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KINETICS OF TOLUENE SORPTION AND DESORPTION IN CA- AND CU-MONTMORILLONITES INVESTIGATED WITH FOURIER TRANSFORM INFRARED SPECTROSCOPY UNDER TWO DIFFERENT LEVELS OF HUMIDITY

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Abstract—Clays in soils or groundwater aquifer materials play roles in the sorption of organic pollutants. The intrinsic sorption kinetics of toluene in dry and humid clay films was investigated by tracking the change of infrared absorbance. Under the humid condition, similar toluene-sorbed intensities were found in Ca- and Cu-montmorillonites. However, a higher intensity of sorbed toluene was found in the Cu-form than in the Ca-form under the dry condition, which indicates a stronger interaction occurring in dry Cu-montmorillonite. The general time scale of sorption of toluene on clays is around 100 s. In both forms of montmorillonite, some portion of toluene was desorbed at an extremely slow rate under the dry condition. Some newly identified peaks were persistent against desorption from montmorillonites, suggesting the existence of irreversibly sorbed species and the possibility of toluene transformation occurring in clay systems.

Keywords—Sorption Toluene Ca-montmorillonite Cu-montmorillonite Fourier transform infrared spectroscopy

INTRODUCTION

Sorption of organic contaminants in soils plays an important role in their transport, fate, and bioavailability in the environment. Although equilibration has often been assumed between the free dissolved phase and the sorbed phase of organic sorbates, the phenomenon of irreversible sorption or slow desorption of organic pollutants in the laboratory or in the field has been reported. A portion of sorbed organic pollutants was released from soil particles slowly. Some fraction was even retained in the particles irreversibly [1,2]. Such retention of the pollutants in soils affects their fate in the environment and the effectiveness of the remediation of contaminated soils and groundwater aquifers.

However, soil is chemically a heterogeneous material with various inorganic and organic constituents. Delineation of the sorption rate and the reversibility of each component is necessary to tell precisely which component contributes the most to the slow sorption and to what extent and to predict the tendency of migration and attenuation of the pollutants in soils.

Numerous researchers have observed that the sorption of volatile organic compounds (VOCs) in soil particles appears to be a biphasic process in which an initial stage of rapid sorption is followed by a slow sorption stage. Karickhoff [3] referred these two stages as ‘‘labile’’ and ‘‘nonlabile’’ stages of sorption. Several researchers interpreted the slow or long-term sorption of VOCs to be the result of intraorganic matter diffusion [4,5]. Some researchers [6,7] suggested that the persistence of organic pollutants in soils resulted from the entrapment of contaminants in soil organic matter. Wu and Gschwend [8] explained the phenomenon of slow sorption by a radial diffusion model in which the sorbate migrates into and out of the aggregates of organic matter and mineral particles by diffusion.

Mineral surfaces as well as soil organic matter could act as contributing sorbents for slow sorption since soil samples with very low organic matter had shown biphasic desorption patterns for VOCs [9,10]. Achoi and Farmer [1] have demonstrated the formation of a resistant fraction of 1,2-dichloroethane on clays mixed with potassium bromine under a dry condition. Clay minerals offer a gigantic surface area for adsorption as well as surface-catalyzed reaction sites that we should not overlook. The clay mineral surfaces and cations in the interlayer can be electron acceptors or donors to provide catalytic capability [11,12]. Delineation of the relative importance of the roles of soil organic matter and soil minerals in sorption vary with the type of pollutants, and a knowledge of the composition of the soils is necessary. This study was conducted to investigate the role of clays on the slow desorption of contaminants from soils.

The gravimetric method with a microbalance has been used to trace the time courses of sorption of VOCs on soil organic matter [13–15] and on oven-dried clay [16,17], all under dry conditions. However, the major constraint associated with gravimetric methods for the investigation of sorption dynamics is the inability to observe the behavior at the molecular level or under a wet condition.

Molecular-level environmental observation, such as spectrometric methods, can be applied to provide information about the relative quantity, the energetic status, and the possible chemical transformation of the compounds.

