-METAL ION-EXCHANGED MONTMORILLONITE STUDIED BY RESONANCE RAMAN SPECTROSCOPY

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Abstract—The adsorption and reaction of thiophene and methylthiophenes in the interlayer of Cu²⁺- and Fe³⁺-montmorillonites were investigated by resonance Raman spectroscopy. Thiophene and 3-methylthiophene polymerized to form cations of polythiophene and polymethylthiophene respectively, which were characterized by absorption bands in the near-infrared region. These polymer cations formed in the interlayer were reduced to their neutral polymers if the clay-polymer complexes were in contact with water, and the formation of their neutral polymers was clearly demonstrated by their resonance Raman spectra. 2,5-Dimethylthiophene in which polymerization was hindered by methyl substitution at the 2 and 5 positions, was oxidized to 2,5-dimethylthiophene cation in the interlayer.

Key Words—Adsorption, Interlayer reaction, Montmorillonite, Polymerization, Raman spectroscopy, Thiophene.

INTRODUCTION

In previous reports the adsorption and reaction of some aromatic molecules on transition-metal ion-exchanged montmorillonites were described on the basis of resonance Raman spectroscopy (Soma *et al.*, 1983a, 1983b, 1984, 1985). The resonance enhancement of Raman scattering allowed a Raman spectrum of a specific adsorbed species to be obtained selectively with no serious interference from the clay mineral itself. The results confirmed that the colored species formed by the adsorption of aromatic molecules in a dry atmosphere on transition-metal ion-exchanged montmorillonites are cationic species, as has been reported in previous infrared (IR) and electron spin resonance (ESR) studies (Mortland and Pinnavaia, 1971; Pinnavaia and Mortland, 1971; Pinnavaia *et al.*, 1974; Rupert, 1973). They also demonstrated that benzene, biphenyl, and p-terphenyl polymerize to form poly-p-phenylene cations in the interlayer.

The poly-p-phenylene cation (synthesized or formed in the interlayer of montmorillonite) is characterized by a strong absorption band extending into the near-IR region. This strong absorption band, due to low energy electronic transitions, is common in doped conjugated organic polymers that have high electrical conductivity (Shirakawa and Yamabe, 1980).

Thiophene adsorbed on Cu²⁺-montmorillonite (Cloos *et al.*, 1973) and on VO²⁺- and Fe³⁺-hectorite (Pinnavaia *et al.*, 1974) has a strong absorption in the infrared region at >1600 cm⁻¹. Synthetic polythiophene doped with certain oxidants is a stable organic

conductor and has a strong broad absorption in the near-IR region (Tourillon and Garnier, 1983; Chung *et al.*, 1984). Thus, polythiophene cations should form from thiophene adsorbed on transition-metal ion-exchanged montmorillonite or hectorite. In this paper, resonance Raman spectra of thiophene and methylthiophenes adsorbed on Cu²⁺- and Fe³⁺-montmorillonites are reported, and the polymerization of thiophene and 3-methylthiophene cations is demonstrated.

EXPERIMENTAL

The Na-montmorillonite used was refined bentonite, mined in Tsukinuno, Yamagata, Japan, and distributed as Kunipia G by Kunimine Industries. The cation-exchange capacity (CEC) of this montmorillonite is about 110 meq/100 g.

Cu²⁺- and Fe³⁺-exchanged montmorillonites were prepared by suspending the Kunipia G material in 0.002 M aqueous acidic solution of metal nitrates (pH = 3) for 20 hr, each solution containing a quantity of cations equal to the CEC of the clay. The colloidal clay was separated by centrifugation, washed once by distilled water, centrifuged again, and freeze-dried. For the montmorillonite, X-ray photoelectron spectroscopy (XPS) showed negligible Na after the ion-exchange.

Thiophene, 3-methylthiophene (purchased from Wako Chemical Industries), 2,5-dimethylthiophene (from Tokyo Chemical Industries), and 2,2'-bithiophene (from Kanto Chemical Company) of guaranteed quality were used as supplied.

