

## Adsorption of Phenols onto 1,1'-Dimethyl-4,4'-bipyridinium-smectites

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(Received April 22, 2002; CL-020347)

Adsorption of phenols (phenol and 2-naphthol) onto the 1,1'-dimethyl-4,4'-bipyridinium (methylviologen: MV<sup>2+</sup>)-smectite intercalation compounds, which were synthesized by ion exchange reactions, led to the change in the color and the basal spacing. The color change was ascribed to the formation of charge-transfer complex of MV<sup>2+</sup> and phenols. The increase in the basal spacing by the reaction with phenols indicates a change in the interlayer microstructure.

Adsorption of organic compounds onto solid surfaces has extensively been investigated from a wide range of scientific and practical viewpoints such as environmental purification and constructing novel functional supramolecular assemblies.<sup>1</sup> The adsorption of organic species into crystalline inorganic solids such as layered materials and zeolites has widely been studied focusing on the thermal and chemical stabilities, and functional properties of the resulting compounds.<sup>2,3</sup>

Smectite group of layered clay minerals is promising materials for organizing guest species since they offer two-dimensional expandable interlayer space and possess various attractive features such as large surface area, swelling and cation exchange ability.<sup>4</sup> The replacement of the interlayer exchangeable cations with organoammonium ion results in the change in the surface properties. Organophilic<sup>5</sup> and microporous materials<sup>6</sup> have been synthesized by the exchange with cationic surfactant and small organic cations (such as tetramethylammonium ion), respectively. The adsorption of hazardous compounds from water has been investigated for the organically modified smectites.<sup>7</sup> The selection of hosts and guests is known to affect the adsorptive properties of the resulting intercalation compounds;<sup>3,6,8</sup> however, the use of attractive  $\pi$ -interactions is yet to be investigated. Here we report adsorptive properties of 1,1'-dimethyl-4,4'-bipyridinium (MV<sup>2+</sup>)-smectites.

MV<sup>2+</sup>-smectites were synthesized from a natural montmorillonite<sup>9</sup> and a synthetic saponite<sup>10</sup> by cation exchange reactions with MV<sup>2+</sup> dichloride. Smectite (1.0 g) suspension was mixed with an aqueous MV<sup>2+</sup> dichloride solution (20 mL) for a day, where the added MV<sup>2+</sup> dichloride amount was just equal to the cation exchange capacities<sup>11</sup> (Table 1). After the aqueous phase was separated by centrifugation, the product was washed with methanol and dried under a reduced pressure. The compositions of the resulting solids are determined by CHN analyses as summarized in Table 1.<sup>12,13</sup> It was shown that the interlayer exchangeable cations of smectites were replaced with MV<sup>2+</sup> ions quantitatively. The basal spacings of the MV<sup>2+</sup>-smectites are summarized in Table 1.<sup>14</sup> Judging from the interlayer expansion (Table 1) and the size of MV<sup>2+</sup> ( $0.63 \times 1.34 \times 0.3$  nm),<sup>15</sup> the adsorbed MV<sup>2+</sup> are thought to be arranged as a monomolecular layer with their molecular planes of pyridinium rings (0.3 nm) parallel to the silicate layers. The UV-vis diffuse reflectance spectra<sup>16</sup> of the MV<sup>2+</sup>-smectites are shown in Figure 1. Absorption band ascribable to MV<sup>2+</sup> was observed at around 280 nm. The band was shifted from that (258 nm) observed

for an MV<sup>2+</sup> dichloride aqueous solution, suggesting that the possible charge-transfer between siloxane surface of smectites and the pyridinium rings and/or change in the molecular conformation of MV<sup>2+</sup>.<sup>17</sup> Considering the occupied area of adsorbed MV<sup>2+</sup> ( $0.63 \times 1.34$  nm<sup>2</sup>/molecule) and surface area of smectites (750 m<sup>2</sup>/g for the montmorillonite and 690 m<sup>2</sup>/g for the saponite),<sup>4b</sup> MV<sup>2+</sup> occupies 80% of the surface of the montmorillonite and 50% of that of the saponite. This means that MV<sup>2+</sup>-smectites possess void space in the interlayer space.

