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Adsorption of tetrakis(*p*-sulfonatophenyl)porphyrin on kaolinite

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Abstract The surface modification of kaolinite to introduce the adsorption sites for anionic species was reported. The introduction of an anion exchange site was as follows; intercalation of 2-aminoethanol into kaolinite by using dimethyl sulfoxide-kaolinite intercalation compound as a precursor and subsequent hydrochlorination of 2-aminoethanol-kaolinite in 1,4-dioxane. The hydrochlorination of 2-aminoethanol-kaolinite was confirmed by the increase in the basal spacing (0.2 nm, corresponding to the diameter of chlorine) and the appearance of the infrared absorption bands due to ammonium groups. The modified kaolinite adsorbed an anionic dye, tetrakis(*p*-sulfonatophenyl)porphyrin, from a N,N-dimethylformamide solution. Initial slope of the adsorption isotherm of tetrakis(*p*-sulfonatophenyl)porphyrin on the hydrochlorinated 2-aminoethanol-kaolinite was steep, showing strong adsorbate-adsorbent interactions. The gallery height after the adsorption of tetrakis(*p*-sulfonatophenyl)porphyrin was close to the thickness of the porphyrin ring, suggesting that tetrakis(*p*-sulfonatophenyl)porphyrin was intercalated as a

monomolecular layer and that chlorine simultaneously deintercalated.

Key Words : Kaolinite, Adsorption, Surface modification, Anion exchange, Tetrakis(*p*-sulfonatophenyl)porphyrin

Introduction

Adsorption of photoactive species onto layered solids has been investigated to control the functions of the adsorbed species [1] by the host-guest and guest-guest interactions. Smectite group of layered clay minerals, which formed by the condensation of sheets of linked $Si(O,OH)_4$ tetrahedra with those of linked $M_{2-3}(OH)_6$ octahedra in a 2:1 proportion, has been used for the guest organization especially cationic dyes. The cation exchange reactions of interlayer cations of smectites with cationic dyes led functional inorganic-organic hybrids with unique nanostructures. The arrangement, the orientation and the spatial distribution of the dyes in the interlayer spaces have been controlled by the layer charge densities of smectites and the molecular structures of the dyes as well as the co-adsorption of photo-inactive guest species. The functions of the intercalation compounds have been varied depending on the arrangement, the orientation and the spatial distribution of the dyes in the interlayer spaces [2].

In contrast, the adsorption of dyes onto kaolinite has scarcely been investigated [3,4], because of the limited ability of kaolinite to accommodate guest species in the interlayer space. Kaolinite is a 1:1 type layered clay with a formula of $Al_2Si_2O_5(OH)_4$, which is composed of two types of interlayer surface, $(SiO)_6$ siloxane surface and aluminol groups on the other side [5]. Due to bonding between these surfaces through hydrogen-bonding, the molecules with relatively larger dipole moment as urea [6,7], formamide [6,7], hydrazine [7,8], dimethyl sulfoxide [9] and methanol [10] have been intercalated. By using these intercalation compounds as precursors, methoxylation of aluminols [11,12] and the intercalation of relatively bulky molecules (alkanediols [13,14], aminoalcohols [15], polyacrylamide [16] and polyols [17]) became possible because of weaker attractive force and greater swelling properties of the precursors.

Here, we report the organic modification of kaolinite to introduce the adsorption sites for anionic species for the first time. The modification was conducted by the intercalation of 2-aminoethanol [15] and the subsequent hydrochlorination of 2-aminoethanol. The successful formation of anion adsorption site was shown by the adsorption of an anionic dye, tetrakis(*p*-sulfonatophenyl)porphyrin (TPPS) (Scheme 1).

Experimental

Materials

Kaolinite (obtained from Kampaku mine, Tochigi, Japan), a reference clay sample of the Clay Science Society of Japan, used as received. Dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), 1,4-dioxane and hydrochloric acid (12 mol/L) were purchased from Kanto Chemical Co., Ltd. 2-Aminoethanol (AEO) and tetrakis(*p*-sulfonatophenyl)porphyrin (α,β,χ,δ-tetraphenylporphine tetrasulfonic acid, abbreviated as TPPS, Scheme 2) were purchased from Tokyo Kasei Kogyo Co. Ltd., and were used as received.