Self-supporting clay films were used for IR spectral

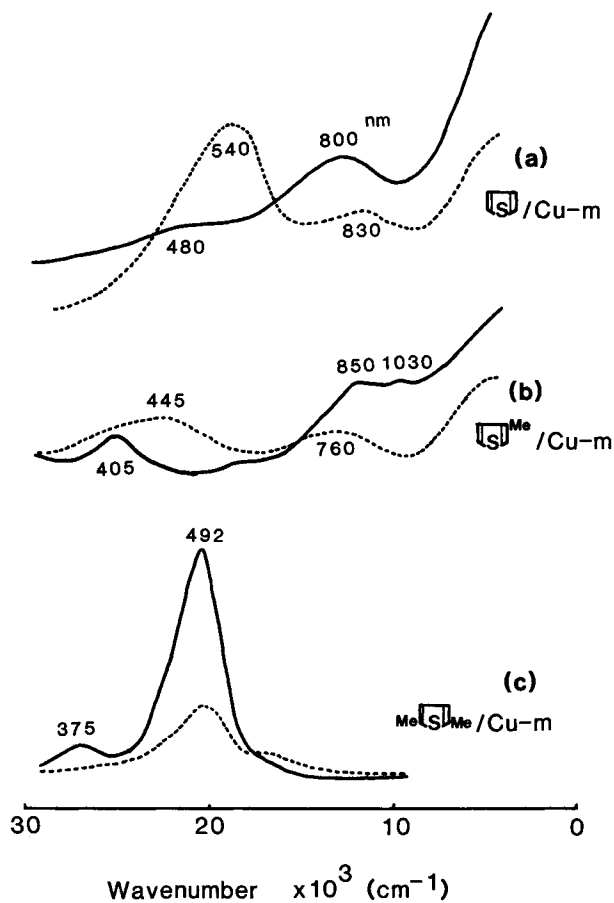


Figure 1. Absorption spectra of (a) thiophene, (b) 3-methylthiophene, and (c) 2,5-dimethylthiophene adsorbed on Cu^{2+} -montmorillonite (Cu-m) in a dry atmosphere (—), and the effect of water immersed in the clay film (---).

measurement. Clay films were formed on the inner surface of a glass ampule for Raman measurement, and the ampule was sealed to avoid the effect of humidity after the adsorption of the thiophenes. Thiophene and methylthiophenes were adsorbed from the vapor phase at room temperature in a desiccator in which barium oxide was used as a drier. 2,2'-Bithiophene was adsorbed from saturated cyclohexane solution onto the clay film which was immersed in the solution and dried in the desiccator. The sealed ampule covered with clay film on the inner surface was fixed on a sample-rotating device and spun at 1000 rpm during the Raman measurement.

Raman spectra excited by an Ar ion laser (457.9, 488.0, 514.5 nm) were measured at room temperature on a JRS 400T Raman spectrometer. Raman spectra with 628.5-nm excitation were recorded on a JASCO R-800 Raman spectrometer equipped with a rhodamine 6G dye laser excited by an Ar ion laser.

XPS data were recorded on a VG ESCA LAB 5 apparatus equipped with $\text{AlK}\alpha$ and $\text{MgK}\alpha$ X-ray

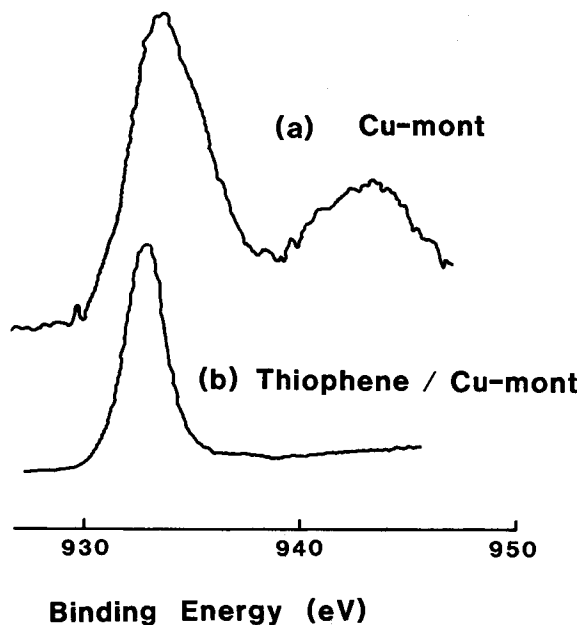


Figure 2. $\text{Cu } 2p_{3/2}$ spectra of Cu-montmorillonite (Cu-mont) and its thiophene complex.