Therefore, via an innovative thin-film/Fourier transform infrared (FTIR) method, this paper seeks to illustrate the sorption and desorption kinetics of VOCs on clay films, to clarify whether a strong interaction exists between toluene and clays, and to identify the molecular-level mechanism that may con-

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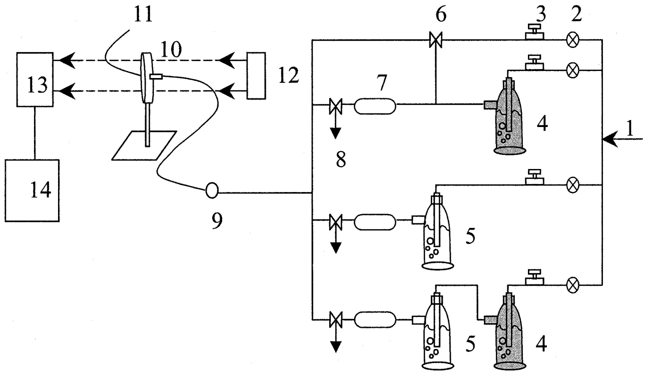

1. HC-free N_2 gas
2. On-off valve
3. Mass flow controller
4. Liquid toluene in a sparge bottle
5. Water in a sparge bottle
6. Three-way valve
7. Mixing chamber
8. Vent
9. Gas sampling port
10. Soil sample on ZnSe window
11. Gas vent
12. Infrared (IR) source
13. MCT (Mercury cadmium telluride) Detector
14. Data processor

Fig. 1. Schematic diagram of sorption and desorption experiments using the infrared spectroscopy method.

tribute to the irreversibility of toluene sorption under dry and humid conditions.

MATERIALS AND METHODS

Montmorillonite (STx-1) was obtained from the Source Clay Mineral Repository of the Clay Minerals Society (Department of Geology, University of Missouri, Columbia, MO, USA). Toluene, the target contaminant, was purchased from Acros Organics (Geel, Belgium). Copper (II) chloride and silver nitrate were also purchased from Acros Organics. Hydrogen peroxide and calcium chloride were obtained from Merck (Darmstadt, Germany). The deionized water used was produced by the Milli-Q reagent water system (Millipore, Bedford, MA, USA).

Preparation of clay films

The clay was treated with 35% hydrogen peroxide, and the fraction with particle sizes smaller than 2 μm was collected by sedimentation method. The Ca(II)- and Cu(II)-exchanged forms of clays were prepared by treating the clay (<2 μm) with 1.0-N solutions of $CaCl_2$ or $CuCl_2$, respectively, then centrifuging and removing the supernatant liquid. The procedure was repeated three times. Excess $CaCl_2$ and $CuCl_2$ were removed by washing with deionized water until the test for chloride with $AgNO_3$ showed a negative result [18]. The treated clay was dried using a freeze dryer and then stored in a sealed bottle before use.

Clay suspensions were homogenized by an ultrasonic oscillator (Branson Ultrasonics, Danbury, CT, USA), and the solid concentration of the suspension was approximately 8 mg/ml. A drop of this clay suspension (0.5 ml) was then deposited on the inner surface of a ZnSe window of a gas cell and allowed to dry to form a thin clay film.

Sorption/desorption experiments traced by FTIR

The schematic diagram of the experimental apparatus is shown in Figure 1. The gas cell had a 5-mm thickness and a 30-mm diameter with two ZnSe windows. All tubings are made of Teflon®. The clay film was purged with 50 ml/min of N_2 gas (hydrocarbon free) for at least 1 d to remove sorbed impurities before each experiment. When humid conditions were required, clay films were then purged with moisturized nitrogen gas. A steady flow of gas was passed through liquid toluene in a bottle and then mixed with a flow of pure N_2 gas to obtain a desired constant concentration of toluene vapor and the same flow rate as the purge gas. The sample cell was purged with nitrogen gas carrying toluene vapor with a constant concentration during sorption experiments under either low relative humidity (below 1%) or high relative humidity (above 95%). The relative humidity was measured at the outlet of the gas cell (component 11, denoted in Fig. 1) with a hygrometer (Oakton, Taiwan, ROC). Desorption experiments were carried out by purging the gas cell with pure N_2 gas at a rate of 50 ml/min for dry experiments or with the moisturized N_2 gas for humid experiments. Experiments were terminated when the change of the intensity of absorbance was not noticeable.