(Insert Scheme 2)

Sample Preparation

Intercalation of AEO into kaolinite by using DMSO-kaolinite as a precursor and the subsequent hydrochlorination of AEO-kaolinite were conducted to give adsorbent, AEOCl-kaolinite. DMSO-kaolinite [9] was prepared by mixing of raw kaolinite (2.0 g) with aqueous DMSO solution (91 %; v/v) for 120 h in a sealed vessel. After centrifugation at 4k rpm for 20 min, the resulting solid was washed with 1,4-dioxane and was subsequently dried under a reduced pressure at room temperature. DMSO-kaolinite (1.0 g) was aged in AEO (50 mL) under nitrogen atmosphere at 443 K for 1 day to exchange DMSO with AEO. After centrifugation (4 krpm, 20 min) and subsequent washing with 1,4-dioxane, the solid product was dried under a reduced pressure at room temperature to give AEO-kaolinite [15]. AEO-kaolinite (0.1 g) was added to the mixture of hydrochloric acid (100 μL, 12 mol/L) with 1,4-dioxane (20 mL) and was allowed to react with hydrochloric acid for 1 day at room temperature. The resulting solid was dried under a reduced pressure at room temperature. This procedure was repeated to give AEOCl-kaolinite.

Adsorption of TPPS on AEOCl-kaolinite from DMF solution

AEOCl-kaolinite (20 or 15 mg) was added to a TPPS DMF solution (6.82×10^{-3} mmol / 20 mL or 1.73×10^{-2} mol / 50 mL) and the mixture was allowed to react for 1 day at 298 K. After centrifugation at 4 krpm for 20 min, the product was washed with DMF and was dried under a reduced pressure. The amount of the adsorbed TPPS was determined from the difference between the initial and equilibrium concentrations of the TPPS solutions. Blank samples containing TPPS DMF solution, without adsorbents, were prepared to estimate vaporization losses and the adsorption on the glass vessel. The concentration of the remaining TPPS in the supernatant was determined by visible absorption spectroscopy.

Characterizations

X-Ray diffraction patterns were obtained using a Rigaku RAD IB using monochromatic Cu Kα radiation, operated at 20 mA and 40 kV. Infrared spectra were recorded on a Shimadzu FT-8200 Fourier-transform infrared spectrophotometer. TG-DTA curves were measured by a Rigaku Thermoplus TG 8120 instrument with a heating rate of 10 K/min using α-Al_2O_3 as the standard material under air. UV-Visible absorption spectra were recorded on a Shimadzu UV 3100 PC spectrophotometer. The diffuse reflectance spectra were recorded on a Shimadzu UV-3100PC spectrometer equipped with an integrated sphere attachment.

Results and Discussion

Preparation of the adsorbent for TPPS

A diffraction peak due to (*001*) with the *d* value of 1.11 nm appeared in the XRD pattern (Fig. 1b) of DMSO-kaolinite. The gallery height (0.39 nm), which was obtained by subtracting the thickness of the aluminosilicate layer (0.72 nm) from the observed basal spacing (1.11 nm), was close to the value (1.116 nm) [9] coincide with the diameter of the methyl group (0.40 nm), suggesting the intercalation of DMSO. In the infrared spectrum of DMSO-kaolinite (Fig. 2A-b), hydroxyl stretching bands at 3695, 3537 and 3502 cm^{-1} presently appeared and corresponded to those at 3690, 3535 and 3499 cm^{-1}, suggesting that intercalation of DMSO resulted from the DMSO breaking the interlayer hydrogen bonds and reforming them [9]. Thus, the formation of DMSO-kaolinite was confirmed.

