Adsorption behavior of phenol for mono, bis and tris(2,2'-bipyridine)nickel(II) and tris(ethylenediamine)nickel(II)-saponite intercalation compounds from aqueous solution

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ABSTRACT

Adsorption of phenol on mono, bis and tris(2,2'-bipyridine)nickel(II)- and tris(ethylenediamine)nickel(II)-saponite intercalation compounds from aqueous solution was examined. Mono, bis and tris(2,2'-bipyridine)nickel(II)-saponites were prepared by the reactions of Ni(II)-form of a synthetic saponite (Sumecton SA) with 2,2'-bipyridine at the molar 2,2'-bipyridine to Ni(II) ratios of 1:1, 2:1 and 3:1. Tris(ethylenediamine)nickel(II)-saponite was prepared by the reactions of the Ni(II)-saponite with ethylenediamine at the molar ratio of 3:1 (ethylenediamine:Ni(II)). X-Ray diffraction and thermal analysis indicated that 2,2'-bipyridine and ethylenediamine were intercalated into Ni(II)-saponite to form mono, bis and tris(2,2'-bipyridine)nickel(II) and tris(ethylenediamine)nickel(II) complexes. The adsorption isotherms of phenol for the mono, bis and tris(2,2'-bipyridine)nickel(II)-saponites did not change by the adsorption of phenol, indicating that the adsorbed phenol existed in the interlayer micropore formed by the pillaring with the complexes. The adsorption of phenol on the tris(ethylenediamine)nickel(II)-saponite was less effective than those on the (2,2'-bipyridine)nickel(II)-saponites, suggesting that the interactions between pyridine rings and phenol played an important role in the adsorption of phenol.

Key words: Adsorption, Organoclays, Phenol, Synthetic saponite, tris(2,2'-bipyridine)nickel(II), tris(ethylenediamine)nickel(II)

INTRODUCTION

Tailor-made adsorbents for purposes as removal and separation of molecules from environment have been required, so that the designing of adsorbents from inorganic (Breck, 1974, Barrer, 1978, Alberti and Bein, 1996) and organic building units (Barrer, 1978, Yaghi et al., 1998, Kitagawa et al., 2004) has been investigated so far. The organic modification of smectites is a way of producing inorganic-organic hybrid adsorbents (Barrer, 1978, Ogawa and Kuroda, 1997). Hydrophobic (Lagaly, 1981) and microporous (Barrer, 1989) nature has been imparted on the surface of smectites by the cation exchange of the interlayer exchangeable cations with organoammonium ions. The combination of hosts with different origin and guests with different molecular structure has been known to affect the adsorption behavior of organic compounds both from water and from vapor (for example, Mortland et al., 1986, Boyd et al., 1988, Lee et al., 1990). In order to meet the requirements to the adsorbents for a wide variety of organic compounds, precise designing adsorbents from the modification of smectites with variable geometry and chemistry is worth investigating further.

The adsorption of aromatic compounds such as alkylbenzenes and phenols on aliphatic ammonium-smectites has been investigated (Barrer, 1989, Xu et al., 1997). On the contrary, there are few examples of the adsorption of the aromatic molecules on aromatic ammonium-smectites (Jaynes and Boyd, 1991, Stevens et al., 1996, Jaynes and Vance, 1999, Sharmasarkar et al., 2000). Moreover, adsorbate-adsorbent interactions are not well understood. Accordingly, further systematic studies on the adsorption of various aromatic com-

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pounds onto organically modified clay are worth conducting to obtain practically important adsorbents as well as to understand the adsorbate-adsorbent interactions. We have reported the adsorption of phenols on the dye-clay intercalation compounds (Okada and Ogawa, 2002, 2003 and 2004). It was shown that the adsorption of 2,4-dichlorophenol from aqueous solution was governed by the charge-transfer interactions or the oxidative coupling reactions between 1,1′-dimethyl-4,4′-bipyridinum-saponite (Okada and Ogawa, 2003) or p-phenylenediammonium-saponite (Okada and Ogawa, 2004) and 2,4-dichlorophenol, respectively.