sources and with a Nicolet signal averager. The sample powder or film was fixed by double-sided sticky tape onto the sample holder of the XPS apparatus. ESR spectra were recorded on a JRS-FE3X X-band spectrometer. The sample was put in an evacuable quartz tube of 5-mm diameter. The powdered samples of adsorbed complexes for the XPS and ESR measurements were prepared in the desiccator by the same procedure as described above.

RESULTS AND DISCUSSION

Adsorption of thiophene, 3-methylthiophene, and 2,2'-bithiophene

When thiophene was adsorbed on Cu^{2+} or Fe^{3+} -montmorillonite under a dry atmosphere, the clay film turned dark blue. An absorption band at about 800 nm and a band extending into the IR region were observed, as shown in Figure 1a. The film turned reddish-purple when water was introduced to it. A new band at about 540 nm appeared, and the intensities of the bands at longer wavelengths decreased but did not completely disappear, as shown in Figure 1a. The spectrum of the "dark-blue" species was restored reversibly when water was removed from the clay film. Similar spectra were observed for the adsorption of 3-methylthiophene, as shown in Figure 1b. The behavior of these absorption bands, when the samples were brought in contact with water, especially of the absorption extending into the IR region, resembled that of benzene adsorbed in the interlayer of Cu^{2+} - or Fe^{3+} -montmorillonite (Pinnavaia and Mortland, 1971; Soma *et al.*, 1983b, 1984).

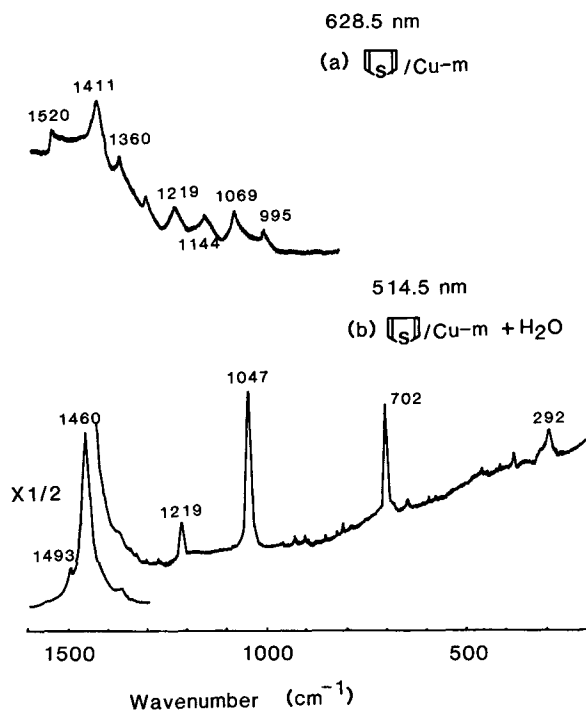


Figure 3. (a) Resonance Raman spectra of thiophene adsorbed on Cu^{2+} -montmorillonite (Cu-m) in a dry atmosphere (628.5-nm excitation) ("dark blue"). (b) Resonance Raman spectrum of the clay complex (a) immersed in water (514.5-nm excitation) ("red purple").