In the XRD pattern (Fig. 1) of the product obtained by the reactions of

DMSO-kaolinite with AEO, a diffraction peak with d_{001} value (1.07 nm, Fig. 1c) was observed with disappearing the (*001*) peak of DMSO-kaolinite (1.11 nm, Fig. 1b). The gallery height (0.35 nm = 1.07 nm - 0.72 nm) observed for AEO-kaolinite was in accordance with the value reported previously [15]. They pointed out [15] that the smaller gallery height (0.35 nm) than the 0.4-nm minimum void space that calculated for AEO was due to some keying in of AEO. A diffraction peak with *d* value of 0.71 nm was observed both for the DMSO- and the AEO-forms, indicating that a certain portion of raw kaolinite remained by these reactions.

The infrared absorption bands for AEO-kaolinite were observed at 3628, 3558 cm^{-1} (ν_{O-H}), 3354, 3311 cm^{-1} (ν_{N-H}) 3074, 2964, 2946, 2889 cm^{-1} (ν_{C-H}) (Fig. 2A-c), 1614 cm^{-1} (δ_{N-H}), 1476 cm^{-1} (δ_{-CH2-}) (Fig. 2B-c), 974 cm^{-1} (δ_{Al-OH}) (Fig. 2C-c). It was reported that bands due to hydroxyl groups hydrogen-bonded with amino group of polyacrylamide appeared at a relatively lower wavenumber region if compared with those of raw kaolinite [16]. Spectral red shifts observed in the present system for the ν_{O-H} bands from 3670 and 3652 cm^{-1} (raw kaolinite, Fig. 2A-a) to 3628 and 3558 cm^{-1} (AEO-kaolinite), respectively, suggest the hydrogen-bonding of the hydroxyls with AEO [15]. In addition, the spectral blue shift of the δ_{Al-OH} band of inner surface kaolinite from 938 cm^{-1} (kaolinite, Fig. 2C-a) to 974 cm^{-1} has also been thought to be due to strong host-guest interactions between AEO moiety and kaolinite [15], <u>but not covalent attachment of AEO to the octahedral sheet of kaolinite [18].</u>

In the DTA curves of the product (Fig. 3), an exothermic peak due to oxidative decomposition of AEO in the range of 210 – 450 °C, which accompanied the mass loss of 7.1 mass % in the corresponding TG curve was observed. From the mass loss, the amount of the immobilized AEO to kaolinite was determined to be $(C_2H_7NO)_{0.5}$ per $Al_2Si_2O_5(OH)_4$ unit.

(Insert Fig.s 1,2 and 3)

By the reactions of AEO-kaolinite with hydrochloric acid, a diffraction peak with d_{001} value of 1.27 nm appeared (Fig. 1d), while the diffraction peak due to the the basal plane (d_{001} = 1.07 nm) of AEO-kaolinite (Fig. 1c) disappeared. The increase in the basal spacing (0.20 nm = 1.27 – 1.07 nm) corresponded to the ionic diameter of chloride (0.18 nm). In the FT-IR spectrum of AEOCl-kaolinite, the absorption bands due to $\nu_{O\text{-}H}$ at 3601 and 3540 cm^{-1}, $\nu_{N\text{-}H+}$ at around 3080 cm^{-1} (Fig. 2A-d) and $\delta_{N\text{-}H+}$ at 1490 cm^{-1} (Fig. 2B-d) were observed. In addition, the absorption band due to $\delta_{N\text{-}H}$ at 1614 cm^{-1} observed for AEO-kaolinite (Fig. 2C-d) disappeared. From the XRD and IR results, hydrochlorination of AEO-kaolinite was shown. As to the $\nu_{O\text{-}H}$ bands, the positions at 3628 and 3558 cm^{-1} for AEO-kaolinite shifted to lower wavenumber regions by the hydrochlorination, suggesting that the protonation of amino groups to ammonium groups led to relatively stronger hydrogen-bonding to the hydroxyl groups of kaolinite. The disappearance of the band at 974 cm^{-1} ($\delta_{Al\text{-}OH}$) by the hydrochlorination was probably attributed to the strong hydrogen-bonding with further spectral blue shift, resulting in perturbation by the lattice vibration region.

The TG curve of AEOCl-kaolinite (Fig. 4) shows mass losses due to dehydration (4 mass %, r.t.-100 °C) and the oxidative decomposition of AEOCl (11 mass %, 230-450 °C). The mass loss due to the oxidative decomposition appeared at the temperature range close to that observed for the AEO-kaolinite, suggesting that AEO was hydrochlorized without desorption.