We have also reported the adsorption of phenols (phenol and chlorinated phenols) onto tris(2,2′-bipyridine)ruthenium(II) (abbreviated as [Ru(bpy)₃]²⁺)-smectites from aqueous solutions (Okada et al., 2005). The adsorption of phenols on the [Ru(bpy)₃]²⁺-smectites from aqueous solutions was confined to Langmuir type isotherms. We have anticipated that the adsorption was governed by the π-interactions between pyridine rings and phenols, however, the interactions are not well understood. In order to discuss the mechanisms of the adsorption as well as show the merit of transition metal-tris(bpy) complexes as organic cations, adsorption behavior of phenol on a synthetic saponite (Sumecton SA) modified with mono, bis and tris(bpy)nickel(II) ([Ni(bpy)₃]²⁺ [n = 1, 2 and 3]) and with tris(ethylenediamine)nickel(II) ([Ni(en)₃]²⁺) is examined in the present study.

EXPERIMENTAL

Materials

Na-saponite (Sumecton SA, obtained from Kunimine Ind. Co., synthesized by a hydrothermal reaction) was used as the host material. Cation exchange capacity (CEC) of the Na-saponite is 71 meq/100 g clay (Ogawa et al., 1992). Nickel dichloride hexahydrate was purchased from Kokusan Kagaku Co. and used as received. 2,2′-Bipyridine (bpy) and ethylenediamine (en) dehydrate were purchased from Kanto Kagaku Co. and used as received.

Preparation of adsorbents

Ni(II)-saponite (2.0 g) was prepared from Na-saponite by cation exchange reaction with an aqueous solution of Ni(II) dichloride hexahydrate (80 mL) at room temperature for 1 day. The added amount of Ni(II) dichloride was ten times (1.69 g) of the CEC of saponite. This procedure was repeated by three times. After the cation exchange reactions, the product was separated by centrifugation (25 krpm for 10 min at 293 K) and washed with acetone/deionized water mixtures repeatedly until a negative AgNO₃ test was obtained. The adsorbed amount of Ni(II) on saponite was determined by ICP analysis to be 70 meq/100 g, showing the quantitative cation exchange.

The Ni(II)-saponite (0.5 g) was allowed to react with 10 mL of aqueous/ethanol (50/50; v/v) bpy solution for 1 day at room temperature to prepare the [Ni(bpy)₃]²⁺-saponites (n = 1, 2 and 3). The molar ratios of the added bpy to Ni(II) in the Ni(II)-saponite were 1:1 (22 mg), 2:1 (44 mg) and 3:1 (66 mg). After centrifugation, the resulting solids were washed with ethanol/deionized water mixture until the absence of bpy in supernatant. The resulting solids were dried under reduced pressure at room temperature.

[Ni(en)₃]²⁺-saponite was prepared by the reaction of the Ni(II)-saponite with en. The Ni(II)-saponite (0.5 g) was allowed to react with 10 mL of aqueous/ethanol (50/50; v/v) solution of en for 1 day at room temperature. The molar ratio of the added en to Ni(II) was 3:1 (0.39 mL). After centrifugation (25 krpm for 10 min at 293 K), the resulting solid was washed with ethanol/deionized water mixture repeatedly. The resulting solid was dried under reduced pressure at room temperature.

Adsorption of phenol

Adsorption of phenol from aqueous solution was conducted as follows; adsorbents (20 mg) were allowed to react with 30 mL of aqueous phenol solution (0.1–2 mM) in 50 mL of glass vessel for 1 day at room temperature under dark. Blank samples containing 30 mL of aqueous solution, without adsorbents, were prepared to estimate vaporization losses and the adsorption on the glass vessel. After the adsorbents were separated by centrifugation (25 krpm for 10 min at 293 K), the concentration of the remaining phenol in supernatant was determined by UV absorption spectroscopy (absorption λ max at 269 nm).

Characterization

X-Ray powder diffraction patterns were obtained by a Rigaku RAD IB diffractometer (monochromatic CuKα) operated at 20 mA, 40 kV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on Rigaku Spectro Ciros CCD. TG-DTA curves were measured by a Rigaku TAS-2000 instrument with a heating rate of 10 K/min under air using α-Al₂O₃ as the standard material. UV-Vis absorption spectra were recorded on a Shimadzu UV 1300 PC spectrophotometer. Nitrogen adsorption isotherms were obtained at 77 K on a BELSORP 28 instrument (Bell Japan Inc.). Prior to the adsorption experiments, the adsorbents were dried at 333 K under vacuum (10⁻¹ torr) for 3 hours. Na-saponite was heat-treated at 773 K for 1 h under air for the determination of the external surface area of saponite. The dehydration was confirmed by the basal spacing of the heat-treated Na-smectites (1.0 nm). Surface areas were determined using BET equation (Brunauer et al., 1938) from the nitrogen adsorption isotherms.