The concentration of the toluene was determined with a Hewlett-Packard 5890II gas chromatographer (Wilmington, DE, USA), equipped with a flame ionization detector and a 30-m × 0.53-mm i.d. × 1.5-μm SPB-5 fused silica capillary column (Supelco, Bellefonte, PA, USA.). The relative vapor concentration of toluene (P/P_0) was around 0.40 or 0.44 under dry or humid conditions, respectively, and was kept constant during each single run of experiment.

The absorbance spectra of an infrared beam passing through the gas cell windows were obtained on the BIO-Rad FTS 40 spectrometer (Randolph, MA, USA) at 2 cm^{-1} resolution by averaging 16 scans in the beginning and followed by 200 scans for long-term monitoring up to 60 d. The Bio-Rad spectrometer incorporated a Michelson interferometer with a KBr beam splitter and a liquid nitrogen–cooled mercury-cadmium-telluride detector. All spectra were ratioed against the optical batch background spectrum before each measurement. No subtraction was performed while obtaining the final spectra.

Synchrotron X-ray diffraction

X-ray diffraction (XRD) of clay samples in a capillary glass tube (1-mm diameter) was measured by using the Synchrotron XRD in the National Synchrotron Radiation Research Center, Taiwan. Samples (approximately 4 mg) in glass tubes were either treated with water to reach a high relative humidity condition or vacuumed and heated around 110°C to reach a dry condition. One hundred microliters of toluene liquid were injected through a septum into the clay samples.

RESULTS AND DISCUSSION

Sorption capacity of clays

The thin-film/FTIR method allows us to monitor the sorption amount and the kinetic behavior of the gas/solid reaction. As shown in Figure 2, three assignments—694 cm^{-1}, 729 cm^{-1}, and 1,493 cm^{-1}—for the adsorbed toluene in Ca-montmorillonite under the dry condition increase with time. The peak area of the assignment of 694 cm^{-1} obtained by integrating the intensity represents the relative sorbed amount.

Comparing the steady absorbance of toluene at wave number 694 cm^{-1} after sorption equilibrium, we found that the amount of adsorbed toluene in both dry clays was higher than that on humid ones (Table 1). Under dry conditions, clay provides more surfaces to toluene molecules than it does under

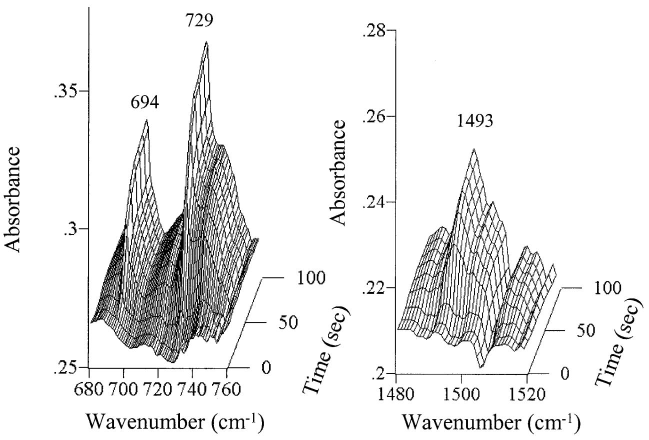

Fig. 2. The time-varying Fourier transform infrared spectra of Ca-montmorillonite exposed to toluene vapor.

wet conditions. This is consistent with the results presented by Chiou [19] and Petersen et al. [20], who have indicated that inorganic matters (e.g., clays) had strong sorbing capacity under the dry condition but were weak adsorbents in aqueous solutions.