(Insert Fig. 4)

Adsorption of TPPS on AEOCl-kaolinite

The adsorption isotherm of TPPS on AEOCl-kaolinite from DMF solution is shown in Fig. 5, together with that on raw kaolinite. TPPS was not adsorbed on raw kaolinite, while was onto AEOCl-kaolinite. The initial slope of the isotherm for AEOCl-kaolinite was steep, showing strong adsorbate-adsorbent interactions. The maximum adsorbed amount was 0.28 mmol (g kaolinite)$^{-1}$, which corresponded to 0.07 mol per $Al_2Si_2O_5(OH)_4$ unit. Hereafter, the products with TPPS adsorbed amounts of 0.05 and 0.07 mol per $Al_2Si_2O_5(OH)_4$ unit designate $TPPS_{0.05}$-kaolinite and $TPPS_{0.07}$-kaolinite, respectively. The change in the XRD pattern by the adsorption is shown in Fig. 6. A diffraction peak with *d* value of 1.23 nm appeared for $TPPS_{0.05}$-kaolinite. The relative contribution of the peak (*d* = 1.23 nm) to that due to the basal plane of AEOCl-kaolinite (1.27 nm) increased with increasing the amount of the adsorbed TPPS. In the XRD pattern of the $TPPS_{0.07}$-kaolinite, the peak due to the basal plane of AEOCl-kaolinite was not observed.

Judging from the observed gallery height (0.54 nm = 1.23 – 0.71 nm) and the size of TPPS (1.7×1.7×0.4 nm estimated by Chem3D, CambridgeSoft®), the adsorbed TPPS is thought to be a monomolecular arrangement with their molecular planes of porphyrin rings (0.4 nm) parallel to the aluminosilicate layer. Considering to the diameter of chloride (0.18 nm) and the basal spacing of AEO-kaolinite (1.07 nm), the decrease in the basal spacing upon the adsorption of TPPS from 1.27 to 1.23 nm can be attributed to the deintercalation of chloride. We deduce that the anion exchange reactions between AEOCl-kaolinite and TPPS are a possible driving force for the adsorption of TPPS. In the infrared absorption spectrum for TPPS-kaolinite (Fig. 7b), the bands due to AEO were ascribable to ($\nu_{N\text{-}H+}$ at around 3080 cm^{-1} and δ_{NH3+} at 1490 cm^{-1}) the ammonium form, showing that interlayer AEO retained ammonium form after the TPPS adsorption. This observation supported the above discussion on the anion exchanges.

(Insert Fig.s 5, 6 and 7)

Diffuse reflectance spectra of $TPPS_{0.05}$- and $TPPS_{0.07}$-kaolinite are shown in Fig.s 8b and 8c, respectively. Two absorption bands ascribable to the porphyrin

Soret bands were observed at 423 and 451 nm (Fig.s 8b and 8c) irrespective of the amount of the adsorbed TPPS. The Soret bands for monomeric free-base TPPS (tetraanion) and for its protonated dianion monomer were reported to be seen at 410 and 432 nm, respectively, in water [19,20]. Akins and his co-workers also reported that the absorption band appeared at around 490 nm when the protonated TPPS dianion formed J-aggregate [20]. Thus, the presently observed two absorption bands (423 and 451 nm) can be ascribed to TPPS monomers (both the free-base and the protonated form). Protons was thought to be supplied from AEOCl in kaolinite to free-base TPPS tetraanions. The ratio of the protonated dianion to the tetraanion is unclear at present. If all of TPPS were adsorbed as tetraanion, the molar ratio of AEOCl to the adsorbed TPPS should be 4. The minimum molar AEOCl / TPPS ratio based on the adsorbed amount per $Al_2Si_2O_5(OH)_4$ unit was ca. 7 (= 0.5 / 0.07), indicating that the anion exchange sites was not fully exchanged with TPPS at least.