RESULTS AND DISCUSSION

Preparation of Ni(II) complex-saponite intercalation compounds

[Ni(bpy)₃]²⁺-saponites (n = 1, 2 and 3)

Fig. 1 shows the XRD patterns of the products obtained by the reactions of Ni(II)-saponite with bpy.
When the reaction of Ni(II)-saponite with bpy was conducted at the molar ratio of 3:1 (bpy: Ni(II)), the basal spacing of Ni(II)-saponite (Fig. 1e, 1.28 nm) increased to 1.76 nm (Fig. 1a), showing the intercalation of bpy into the interlayer space of Ni(II)-saponite. The gallery height of the product was determined by subtracting the thickness of silicate layer (0.96 nm) from the observed basal spacing (1.76 nm) to be 0.80 nm. Formation of [M(bpy)]\textsuperscript{2+}-hectorite (M = Cu\textsuperscript{2+}, Fe\textsuperscript{2+} and Ru\textsuperscript{2+}) (Traynor et al., 1978), [Co(bpy)]\textsuperscript{3+}-montmorillonite (Ogawa et al., 1991) and [Ru(bpy)]\textsuperscript{2+}-TSM (Ogawa et al., 1993) intercalation compounds with the gallery heights of 0.8 nm has been reported. The formation of [M(bpy)]\textsuperscript{2+} (M = Co\textsuperscript{2+}, Mn\textsuperscript{2+}) intercalation compounds with the gallery heights of 0.8 nm has been reported.

In order to discuss the effect of the \pi-interactions between phenol and pyridine rings on the adsorption of phenol, [Ni(bpy)]\textsuperscript{2+}- and [Ni(bpy)]\textsuperscript{2+}-saponites were synthesized and used as adsorbents. It was reported that the [Ni(bpy)]\textsuperscript{2+} dichlorides (n = 1 and 2) were obtained by the heat-treatment of [Ni(bpy)]\textsuperscript{2+} dichloride heptahydrate under air (Lee et al., 1964, Natu et al., 1982). Accordingly, [Ni(bpy)]\textsuperscript{2+} and [Ni(bpy)]\textsuperscript{2+}-saponites were attempted to synthesize by the vaporization of bpy from the [Ni(bpy)]\textsuperscript{2+}-saponite by the heat-treatment (at 723 and 813 K for the [Ni(bpy)]\textsuperscript{2+}-saponite and the [Ni(bpy)]\textsuperscript{2+}-saponite, respectively, with a heating rate of 10 K/min) under air. However, the heat-treatment of the [Ni(bpy)]\textsuperscript{2+}-saponite resulted in the carbonization of the interlayer [Ni(bpy)]\textsuperscript{2+} to give black colored product. Thus, the quantitative decomposition of bpy was not succeed. Therefore, the reactions of Ni(II)-saponite with bpy solution at the mixing molar ratio of 1:1 and 2:1 (bpy:Ni(II)) were conducted to synthesize [Ni(bpy)]\textsuperscript{2+}- and [Ni(bpy)]\textsuperscript{2+}-saponites.

The TG curve of the product prepared by the reactions of Ni(II)-saponite with bpy at the mixing molar ratio of 2:1 (bpy:Ni(II)) showed the mass loss of 9.3% due to the oxidative decomposition of bpy. The

![Diagram](image-url)

**Fig. 1.** XRD patterns of the Ni(II)-, [Ni(bpy)]\textsuperscript{2+}- (n = 1, 2 and 3) and [Ni(en)]\textsuperscript{2+}-saponites.