The averaged values of the intensity of toluene sorbed in Ca- and Cu-montmorillonite are similar under humid conditions. Goss and Eisenreich [21] had illustrated that the adsorbed water film at near 100% relative humidity was apparently thick enough to diminish the influence of the mineral surface toward the sorbate. This result agrees with our result of having a similar adsorption amount for different cation-exchanged clays under high humidity.

Kinetics of toluene sorption in clays

The gas–phase spectra of toluene can be identified by referring to the band assignments of toluene made by Lau and Snyder [22]. Referring to the absorbance spectrum of vapor-phase toluene, three normal modes are selected to be the characteristics [18] for the physically adsorbed toluene molecules in montmorillonite: the C-H out-of-plane skeletal vibration at 694 cm^{-1}, the C-H out-of-plane deformation vibration at 729 cm^{-1}, and the C-C stretching vibration at 1,493 cm^{-1} (Fig. 2).

Sorption equilibrium was achieved in a few minutes for all experiments in this study (Figs. 3 and 4). Johnston et al. [23] had studied the vapor-phase sorption of *p*-xylene on a self-supporting montmorillonite film. They also observed that only a few minutes were needed to reach the equilibrium. Our results were consistent with their observations.

The sorption rate is higher than the desorption rate, which suggests that sorption of toluene in clays is easier than desorption. In addition, in both types of clays, some persistent fraction exists that took a long period of time to be removed under the dry condition. Some toluene molecules could be trapped in clay matrix during the sorption process.

Table 1. The equilibrium infrared absorbance intensity of toluene sorbed on clays[a]

	Ca-montmorillonite	Cu-montmorillonite
Dry condition	0.57, 0.49	1.27, 1.33
Humid condition	0.28, 0.29	0.24, 0.34

[a] The gas concentration (P/P_0) were 0.40 and 0.44 under dry and humid conditions, respectively. Each experiment was duplicated.

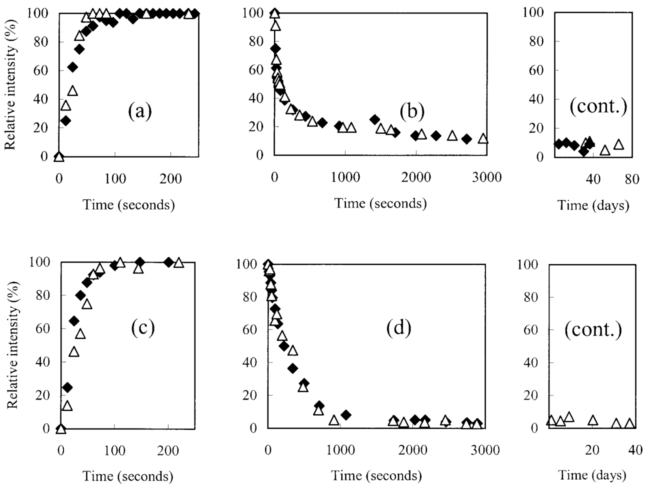

Fig. 3. The sorption (**a**) and desorption (**b**) of toluene on air-dried Ca-montmorillonite and sorption (**c**) and desorption (**d**) of toluene on hydrated Ca-montmorillonite indicated by the relative absorbance intensity at 694 cm^{-1} by Fourier transform infrared spectrophotometry.

Sorption kinetics of toluene in Ca-montmorillonite

Figure 3 shows the amount of sorbate in Ca-montmorillonite varying over time during the experiments under dry and humid conditions, respectively. It took about 80 s for toluene in Ca-montmorillonite to reach equilibrium under the dry condition. During the desorption process, a residual fraction (~10% of the total) resistant against desorption was observed through 60 d of desorption. The results of duplicated experiments were in good agreement. Under the humid condition, it took about 100 s to reach equilibrium (Fig. 3c). However, the rate of desorption in the humid condition is faster than that in the dry condition. No residual of toluene was evident in the duplicated experiments in humid conditions.