The Soret band for the free-base TPPS in methanol was observed at 423 nm (Fig. 8a), which is a longer wavelength region compared to that in water (410 nm) [19,20]. We assume that TPPS-kaolinite have the 423- and 451-nm absorption bands, which were seen in longer wavelength regions than monomeric TPPS in water (410 and 432 nm), as a result of the interactions between TPPS and AEO in kaolinite.

(Insert Fig. 8)

Conclusions

Organic modification of kaolinite (Kampaku) with 2-aminoethanol and subsequent hydrochlorination of 2-aminoethanol were conducted to introduce the adsorption site for anionic species. The successful formation of an anionic exchange site was shown by the adsorption of an anionic dye, tetrakis(*p*-sulfonatophenyl)porphyrin.

Acknowledgment

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Figure captions

Fig. 1 XRD patterns of (a) kaolinite, (b) DMSO-kaolinite, (c) AEO-kaolinite and (d) AEOCl-kaolinite

Fig. 2 FT-IR spectra of (a) kaolinite, (b) DMSO-kaolinite, (c) AEO-kaolinite and (d) AEOCl-kaolinite

Fig. 3 TG-DTA curves of (a) kaolinite and (b) AEO-kaolinite

Fig. 4 TG-DTA curves of AEOCl-kaolinite

Fig. 5 Adsorption isotherms of TPPS on kaolinite (open circle) and AEOCl-kaolinite (filled circle) from DMF solution

Fig. 6 XRD patterns of (a) kaolinite, (b) AEOCl-kaolinite, (c) TPPS$_{0.05}$-kaolinite and (d) TPPS$_{0.07}$-kaolinite

Fig. 7 FT-IR spectra of (a) AEOCl-kaolinite and (b) recorded after the adsorption of TPPS on (a).

Fig. 8 Absorption spectra of (a) TPPS methanol solution, (b) TPPS$_{0.05}$-kaolinite and (c) TPPS$_{0.07}$-kaolinite

Scheme 1 Schematic drawing of the structural change in the hydrochlorination of aminoethanol and subsequent adsorption of TPPS in the interlayer space of kaolinite

Scheme 2 The molecular structure of tetrakis(*p*-sulfonatophenyl)porphyrin

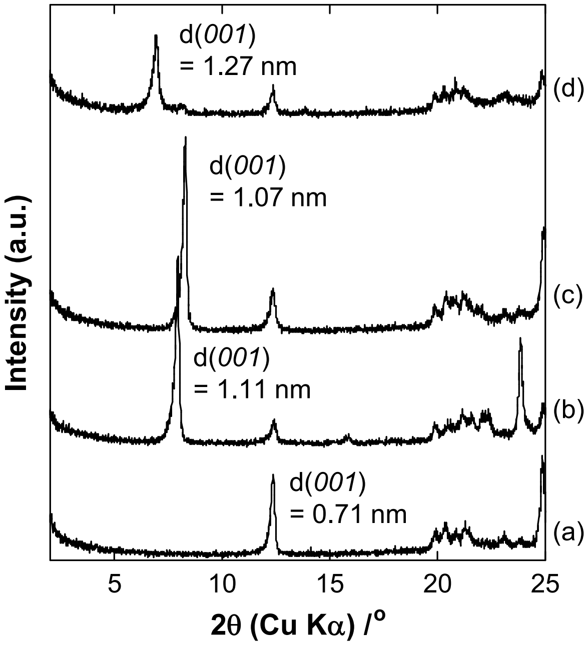


Figure 1 XRD patterns of (a) kaolinite, (b) DMSO-kaolinite, (c) AEO-kaolinite and (d) AEOCl-kaolinite