ESR showed that most of the Cu^{2+} and Fe^{3+} ions were reduced to Cu^+ and Fe^{2+} during the formation of the "dark-blue" species. A sharp signal due to a cation radical were observed simultaneously, as has been reported for thiophene adsorbed on Fe^{3+} -hectorite (Pinnavaia *et al.*, 1974). The addition of water to the "dark-blue" species recovered the signal of the Cu^{2+} or Fe^{3+} ions, and the signal due to cation radicals disappeared. Thus, the "dark-blue" species appears to be an oxidized product of thiophene, as has been pointed out previously (Cloos *et al.*, 1973; Pinnavaia *et al.*, 1974), and the "reddish-purple" species appears to be its reduced form. Figure 2 shows XPS $\text{Cu } 2p_{3/2}$ spectra of Cu-montmorillonite with (Figure 2b) and without adsorbed thiophene (Figure 2a). The $\text{Cu } 2p_{3/2}$ spectrum of Cu-montmorillonite has a satellite structure characteristic of the paramagnetic Cu^{2+} ion at the higher energy side of the main peak. The disappearance of this characteristic satellite in spectra of the thiophene-treated sample demonstrates the reduction of Cu^{2+} to Cu^+ , in accord with the ESR results.

Resonance Raman spectra of thiophene and 3-methylthiophene adsorbed on Cu-montmorillonite in a dry atmosphere ("dark-blue" species) are shown in Figures 3a and 4a. Resonance Raman spectra of the "reddish-purple" species formed when the "dark-blue" species

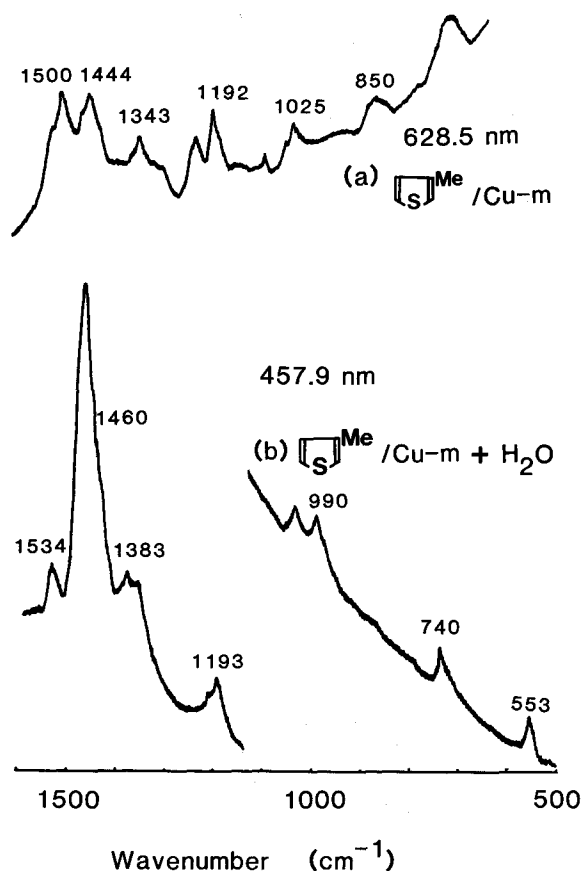


Figure 4. (a) Resonance Raman spectra of 3-methylthiophene adsorbed on Cu^{2+} -montmorillonite (Cu-m) in a dry atmosphere (628.5-nm excitation) ("dark blue"). (b) Resonance Raman spectrum of the clay complex (a) immersed in water (514.5-nm excitation) ("red purple").

was brought into contact with water are shown in Figure 3b for thiophene and in Figure 4b for 3-methylthiophene. The spectra in Figures 3b and 4b coincide with those of neutral polythiophene and polymethylthiophene synthesized electrochemically (Yong and Renyuan, 1985; Akimoto *et al.*, 1984, 1986), in which thiophenes were polymerized at the 2 and 5 positions of the thiophene ring. The main Raman bands observed in the clay complexes and in the electrochemically generated polymers are summarized in Table 1. The bands at about 1490, 1460, 1220, 1050, and 702 cm^{-1} are assigned respectively to the $\text{C}_2=\text{C}_3$ and $\text{C}_4=\text{C}_5$ antisymmetric stretching, $\text{C}_2=\text{C}_3$ and $\text{C}_4=\text{C}_5$ symmetric stretching, inter-ring C-C stretching, CH in-plane bending, and ring deformation. The Raman spectra of the "dark-blue" species correspond to those of doped (oxidized) polythiophene (=polythiophene cation) and doped polymethylthiophene (=polymethylthiophene cation) that were electrochemically synthesized (Akimoto *et al.*, 1984), although some differences are present, e.g., frequency shifts of the ring-stretching bands.