In the thin-film/FTIR experimental system, the width of the cell's inner space is approximately 5 mm. The time scale of diffusion through the boundary layer, estimated by the relationship $t = (\Delta x)^2/D_a$, where Δx is the thickness of the boundary layer (exaggeratedly assuming the same as that of the inner space) and D_a is the gaseous diffusivity of toluene [24], is

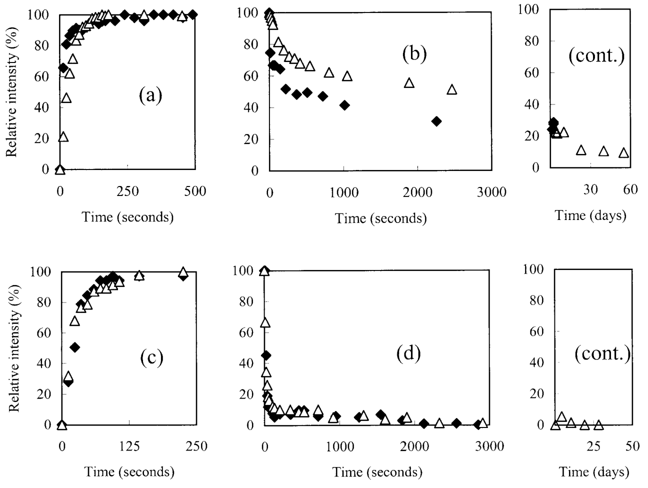

Fig. 4. The sorption (**a**) and desorption (**b**) of toluene on air-dried Cu-montmorillonite and sorption (**c**) and desorption (**d**) of toluene on hydrated Cu-montmorillonite indicated by the relative absorbance intensity at 694 cm^{-1} by Fourier transform infrared spectrophotometry.

Table 2. The pseudo-first-order rate constant of sorption and desorption (per minute)

	Sorption	Desorption
Ca-montmorillonite in dry condition	2.94	0.53
	4.50	0.61
Ca-montmorillonite in humid condition	2.50	0.20
	2.81	0.22
Cu-montmorillonite in dry condition	1.85	0.096
	1.78	0.090
Cu-montmorillonite in humid condition	2.90	0.91
	2.12	0.82

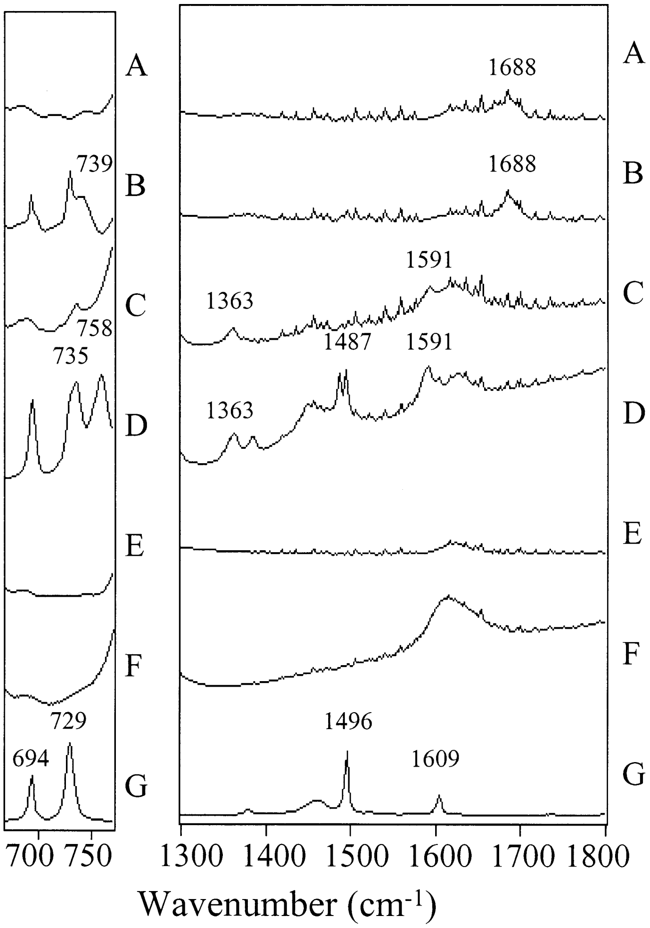

Fig. 5. The Fourier transform infrared spectra of toluene on Ca-montmorillonite desorbed with nitrogen gas under the dry condition after 60 d (A) and Ca-montmorillonite after sorption equilibrium (B), Cu-montmorillonite desorbed with nitrogen gas after 60 d (C) and Cu-montmorillonite after sorption equilibrium (D). (E) denotes pure Ca-montmorillonite, (F) denotes pure Cu-montmorillonite, and (G) denotes pure gaseous toluene.