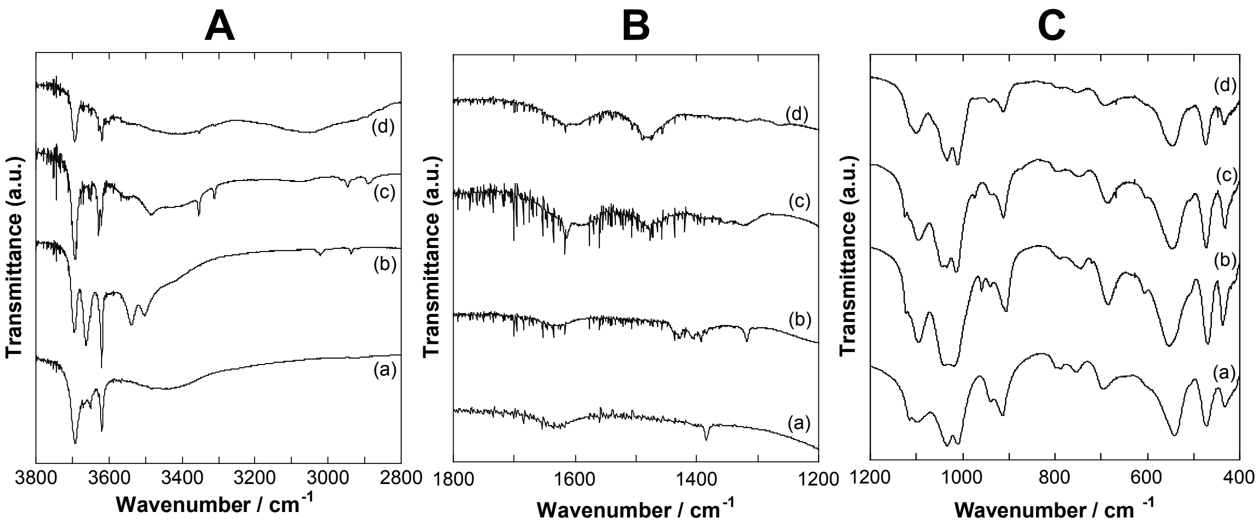


Figure 2 FT-IR spectra of (a) kaolinite, (b) DMSO-kaolinite, (c) AEO-kaolinite and (d) AEOCl-kaolinite