Table 1. Properties of the MV<sup>2+</sup>-smectites

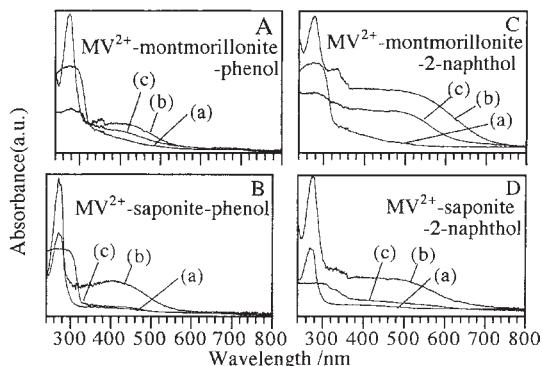
Hosts	Montmorillonite	Saponite
Chemical composition (mass%)		
Carbon	6.8	4.1
Nitrogen	1.2	0.66
Amounts of adsorbed MV <sup>2+</sup> (meq/100 g of clay)	116	71
Cation exchange capacity (meq/100 g of clay)	119	71
Basal spacing (nm)	1.27	1.31
Interlayer expansion (nm)	0.31	0.35
color (basal spacing/nm)		
Reaction with phenol: 1 1 extracted with water	yellow (1.47) colorless (1.27)	yellow (1.48) colorless (1.31)
Reaction with 2-naphthol: 2 2 extracted with ethanol	orange (1.57) light-orange (1.39)	orange (1.62) colorless (1.31)

Reaction of phenols with MV<sup>2+</sup>-smectites was carried out by mixing MV<sup>2+</sup>-smectites and neat phenols<sup>18</sup> at room temperature and subsequent removal of excess phenols under a reduced pressure. By the reaction with phenol the color of MV<sup>2+</sup>-montmorillonite changed from colorless to yellow. The diffuse reflectance spectrum of the product (Figure 1A-b) showed a new absorption band (ca. 420 nm), which was not observed for MV<sup>2+</sup>-montmorillonite, an MV<sup>2+</sup> dichloride solution (258 nm) and an aqueous phenol solution (270 nm). It was reported that the absorption maximum of the MV<sup>2+</sup> dichloride-phenol charge-transfer band in methanol solution appeared at 372 nm.<sup>19</sup> Thus, it was thought that the color change was due to the formation of charge-transfer complex of MV<sup>2+</sup> and phenol in the interlayer space of montmorillonite. Judging from the reduction potential of MV<sup>2+</sup>-smectites<sup>20</sup> and the oxidation potential of phenols,<sup>21</sup> phenols act as electron donor for the MV<sup>2+</sup>-montmorillonite. The difference in the size and microstructure of the charge-transfer complex in solution and in the interlayer space of clays as well as the interactions with surface of silicate layer and the complex was thought to be possible reasons for the difference in the absorption maxima between the present product and the reported MV<sup>2+</sup> dichloride-phenol complex.

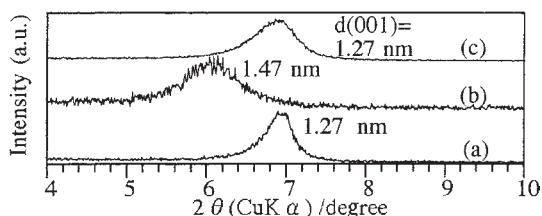
The basal spacing of the MV<sup>2+</sup>-montmorillonite changed from 1.27 nm (Figure 2a) to 1.47 nm (Figure 2b) by the reaction with phenol, indicating that phenol molecules were intercalated into the interlayer space to change the interlayer microstructure as schematically shown in our Graphical abstract. By washing with water,<sup>22</sup> the color disappeared and the basal spacing decreased to be

1.27 nm (Figure 2c), which was identical to that of the  $MV^{2+}$ -montmorillonite, indicating the desorption of phenol. The absorption band observed at 270 nm (Figure 1A-b) was ascribable to the  $\pi$ - $\pi^*$  absorption bands of the formed complex. The sharpness of the absorption band was thought to be derived from the host-guest interactions, though the exact origin was not clear at present.