**Table 1.** Properties of the transition metal complex-clay intercalation compounds

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basal spacing (gallery height) (nm)</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>Ligand content (mass %)</th>
<th>Amount of adsorbed bpy or en (mmol/100 g clay)</th>
<th>Molar ratio of the amount of intercalated bpy or en to Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(bpy)]\textsuperscript{2+}-saponite</td>
<td>1.76 (0.80)</td>
<td>244</td>
<td>16</td>
<td>108</td>
<td>3.0</td>
</tr>
<tr>
<td>[Ni(bpy)]\textsuperscript{2+}-saponite</td>
<td>1.65 (0.69)</td>
<td>223</td>
<td>9.3</td>
<td>67</td>
<td>1.9</td>
</tr>
<tr>
<td>[Ni(bpy)]\textsuperscript{2+}-saponite</td>
<td>1.37 (0.41)</td>
<td>158</td>
<td>5.0</td>
<td>39</td>
<td>1.1</td>
</tr>
<tr>
<td>[Ni(en)]\textsuperscript{2+}-saponite</td>
<td>1.39 (0.43)</td>
<td>231</td>
<td>5.9</td>
<td>107</td>
<td>3.0</td>
</tr>
<tr>
<td>[Ru(bpy)]\textsuperscript{2+}-saponite</td>
<td>1.77 (0.81)</td>
<td>256</td>
<td>14</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)]\textsuperscript{2+}-montmorillonite</td>
<td>1.76 (0.80)</td>
<td>48</td>
<td>19</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)]\textsuperscript{2+}-TSM</td>
<td>1.77 (0.81)</td>
<td>60</td>
<td>19</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>Ni(II)-saponite</td>
<td>1.28 (0.32)</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-saponite</td>
<td>1.23 (0.27)</td>
<td>135</td>
<td>—</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)Okada et al. (2005).
mass loss of 5.0% due to the oxidative decomposition of bpy was observed for the product prepared at the mixing molar ratio of 1:1 (bpy:Ni(II)). From these mass losses, the amounts of the immobilized bpy on Ni(II)-saponite were determined to be 67 (for 2:1 = bpy:Ni(II)) and 39 mmol/100 g clay for (1:1 = bpy:Ni(II)). The amounts of the immobilized bpy correspond to the molar immobilized bpy to Ni(II) molar ratios of 1.9 (at the mixing molar ratio of 2:1 [bpy:Ni(II)]) and 1.1 (at the mixing molar ratio of 1:1 [bpy:Ni(II)]).

Fig. 1b and 1c show the XRD patterns of the products obtained by the reaction of Ni(II)-saponite with bpy at the mixing molar ratios of 2:1 and 1:1 (bpy:Ni(II)), respectively. The basal spacings of the products were 1.65 nm (bpy:Ni(II)=2:1) and 1.37 nm (bpy:Ni(II)=1:1). The (001) diffraction peak obtained by the reactions at the mixing ratio of 2:1 (bpy:Ni(II)) did not split (Fig. 1b), suggesting that the reactions prevented the formation of the mixture of the [Ni(bpy)]^{2+} and the [Ni(bpy)_3]^{2+}-saponites. The size of [Ni(bpy)]^{2+} was estimated from the result of the crystal structure determination of [Ni(bpy)_2NO_2]NO_3 (Finney et al., 1981). [Ni(bpy)_2NO_2]NO_3 crystal has C_{2h} symmetry and the cross-sectional area of the mirror plane for [Ni(bpy)_2NO_2]^+ is 0.67 × 1.16 nm^2. Judging from the gallery height of the [Ni(bpy)]^{2+}-saponite (0.69 nm) and the cross-sectional area, we assumed that the intercalated [Ni(bpy)]^{2+} arranged as a monomolecular coverage with their C_{2h} symmetry axis parallel to the silicate layer. A single (001) diffraction peak was also observed for the product with the bpy:Ni(II) ratio of 1:1. Considering the gallery height of the [Ni(bpy)]^{2+}-saponite (0.41 nm) and the thickness of [Ni(bpy)]^{2+} (0.42 nm) based on the crystal structure determination of [Ni(bpy)(H_2O)_4]SO_4 (Healy et al., 1984), the interlayer [Ni(bpy)]^{2+} was considered to arrange as a monomolecular layer. Thus, the syntheses of the [Ni(bpy)]^{2+}-saponite intercalation compounds (n=1 and 2) were shown.

[Ni(en)]^{3+}-saponite

The TG curve of the product prepared by the reactions of Ni(II)-saponite with en (the mixing molar ratio of 3:1 [en:Ni(II)]) showed a weight loss of 9.0 mass % due to the oxidative decomposition of en. From the mass loss, the amount of the adsorbed en was determined to be 107 mmol/100 g clay, corresponding to the molar ratio of the immobilized en to Ni(II) of 3.0:1. The molar ratio indicates that the immobilized en formed [Ni(en)]^{3+}. The basal spacing increased by the reaction of Ni(II)-saponite with en to 1.39 nm (Fig. 1d), whose gallery height was 0.43 nm. The gallery height of [Co(en)]^{3+}-saponite (0.47 nm) indicated that the intercalated [Co(en)]^{3+} arranged as a monomolecular coverage with their 3-fold symmetry axis perpendicular to the surface of silicate layer (Kaneyoshi et al., 1993). Considering the gallery height of the [Ni(en)]^{3+}-saponite (0.43 nm), it seems that the interlayer [Ni(en)]^{3+} arranged in a similar manner.