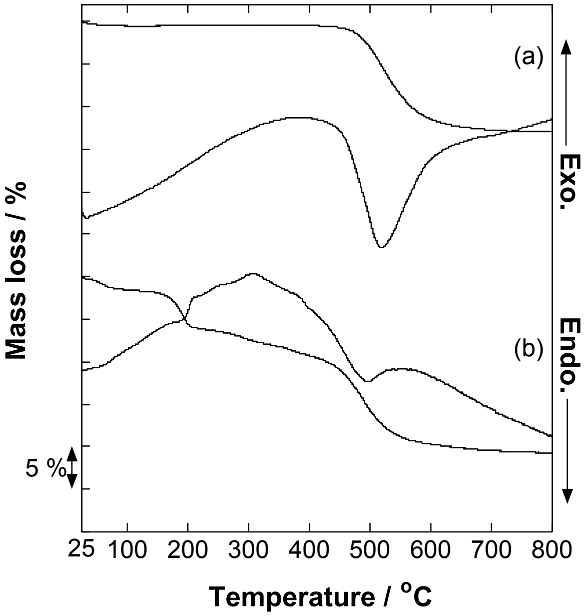


Figure 3 TG-DTA curves of (a) kaolinite and (b) AEO-kaolinite

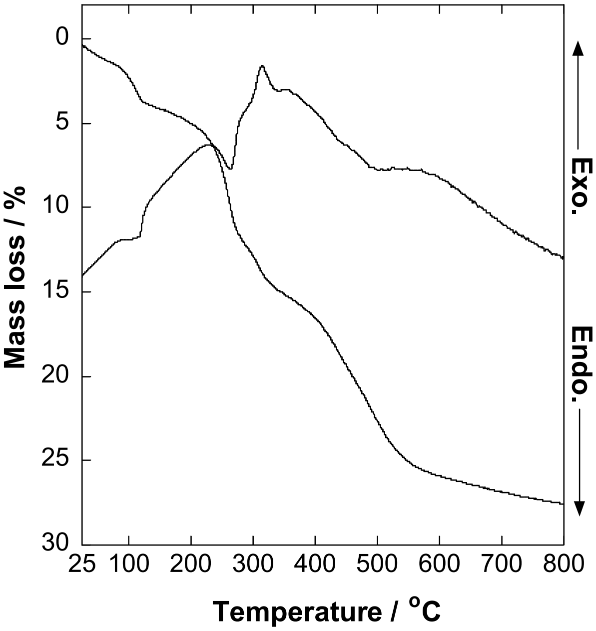


Figure 4 TG-DTA curves of AEOCl-kaolinite

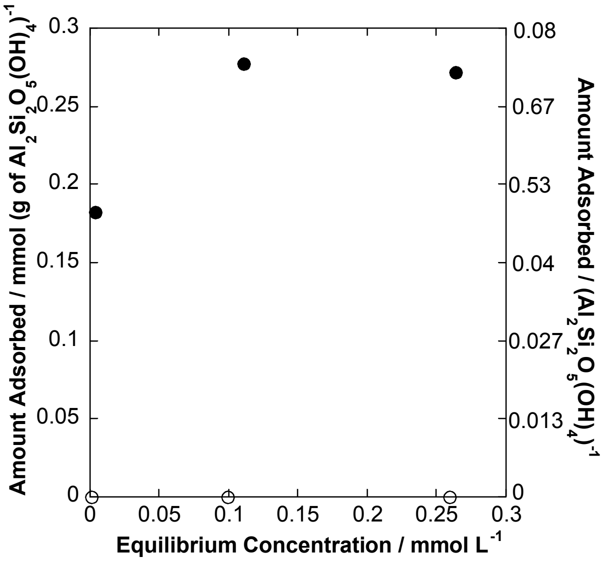


Figure 5 Adsorption isotherms of TPPS on kaolinite (open circle) and AEOCl-kaolinite (filled circle) from DMF solution.

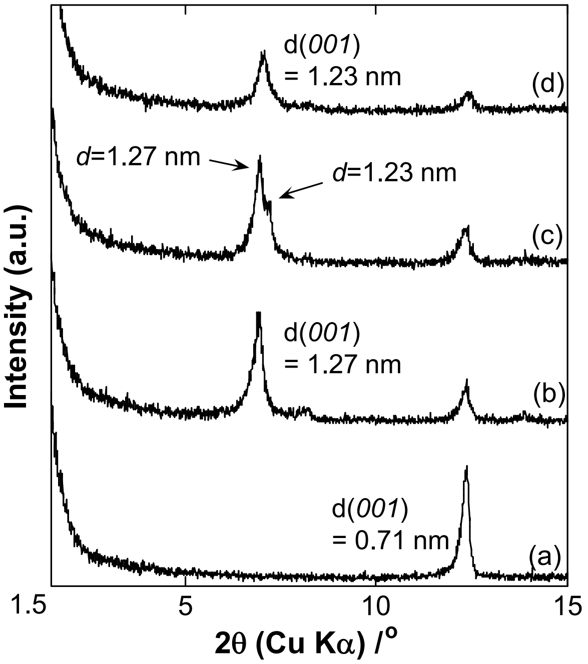


Figure 6 XRD patterns of (a) kaolinite, (b) AEOCl-kaolinite, (c) $TPPS_{0.05}$-kaolinite and (d) $TPPS_{0.07}$-kaolinite