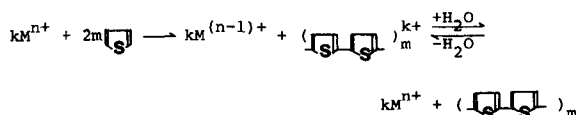
Table 1. Observed Raman bands (cm^{-1}) of polythiophene and polymethylthiophene.

Synthesized polythiophene ¹	Formed in interlayer of Cu-montmorillonite		Synthesized polymethylthiophene ²
	Thiophene	3-Methylthiophene	
1498	1493	1534	1524
1461	1460	1460	1463
		1383	1363
1222	1219	1193	1212
			1187
1045	1047	990	984
701	702	740	721
		553	548

¹ Akimoto *et al.* (1986).

² Akimoto *et al.* (1984).

From the above results, the following reactions similar to the reaction of benzene probably took place in the interlayer of the montmorillonite:



The polythiophene cation was formed also from the adsorption of 2,2'-bithiophene on Cu^{2+} -montmorillonite. The same dark-blue color developed during the adsorption of 2,2'-bithiophene, and this species changed reversibly to the "reddish-purple" species on contact with water. A comparison of the resonance Raman spectrum of this "reddish-purple" species with that of the species formed from thiophene (Figure 5) shows the essential identity of the two.

Characterization of polythiophenes formed in the interlayer

The amount of polythiophene formed from thiophene adsorbed in the interlayer was estimated from the quantitative analysis of the resonance Raman spectra. Electrochemically synthesized polythiophene and a polythiophene-Cu-montmorillonite complex ("reddish-purple" form) were each weighed, powdered and mixed with Na_2SO_4 as an internal standard. Polythiophenes used for the quantitative analysis were in the neutral form. The powder, spread on an adhesive tape, was spun at 1000 rpm on the rotating device, and resonance Raman spectra were measured. Based on the intensity ratio of the band at 1460 or 1047 cm^{-1} for neutral polythiophene and that at 994 cm^{-1} for Na_2SO_4 , the number of thiophene units of polythiophene formed in the interlayer was estimated to be about 140–240 mmole/100 g clay for Cu-montmorillonite. Quantitative analysis of XPS showed that the amount of interlayer metal ions in montmorillonite was consistent with the CEC, the same as the bulk structure (Seyama Soma, 1984).

Thus, the amount of thiophene adsorbed was esti-

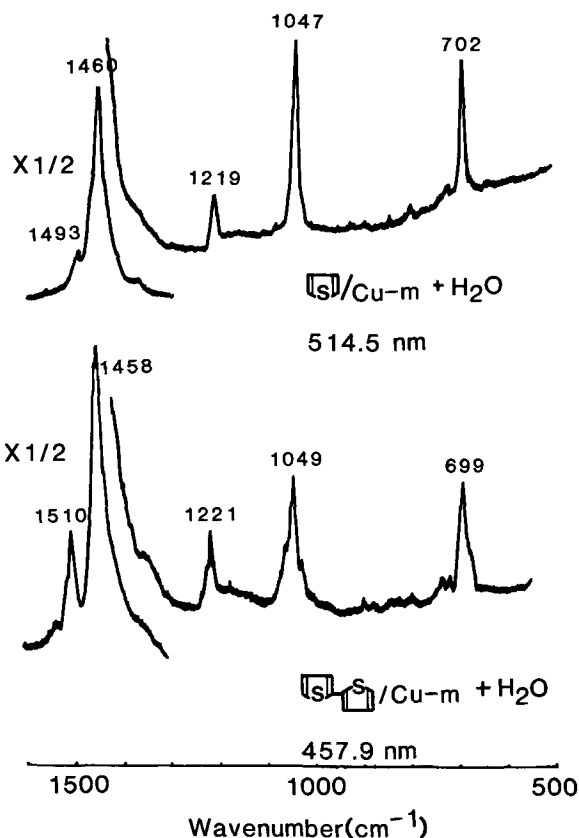


Figure 5. Resonance Raman spectra of polythiophene formed from the adsorption of (a) thiophene and (b) 2,2'-bithiophene on Cu^{2+} -montmorillonite (Cu-m) (514.5 and 457.9-nm excitations respectively).