Adsorption of phenol on the [Ni(bpy)_x]^{2+}-saponites (n = 1, 2 and 3) and [Ni(en)_3]^{2+}-saponite from aqueous solution

Fig. 2 shows the adsorption isotherms of phenol on the [Ni(bpy)_x]^{2+}-saponites (n = 1, 2 and 3) and [Ni(en)_3]^{2+}-saponite from aqueous solution. According to the Giles classification (Giles et al., 1960), the adsorption isotherms of phenol for the [Ni(bpy)_n]^{2+}-saponites (n = 1, 2 and 3) were type-L, showing strong adsorbate-adsorbate interactions. On the contrary, the adsorption isotherm of phenol for the [Ni(en)_3]^{2+}-saponite (Fig. 2) was S-type (Giles et al., 1960), which are characteristic of weak adsorbate-adsorbent interactions, causing adsorption at relatively low concentration (<ca. 1.0 mM) to be small. There is an upsweep at the equilibrium concentration of ca. 1.0 mM, indicating adsorbate-adsorbent interactions promoted the adsorption of phenol.

The adsorption isotherms were fitted to the Langmuir equation (Langmuir, 1918) as,

\[ C_e/Q = K_L C_e + b \]

where slope (K_L) and the intercept (b) are constants related to maximum adsorbed amount and binding energy, respectively. Q and C_e designate the adsorbed amounts of phenol and the equilibrium concentrations, respectively. Langmuir parameters based on the adsorption isotherms are presented in Table 2. Jaynes and Boyd (1991) proposed that the adsorption can be conformed to Langmuir model when the r^2 value (correlation coefficient for Langmuir equation) is larger than 0.89. The r^2 values shown in Table 2 are larger than 0.89, indicating that the isotherms are empirically consistent with Langmuir model. The adsorption capacities derived from Langmuir plots of the isotherms
Adsorption Behavior of Phenol

TABLE 2. Parameters of the adsorption data fitted to Langmuir and Freundlich equations

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Type</th>
<th>Adsorption capacity ($Q_{max}$) (mmol g⁻¹)</th>
<th>Molar ratio of phenol to bpy</th>
<th>b</th>
<th>The linearity for Langmuir equation</th>
<th>$K_L$ (mmol g⁻₁ mM⁻¹/²)</th>
<th>Freundlich affinity index (N)</th>
<th>The linearity for Freundlich equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(bpy)]₃²⁺-saponite</td>
<td>L</td>
<td>0.25</td>
<td>0.23</td>
<td>2.9</td>
<td>0.953</td>
<td>0.18</td>
<td>1.20</td>
<td>0.976</td>
</tr>
<tr>
<td>[Ni(bpy)]₂²⁺-saponite</td>
<td>L</td>
<td>0.12</td>
<td>0.18</td>
<td>4.2</td>
<td>0.914</td>
<td>0.12</td>
<td>1.15</td>
<td>0.991</td>
</tr>
<tr>
<td>[Ni(bpy)]¹⁺-saponite</td>
<td>L</td>
<td>0.07</td>
<td>0.18</td>
<td>4.9</td>
<td>0.887</td>
<td>0.094</td>
<td>1.17</td>
<td>0.973</td>
</tr>
<tr>
<td>[Ni(en)]²⁺-saponite</td>
<td>S</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Ru(bpy)]₃²⁺-saponite¹</td>
<td>L</td>
<td>0.19</td>
<td>0.17</td>
<td>2.7</td>
<td>0.994</td>
<td>0.20</td>
<td>1.56</td>
<td>0.991</td>
</tr>
<tr>
<td>[Ru(bpy)]₂²⁺-montmorillonite¹</td>
<td>L</td>
<td>0.18</td>
<td>0.11</td>
<td>1.2</td>
<td>0.997</td>
<td>0.35</td>
<td>1.95</td>
<td>0.994</td>
</tr>
<tr>
<td>[Ru(bpy)]₁²⁺-TSM²</td>
<td>L</td>
<td>0.10</td>
<td>0.06</td>
<td>3.1</td>
<td>0.889</td>
<td>0.093</td>
<td>1.59</td>
<td>0.995</td>
</tr>
</tbody>
</table>

¹ Okada et al. (2005), ² Giles classification.