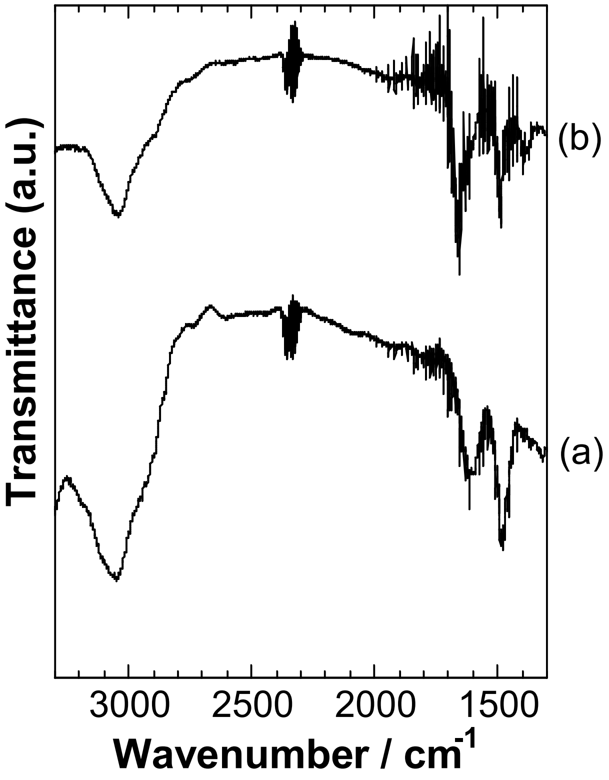


Figure 7 FT-IR spectra of (a) AEOCl-kaolinite and (b) recorded after the adsorption of TPPS on (a).

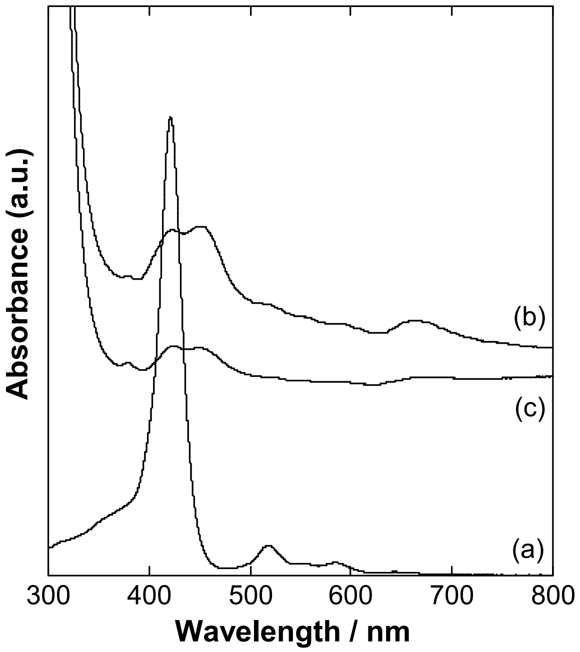
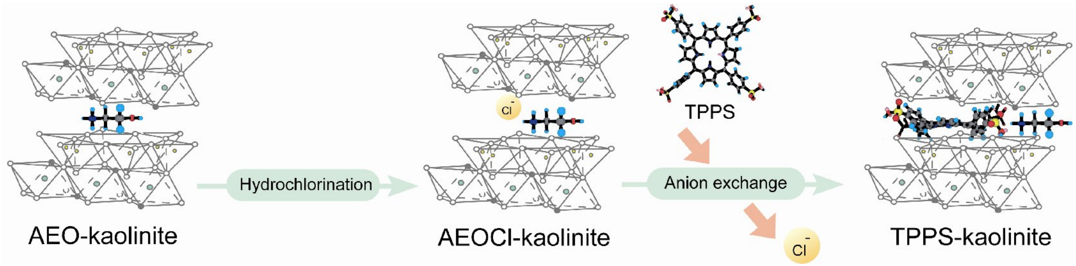
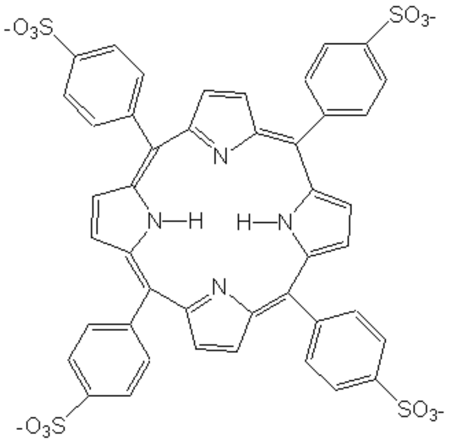


Figure 8 Absorption spectra of (a) TPPS methanol solution, (b) $\text{TPPS}_{0.05}$-kaolinite and (c) $\text{TPPS}_{0.07}$-kaolinite



Scheme 1 Schematic drawing of the structural change in the hydrochlorination of aminoethanol and subsequent adsorption of TPPS in the interlayer space of kaolinite



Scheme 2 The molecular structure of tetrakis(*p*-sulfonatophenyl)porphyrin