2.75 s. Since the thickness of the clay films is around 6 μm, the time scale of diffusion across the film is only 6 s. No mass transfer limitation through the clay film should occur. This system is clearly not a gas-phase boundary layer–limited case, and the sorption kinetics is controlled by the intrinsic sorption of the clay particles.

The adsorption of organic contaminant on soil aggregates has been widely discussed in the literature. Arocha et al. [16] studied the adsorption kinetics of toluene on two soil agglomerates, Yolo silt loam and Na-montmorillonite, and indicated that soil was a biporous sorbent. By proposing that the slow stage was controlled by slower diffusion and adsorption in intragrain micropores, they estimated the macropore and micropore diffusivities in clay. Morrissey and Grismer [17] also estimated these diffusivities in montmorillonite from the experimental results by using a gravimetric method. According to these two papers, the micropore diffusivities of toluene in montmorillonite range from 3.7×10^{-12} to 3.5×10^{-15} cm^2/s, respectively.

The time needed to reach 50% sorption equilibrium can be predicted from the equation $t \approx 0.03\ r^2/D$, in which r is the radium [8,25]. If the micropore diffusion is the control factor, the calculated micropore diffusivity of this study is about 6×10^{-12} cm^2/s for a particle size of 2 μm, which is in good agreement with the results of Arocha et al. [16] and Morrissey and Grismer [17]. Thus, micropore diffusion is a possible controlling mechanism of the sorption kinetics of toluene in clays; otherwise, the slow sorption is attributed to the intrinsic reaction between the sorbent and the sorbate.

Sorption kinetics of toluene on Cu-montmorillonite

It took about 150 s for Cu-montmorillonite to reach equilibrium under the dry condition (Fig. 4). The small difference between the two duplicated experiments might result from the slight difference of clay thickness. The desorption rate was lower than that of Ca-montmorillonite under the same condition. The sorbed toluene could not be desorbed completely either. The residual fraction was approximately 10% of the maximum sorbed amount after 60 d of desorption. Under the humid condition, the rates of sorption and desorption were faster than those under the dry condition (Fig. 4). However, unlike that in the dry condition, the absorbance of peak 694 cm^{-1} showed no residual after long-term desorption in the humid condition.

The estimated first-order rate constants according to the growing and decaying of the intensity at wave number 694 cm^{-1} in Figures 3 and 4 are listed in Table 2. The rate constant ranges from 1.8 to 4.5 min^{-1} for sorption and 0.09 to 0.9 min^{-1} for desorption. For Ca-montmorillonite, the desorption rates are lower than sorption rates by approximately one order of magnitude; moreover, the rate constants in a dehydrated condition are slightly higher than those in humid conditions. As a result of the hydration of clays, toluene molecules spend more time for diffusion in the intra-aggregate water films. As a consequence, the migration of toluene in Ca-montmorillonite under high humidity was retarded.

However, the sorption/desorption kinetics of toluene in Cu-montmorillonite under the humid condition is faster than those under the dry condition. Furthermore, Cu-montmorillonite under the dry condition has the lowest sorption/desorption rate constants and the highest sorbing capacity (Tables 1 and 2).

FTIR spectral analysis of toluene sorption

Under the dry condition, the FTIR spectra of the two cation-exchanged montmorillonites exposed to toluene vapor are shown in Figure 5. For the purpose of comparison, a reference spectrum of vapor-phase toluene and the spectra of Ca- and Cu-montmorillonite without toluene are included.