The adsorption of phenol on organically modified smectites from aqueous solution has been reported so far (Mortland et al., 1986, Lawrence et al., 1998, Borisover et al., 2001). Cetyltrimethylammonium-smectite did not adsorb phenol at all, where phenol interacted strongly with water and was not attracted sufficiently to the hydrophobic surface of the cetyltrimethylammonium-smectite (Mortland et al., 1986). The adsorption isotherm of phenol on tetramethylphosphonium-smectite from aqueous solution was type-S (Giles et al., 1960) and the adsorbed amount was ca. 0.3 mmol/g at the equilibrium concentration of 1.2 mM (Lawrence et al., 1998). On the contrary, dye-clay intercalation compounds (i.e. crystal violet-smectite) adsorbed phenol from aqueous solution (L type isotherm) and the maximum adsorbed amount of phenol on crystal violet-smectite was ca. 0.08 mmol/g (Borisover et al., 2001). In the present system, the adsorption was L-type and the adsorbed amounts of phenol on the [Ni(bpy)]ₙ²⁺-saponites (n = 1, 2 and 3) (0.07–0.25 mmol/g) are close to that on crystal violet-smectite (Borisover et al., 2001). These observations suggest that the interactions between phenol and the interlayer organic cations containing aromatic rings played an important role in the adsorption of phenol.

The basal spacings of the [Ni(bpy)]ₙ²⁺-saponites (n = 1, 2 and 3) (Table 1) did not change upon the adsorption of phenol, indicating that the adsorbed phenol existed in the interlayer spaces. The formation of the nanospace was confirmed by the nitrogen adsorption isotherms shown in Fig. 3 as reported for the [Ru(bpy)]ₙ²⁺-clay systems (Okada et al., 2005). According to the BDDT classification (Brunauer et al., 1940), these adsorption isotherms were type-I isotherms, showing microporosity for nitrogen with only a small macroporous contribution (Yang and Bein, 1993). The surface areas derived from the nitrogen adsorption isotherms are listed in Table 1. The surface area of Na⁺-saponite (135 m²/g) was due to the external surface, because the interlayer space should be collapsed under the conditions for the nitrogen adsorption isotherm measurement (Okada et al., 2005). The surface areas of the [Ni(bpy)]ₙ²⁺-saponites (244, 223 and 158 m²/g) for the [Ni(bpy)]₃²⁺, the [Ni(bpy)]₂²⁺- and the [Ni(bpy)]¹⁺-saponites, respectively) and the [Ni(en)]₃²⁺-saponite (231 m²/g) were larger than that of Na⁺-saponite (135 m²/g) (Table 1). The increased surface areas of the [Ni(bpy)]ₙ²⁺-saponites (n = 1, 2 and 3) and the [Ni(en)]₃²⁺-saponite were ascribed to the formation of the interlayer micropore created by the [Ni(bpy)]ₙ²⁺ (n = 1, 2 and 3) or [Ni(en)]₃²⁺. The volumes of the pore formed by [Ni(bpy)]ₙ²⁺ (n = 1, 2 and 3) were estimated from the geometry of the [Ni(bpy)]ₙ²⁺-saponites (n = 1, 2 and 3), the gallery heights, the amounts of immobilized [Ni(bpy)]ₙ²⁺ (n = 1, 2 and 3) and the ideal surface area of saponite as reported for tetramethylammonium-saponite (Ogawa...
et al., 1994) and for [Ru(bpy)3]2+-clays (Okada et al., 2005). The interlayer volume is obtained by multiplying the gallery height of [Ni(bpy)]n2+-saponites (8.0 x 10^-7, 6.9 x 10^-7, and 4.1 x 10^-7 cm for [Ni(bpy)]n2+, [Ni(bpy)]n2+- and [Ni(bpy)]n2+-saponite, respectively) by half of the ideal surface area of saponite (3.4 x 10^-5 cm²/g) to be 0.27, 0.23, and 0.14 cm³/g for [Ni(bpy)]n2+, [Ni(bpy)]n2+- and [Ni(bpy)]n2+-saponite, respectively. The volume of [Ni(bpy)]n2+(n = 1, 2 and 3) occupied in the interlayer space (0.68, 0.50 and 0.33 nm²/dication for n = 1, 2 and 3, respectively) is obtained by multiplying the volume of [Ni(bpy)]n2+ by the amounts of immobilized [Ni(bpy)]n2+ on saponite (0.36, 0.34 and 0.39 mmol/g for [Ni(bpy)]n2+, [Ni(bpy)]n2+ and [Ni(bpy)]n2+–saponite, respectively) to be 0.14, 0.10 and 0.077 cm³/g for [Ni(bpy)]n2+, [Ni(bpy)]n2+– and [Ni(bpy)]n2+–saponite, respectively. The pore volume is calculated by subtracting the volume occupied by the immobilized [Ni(bpy)]n2+ from the interlayer volume to be 0.13, 0.13 and 0.062 cm³/g for [Ni(bpy)]n2+, [Ni(bpy)]n2+– and [Ni(bpy)]n2+–saponite, respectively. The volumes of adsorbed phenol are determined by multiplying the volume of phenol (0.162 nm²/molecule) (Caturia et al., 1988) by the adsorbed amounts of phenol (0.25, 0.12 and 0.07 mmol/g for [Ni(bpy)]n2+, [Ni(bpy)]n2+– and [Ni(bpy)]n2+–saponite, respectively) to be 0.016, 0.0074 and 0.0043 cm³/g for [Ni(bpy)]n2+, [Ni(bpy)]n2+– and [Ni(bpy)]n2+–saponite, respectively. The adsorption isotherm of phenol (Fig. 2). The difference in the adsorption behavior of phenol between the [Ni(bpy)]n2+-saponites (n = 1, 2 and 3) and the [Ni(en)]n2+–saponite systems was observed in the adsorption isotherms of phenol (Fig. 2). The difference indicates that the interactions between pyridine rings and phenol play an important role in the adsorption of phenol. This consideration was supported by comparisons of the gallery height, which directly correlates with pore size, and of the surface area between the [Ni(en)]n2+– and the [Ni(bpy)]n2+-saponite systems. The gallery height of the [Ni(en)]n2+–saponite (0.39 nm) was close to that of the [Ni(bpy)]n2+-saponite (0.41 nm), and the surface area of the [Ni(en)]n2+–saponite (231 m²/g) was larger compared to that of the [Ni(bpy)]n2+–saponite (158 m²/g) (Table 2). The adsorption isotherm of phenol for the [Ni(en)]n2+–saponite conformed to S-type, showing that the adsorption of phenol in the interlayer space as well as on the external surface did not occur even when the interlayer micropore was formed by the intercalation of [Ni(en)]n2+. This fact suggested that the contribution of the adsorption on the external surface of the [Ni(bpy)]n2+–saponites (n = 1, 2 and 3) was quantitatively minor. It was reported that the trimethylphenylammonium-smectite with larger surface area was capable of accommodating larger amount of aromatic hydrocarbons from aqueous solution (Jaynes and Boyd, 1991, Stevens et al., 1996). In the present system, the [Ni(bpy)]n2+-saponite shows strong phenol-adsorbent interactions despite of smaller surface area of the [Ni(bpy)]n2+–saponite compared to that of the [Ni(en)]n2+–saponite, supporting that the interactions of phenol with pyridine ring are a driving force for the adsorption on the [Ni(bpy)]n2+–saponites.