ated by S 2p and Si 2s line intensities of XPS, assuming that the distribution of thiophene molecules in the interlayer was homogeneous. The S/Si ratio in the thiophene-treated Cu-montmorillonite was 0.25, corresponding to about 250 mmole/100 g clay, in agreement with the result from the resonance Raman spectra. The amount of thiophene in the interlayer (140–240 mmole/100 g clay) was 3–5 times the amount of Cu ion in the interlayer (55 mmole/100 g). Accordingly, thiophene oxidized by Cu^{2+} probably acted as an initiator of the polymerization reaction involving adsorbed thiophene.

The wavelength of the absorption band in the visible region is known to correlate to the length of conjugated polymers (Bredas *et al.*, 1983). Polythiophene formed in the interlayer of montmorillonite had an absorption band at 540 nm, as shown in Figure 1, whereas that synthesized electrochemically had a band at shorter wavelength, 460 nm (Akimoto *et al.*, 1984). The conjugation length of polythiophene in the interlayer of montmorillonite was estimated by the absorption band at 540 nm, using Bredas' method (the valence effective Hamiltonian technique, Bredas *et al.*, 1983), to be about

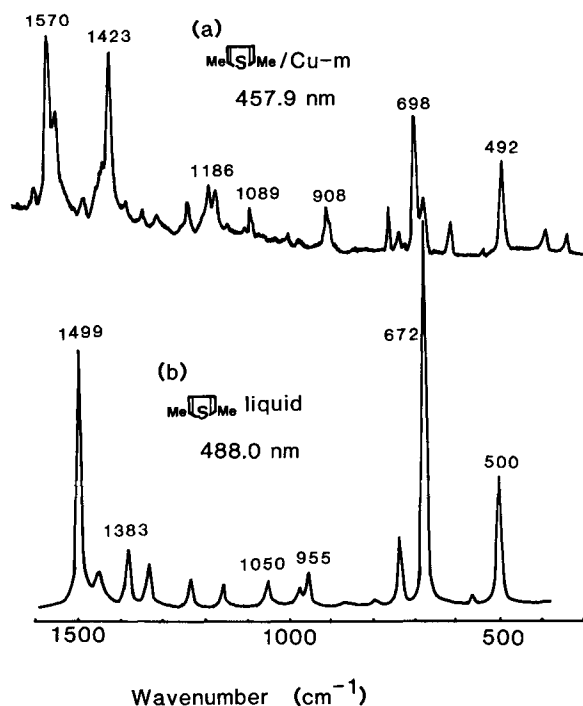


Figure 6. Resonance Raman spectrum of (a) 2,5-dimethylthiophene adsorbed on Cu^{2+} -montmorillonite (Cu-m) in a dry atmosphere (457.9-nm excitation) and (b) Raman spectrum of liquid 2,5-dimethylthiophene.

25, which corresponded to the chain length of about 9 nm. On the other hand, polymethylthiophene formed in the interlayer of montmorillonite had an absorption at a shorter wavelength compared with that synthesized electrochemically—445 nm for adsorbed polymethylthiophene and 485 nm for the synthesized polymer. Thus, the conjugation length of polythiophene formed on montmorillonite appears to be longer compared with that synthesized electrochemically, whereas the conjugation length of polymethylthiophene formed on montmorillonite appears to be shorter than that synthesized electrochemically. This difference may have been caused by steric hindrance against adsorption of methylthiophene.