For Cu-montmorillonite, two normal modes (694 and 1493 cm^{-1}) were observed and unshifted (<2 cm^{-1}). However, the band of C-H out-of-plane deformation vibration split into two peaks and was shown around 735 cm^{-1}. This C-H out-of-plane moiety is known to be quite sensitive to its surrounding [18];

for instance, similar shifts were observed for toluene in the solid state [26]. The shift indicates an external force exerted toward the C-H bond, which is likely a strong physical attraction.

In addition to the three normal models, new vibrational bands at 758, 1,363, 1,487, and 1,591 cm^{-1} appeared in the 600 to 1,700 cm^{-1} region after 1 d. Unlike the physically induced shift, the CH_3 deformation was shifted to a frequency lower than that of free toluene by 17 cm^{-1} (1,380–1,363 cm^{-1}), and two C-C stretching modes of the complexed toluene were shifted in the same direction by 9 to 18 cm^{-1} (1,496–1,487 cm^{-1} and 1,609–1,591 cm^{-1}). Furthermore, the shift toward high frequency for the band of vibration from 729 cm^{-1} to 758 cm^{-1} is 4.8 times larger than that for the physically adsorbed form. This result indicates that some toluene molecules could have been chemically bound to Cu-montmorillonite. Pinnavaia and Mortland [18] reported similar peaks for adsorbed toluene in dehydrated clays. These peaks supposedly represented the physical adsorption to the silicate structure and complex formation with the copper (II).

During sorption, the color of the dry toluene/Cu-montmorillonite film changed from light blue to light green and stayed at light green even after purging with a moisturized clean gas. The different colors may be attributed to different clay-organic complexes. Doner and Mortland [27] and Pinnavaia et al. [28] indicated that the exposing of partially dehydrated Cu-montmorillonite to benzene vapor resulted in the formation of a green surface complex designated as the type I complex. However, a red type II complex was produced when benzene sorbed onto strongly dehydrated Cu-montmorillonite. Johnston et al. [23] also observed that the color of the dry *p*-xylene/Cu-montmorillonite complex turned from dark orange-brown to light orange and suggested that there was a single electron transfer reaction between *p*-xylene and Cu-montmorillonite based on the analysis of the spectra. Thus, the chemisorption of toluene could be a result of a single electron transfer reaction that is similar to what occurred for the benzene/Cu-montmorillonite pair [27,28].

For Ca-montmorillonite, in addition to the physically sorption modes, two new peaks (739 and 1,688 cm^{-1}) grew with time consistently in some experimental sets. The emergence of the peak 739 cm^{-1}, a peak representing important adsorption forces, may have resulted from an interaction of the π-electrons of toluene molecules and hydroxyl groups or oxygen atoms of clays. This phenomenon has been observed for toluene on a silica surface [29] and a clay surface [18]. However, the broad band at 1,688 cm^{-1} has no matching band in the spectra of gaseous toluene or liquid toluene. Since it is located near the band frequency for carbonyl stretching, it might suggest the existence of carbonyl functional group. Carboxylation has also been proposed in a chloroethane/clay system [30] and a toluene/clay system [31]. Ca-montmorillonite may also have some catalytic ability to transform or degrade toluene molecules.

Few new peaks were observed in the spectra of toluene sorbed on Ca-montmorillonit, and the color of Ca-montmorillonite in all experiments did not change at all. How toluene was bound in these two systems seems to be different but might be due to the energy barrier of d-orbital occupation of calcium being too high to carry out the single electron transfer reaction.

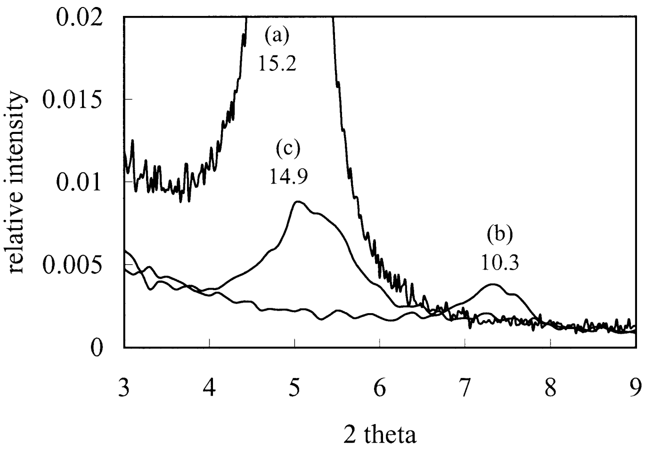

Fig. 6. X-ray diffraction spectra of dehydration of Ca-montmorillonite from (a) to (b) and sorption of toluene on Ca-montmorillonite from (b) to (c).