A similar adsorption behavior of phenol was observed for  $MV^{2+}$ -saponite system. The basal spacings and the color upon adsorption and desorption of phenol are listed in Table 1. When the adsorption of phenol onto  $MV^{2+}$ -saponite from aqueous solution was conducted, the basal spacing did not change and the absorption band ascribable to charge-transfer complex appeared at ca. 380 nm. The absorption band appeared in a shorter wavelength region if compared with that observed for the product obtained by the reaction with neat phenol (Figure 1B-b; ca. 420 nm). The variation suggests the difference in the states of the charge-transfer complexes.



**Figure 1.** The diffuse reflectance spectra of (A)  $MV^{2+}$ -montmorillonite-phenol, (B)  $MV^{2+}$ -saponite-phenol, (C)  $MV^{2+}$ -montmorillonite-2-naphthol, (D)  $MV^{2+}$ -saponite-2-naphthol. a: before adsorption of phenols, b: after adsorption of phenols, c: the products obtained by washing of b with water or ethanol.



**Figure 2.** X-ray powder diffraction patterns of (a)  $MV^{2+}$ -montmorillonite, (b)  $MV^{2+}$ -montmorillonite-phenol and (c) the product obtained by washing of (b) with water.

When the  $MV^{2+}$ -saponite-phenol was washed with water, the charge transfer band at ca. 420 nm disappeared (Figure 1B-c). On the contrary, the diffuse reflectance spectra of the washed  $MV^{2+}$ -montmorillonite-phenol (Figure 1A-c) indicated that a significant fraction of the adsorbed phenol remained in the interlayer space. The absorbance at ca. 270 nm decreased after the washing supporting that the bands was derived from the charge-transfer complex.

Adsorption of 2-naphthol onto the  $MV^{2+}$ -smectites also occurred. By the reaction with 2-naphthol,  $MV^{2+}$ -smectites changed its color from colorless to orange. In the diffuse reflectance spectrum of the  $MV^{2+}$ -montmorillonite-2-naphthol, a new absorption band appeared at ca. 500 nm (Figure 1C-b), which was not observed for a 2-naphthol ethanol solution (270, 320 nm), indicating the formation of the charge-transfer complex of  $MV^{2+}$  and 2-naphthol.<sup>19</sup> In the saponite system, a similar absorption spectrum was obtained (Figure 1D-b). By the reaction with 2-naphthol, the

basal spacing increased (Table 1) to show the adsorption of 2-naphthol into the interlayer space of  $MV^{2+}$ -smectites (See Graphical abstract). The desorption of 2-naphthol from  $MV^{2+}$ -saponite-2-naphthol was possible by washing with ethanol as observed for the  $MV^{2+}$ -smectites-phenol systems. On the contrary, a significant amount of 2-naphthol remained in the interlayer space for the  $MV^{2+}$ -saponite-2-naphthol (Figure 1D-c).

On the other hand, it was difficult to extract 2-naphthol from  $MV^{2+}$ -montmorillonite-2-naphthol. The diffuse reflectance spectra of the  $MV^{2+}$ -montmorillonite-2-naphthol obtained by washing with ethanol<sup>22</sup> showed an absorption band at ca. 500 nm (Figure 1C-c). The basal spacing of the product was 1.39 nm, suggesting that a certain portion of 2-naphthol remained in the interlayer space. It is known that the expandability of the interlayer space of smectite correlates to electrostatic interaction, which depends on layer charge and position of cations.<sup>23</sup> The difference in the surface charge density of two smectites plays an important role in the observed difference in the guest binding properties.

This work demonstrated that the unique adsorption behavior of phenols onto  $MV^{2+}$ -smectite intercalation compounds. The adsorption was thought to occur through charge-transfer complex formation and such interactions resulted in the changes in the color and the microstructures. The color-change signatures upon the adsorption of phenols may be applied for the colorimetric sensing for the purpose of hazardous aromatic compounds detector. There are many reports on the clay-dye intercalation compounds,<sup>24</sup> however, the adsorptive properties of them are yet to be investigated. The adsorptive properties of various clay-dye intercalation compounds are worth investigating as possible smart adsorbents.

#### References and Notes

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- 13 The CHN analysis was performed on a Perkin Elmer 2400 II instrument.
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