The difference in the adsorption behavior is also expressed by the variation of the values for the Freundlich affinity index (N) as listed in Table 2. The Freundlich equation (Freundlich, 1926) is expressed as,

\[ Q = K_f C^1/N \]

where \( K_f \) (mmol g⁻¹) and N are constants pertaining to maximum adsorbed amount and a conditional index which describes the shape of the isotherm (empirical adsorption characteristics), respectively. The N values that are less than 1 ([Ni(en)]n2+–saponite system) and greater than 1 ([Ni(bpy)]n2+–saponite [n = 1, 2 and 3] systems) represent isotherms having concave and convex up curvatures, respectively (Fig. 2). Evaluation using the Freundlich model to describe the adsorption of phenol from aqueous solution on a synthetic zeolite, Na-Y (\( K_f = 0.3 \) mmol g⁻¹ (mmol L⁻¹)¹/N, \( N = 1.7 \)) and on activated carbon (\( K_f = 1.9 \) mmol g⁻¹ (mmol L⁻¹)¹/N, \( N = 5.88 \)) was done (Okolo et al., 2000), and they indicated that these adsorbents had high affinity toward phenol molecule. In organically pillared smectite systems, there is an example of using the Freundlich model to discuss the adsorption behavior of aromatic hydrocarbons for trimethylphenylammonium-smectite from aqueous solutions (Sharmasarkar et al., 2000). The value with \( N > 1 \) indicated conformity of the isotherm to multilayer formation at the clay surfaces and was attributed to the interactions between adsorbates and subsequent aggregation in the pattern of a surface monolayer (Sharmasarkar et al., 2000). Considering the fact that the amount of the immobilized [Ni(bpy)]n2+ and the gallery height were close to those of the [Ru(bpy)]n2+-saponite (Table 1), the pore volume of the [Ni(bpy)]n2+–saponite is possibly close to that of the [Ru(bpy)]n2+-saponite. On the contrary, the values for the Freundlich affinity index (N) for the [Ru(bpy)]n2+–saponite (\( N = 1.59 \)) and the [Ni(bpy)]n2+–saponite (\( N = 1.20 \)) systems are shown to be different (Table 2). The difference in the value was thought to be derived from the variation of the pore size.