The length of conjugated segments also correlates to the frequency of the $\text{C}_2=\text{C}_3$ and $\text{C}_4=\text{C}_5$ antisymmetric stretching vibration at about 1500 cm^{-1} . Polythiophene, having a longer conjugation length, shows a lower frequency (Akimoto *et al.*, 1985). As shown in Table 1, this relation confirms the above conclusion concerning the conjugation length of polythiophene formed in the interlayer of clay and synthesized electrochemically. Adapting this relation in the montmorillonite-polythiophene complexes in Figure 5, the conjugation length of polythiophene formed from thiophene (1493 cm^{-1}) appears to be longer than that from 2,2'-bithiophene (1510 cm^{-1}).

In the XPS measurement, the area intensity of the $\text{Cu } 2p_{3/2}$ peak (including the satellite for Cu-montmorillonite without thiophene) relative to those of peaks due to elements in the montmorillonite structure, e.g., Si, Al, and Mg, increased remarkably after the adsorption of thiophene. The Cu/Si ratio for the thiophene-treated sample reached a level 5 times as great as that for the untreated Cu-montmorillonite, whereas the latter ratio was consistent with the CEC of the montmorillonite ($\sim 100\text{ meq}/100\text{ g}$ clay). Taking the surface sensitivity of XPS into account, the increase of the Cu^+ ions for thiophene-treated sample in XPS measurement suggests that Cu^+ ions migrated to the surface of montmorillonite during the formation of polythiophene cations.

The ESR signal due to the polythiophene cation radical on Cu-montmorillonite had a g-factor of 2.0024, which is slightly lower than that reported for adsorbed thiophene on Fe-hectorite (Pinnavaia *et al.*, 1974) and close to that for the free electron and for hydrocarbon cation radicals in metal-ion-exchanged montmorillonite. This implies that no significant amount of spin density was on the sulfur atom. Otherwise, the spin-orbit interaction with the sulfur atom would have increased the g-factor. The same result has been reported for doped synthetic polymethylthiophene (Tourillon *et al.*, 1984). The spin concentration estimated from the intensity of ESR signal was only about 1% of Cu^{2+} ions reduced. Thus, the polythiophene cation in the interlayer of clay was essentially diamagnetic, also consistent with what has been suggested for doped polythiophene, i.e., two monocationic radical segments (polaron) in the polythiophene tend to fuse into a more stable dication segment (bipolaron) (Bredas *et al.*, 1981).

Adsorption of 2,5-dimethylthiophene

The spectrum of 2,5-dimethylthiophene adsorbed on Cu^{2+} - or Fe^{3+} -montmorillonite is quite different from those of adsorbed thiophene and 3-methylthiophene, as shown in Figure 1. The absorption band extending into the IR region is absent, and no new band was observed in the visible region when water was introduced to the clay. An ESR signal due to the cation radical was observed in the formation of the adsorbed species having an absorption at 492 nm, and the signal due to Cu^{2+} ions was reduced.

Raman bands of 2,5-dimethylthiophene adsorbed on Cu^{2+} -montmorillonite had narrower band widths than those of adsorbed thiophene which formed polymer in the interlayer, as shown in Figure 6. The IR spectrum of adsorbed 2,5-dimethylthiophene, as compared with that of free 2,5-dimethylthiophene (Figure 7), showed large differences in intensities of ring-stretching (1550 cm^{-1}) and CH in-plane deformation (1230 cm^{-1}) bands. Also, the spectrum was different from that of thiophene or 3-methylthiophene adsorbed