Sorption of toluene into interlayers of Ca-montmorillonite

During the dehydration period of Ca-montmorillonite, the d-spacing of Ca-montmorillonite decreased from 15.2 to 10.3 Å as seen in the X-ray diffraction spectra in Figure 6. After toluene was introduced into the capillary tube, the d-spacing of Ca-montmorillonite increased to 14.1 Å, and the final d-spacing is 14.9 Å. Toluene molecules could obviously enter into the interlayer of Ca-montmorillonite.

For Cu-montmorillonite, a d-spacing of 15.8 Å on adsorption of toluene has been reported [18]. Hinedi et al. [32] proposed that polymerization of benzene occurred in Cu-montmorillonite in the interlayers. This could occur with toluene in Cu-montmorillonite. However, no spectroscopic evidence has been suggested that this reaction occurs between toluene and Ca-montmorillonite.

The toluene molecules have opportunities to enter the clay interlayer and form π-system–hydrogen bondings with silanols or π-complexes with Ca^{2+} [29,33]. Then some reactions, such as oxidation (resulting carbonyl or C-O) and benzene ring opening, may occur because the activation energy is lowered for these reactions when the adsorbate molecules is very close to clay matrix in the interlayers [34]. Some of the toluene molecules and their transformation products might have been strongly trapped in the micropores or the interlayers of Ca-montmorillonite because of these strong sorbent-sorbate interactions.

Irreversible sorption

Irreversible sorption was observed for Cu-montmorillonite. It took approximately 20 d for Cu-clay under the dry condition to reach a stable absorbance intensity (Fig. 4b). Extended time may be necessary for breaking the previously mentioned strong interaction between toluene and Cu-montmorillonite under an anhydrous condition.

The irreversible sorption of toluene on montmorillonite has also been observed by using the gravimetric method [17]. The authors of that paper indicated that the sorption processes would not be completed instantaneously because of the limitation of the diffusion of the sorbate into the sorbent matrix. They also observed a residual amount, 30% of the maximum sorbed amount, after several hours under an air-dried condition. Hundal et al. [35] studied the sorption of phenanthrene on smectites and indicated that the sorption of this aromatic compound by smectites was a physical phenomenon. They also concluded that the capillary condensation into a network of nano- or micropores created by quasicrystals was likely to be a dominant mechanism of this aromatic retention by smectites. Several studies [1,36–38] proposed that the existence of the network of narrow pores in clay minerals could limit the rates of both sorption and desorption for organic species.

In this study, the adsorption and desorption FTIR spectra revealed a persistent fraction about 10% of the total under the dry condition. However, no residual peak on the FTIR spectra was observed under a humid condition after the short-term equilibrium. This indicates that water molecules may cover the strong binding sites so that the hydrated clay surface and cations on it are not able to provide strong reaction sites for irreversible sorption.

CONCLUSION

A thin-film/FTIR method enables us to investigate the intrinsic sorption and desorption behaviors as well as the spectroscopic pattern of sorbed species in short ($<$1 min) or long ($>$ weeks) period of time instantaneously, to identify the persistent fraction, and to trace the sorption kinetics at the same time. The intrinsic sorption time scale of toluene in clays is just a few minutes. The persistency of toluene against desorption was found in Ca-montmorillonite, which could result from the chemical bindings and the entrapment of toluene by the structural stereo-hindrance of nano- or micropores in montmorillonite. The observed persistence of toluene in Cu-montmorillonite may be caused by the stereo-hindrance and the formation of complexes between toluene and Cu-montmorillonite. Infrared spectra indicate strong interaction between the cation-exchanged anhydrous montmorillonites and toluene.

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