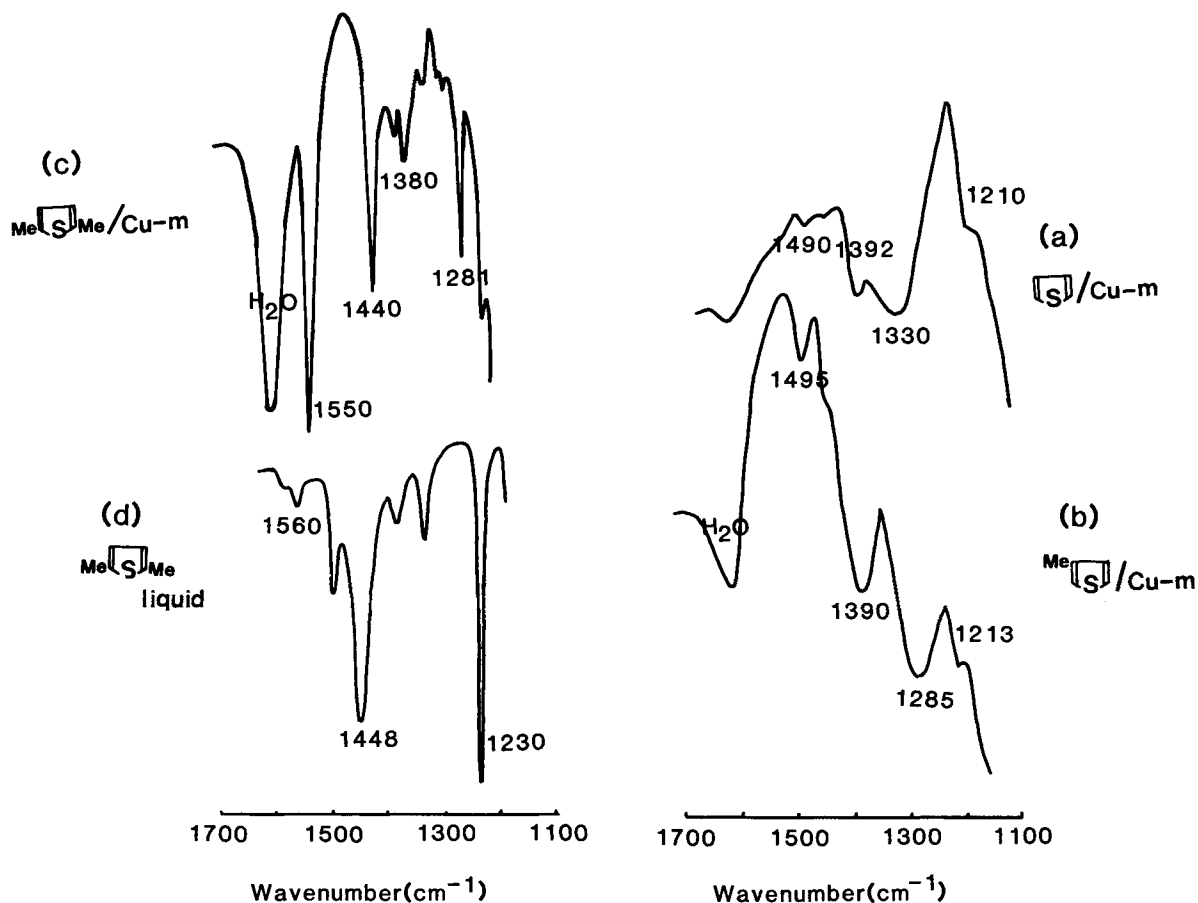


Figure 7. Infrared spectra of (a) thiophene, (b) 3-methylthiophene, (c) 2,5-dimethylthiophene adsorbed on Cu^{2+} -montmorillonite (Cu-m), and (d) the spectrum of liquid 2,5-dimethylthiophene.

which had broad absorption bands because of the formation of polymers, as shown in Figure 7. Although no reference spectrum of the 2,5-dimethylthiophene cation exists, from ultraviolet, Raman, and ESR spectra the cation radical of 2,5-dimethylthiophene must form on adsorption on Cu^{2+} -montmorillonite. The inactivity of 2,5-dimethylthiophene toward polymerization resembles that of para-disubstituted benzenes (Soma *et al.*, 1983a, 1984).

CONCLUSION

The formation of polythiophene and polymethylthiophene in the adsorption of thiophene and 3-methylthiophene on Cu^{2+} - and Fe^{3+} -montmorillonites has been demonstrated using resonance Raman spectroscopy. This polymerization reaction is considered to proceed through the oxidation of thiophene by the interlayer metal ion, wherein the thiophene cation acts as the initiator to form the polythiophene cation.

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