The pore sizes should correlate with the gallery heights of [M(bpy)]n2+-clays (M = Ru and Ni) and the average distances between adjacent [M(bpy)]n2+. Considering the diameter of [Ni(bpy)]n2+ (1.0 nm), the average size of the pore in the [Ni(bpy)]n2+–saponite was calculated by subtracting the diameter of [Ni(bpy)]n2+ from the intermolecular distance (1.4 nm) to be 0.4 x 0.8 nm². Judging from the molecular size of phenol (0.7 x 0.8 x 0.3 nm³ estimated from Chem3D, CambridgeSoft®) and the calculated pore size, phenol can be intercalated into the interlayer space of the
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[\text{Ni(bpy)}_3]^{2+}\text{-saponite. It has been pointed out that the }[\text{Ru(bpy)}_3]^{2+}\text{ aggregates in the interlayer spaces of montmorillonite (Ghosh and Bard, 1984) and fluoro-
tetrasilicic mica (TSM) (Ogawa et al., 1993, 2000) by the intermolecular interactions between adjacent }[\text{Ru(bpy)}_3]^{2+}. \text{ We mentioned in the previous paper that the }
\text{aggregation possibly affected the pore size distribution for the }[\text{Ru(bpy)}_3]^{2+}\text{-montmorillonite (Kunipia F) and the }[\text{Ru(bpy)}_3]^{2+}\text{-TSM systems (Okada et al., 2005). The difference in the adsorbed amount of phenol between the }[\text{Ru(bpy)}_3]^{2+}\text{-montmorillonite (0.18 mmol/g) and the }[\text{Ru(bpy)}_3]^{2+}\text{-TSM (0.10 mmol/g) systems was observed despite of the fact that the gallery height (0.80 nm) and the adsorbed amount of }[\text{Ru(bpy)}_3]^{2+}\text{ on montmorillonite (112 meq/100 g) were close to those on TSM system (gallery height: 0.81 nm, adsorbed amount of }[\text{Ru(bpy)}_3]^{2+}:\text{ 110 meq/100 g). The high affinity of phenol toward the }[\text{Ru(bpy)}_3]^{2+}\text{-montmorillonite is designated by the fact that the }N\text{ value for the }
[\text{Ru(bpy)}_3]^{2+}\text{-montmorillonite system (1.95) was larger compared to that of the }[\text{Ru(bpy)}_3]^{2+}\text{-TSM system (1.59) (Table 2). We assumed that the aggregation of the }[\text{Ru(bpy)}_3]^{2+}\text{ in montmorillonite yielded the formation of the nanopore with the size to match that of phenol molecule. From the comparison of the }N\text{ value for the }
[\text{Ni(bpy)}_3]^{2+}\text{-saponite system (1.20) with that for the }[\text{Ru(bpy)}_3]^{2+}\text{-saponite system (1.56), the size matching between the nanopore and phenol may not occur in the }
[\text{Ni(bpy)}_3]^{2+}\text{-saponite system, so that the interlayer }
[\text{Ni(bpy)}_3]^{2+}\text{ ions were thought to immobilize distribute evenly on saponite. In other words, tris-chelated bpy-
saponite with uniform distribution of the complex can be obtained through the reactions of transition-metal form-
saponite with bpy.

The adsorption capacity of phenol increased with the }n\text{ number of the }[\text{Ni(bpy)}_n]^{2+}\text{-saponites }n=1, 2\text{ and }3. \text{ In the }[\text{Ni(bpy)}_n]^{2+}\text{ and }[\text{Ni(en)}_3]^{2+}\text{-saponite systems, it is difficult to estimate pore size because the direction of the immobilized }[\text{Ni(bpy)}_n]^{2+}\text{ and }[\text{Ni(en)}_3]^{2+}\text{ in the interlayer space has not be clear. The variation of the adsorption capacity is affected by the gallery height, which directly correlates with the pore size. The values of Freundlich affinity index is approximately constant }
(N=1.2, \text{ Table 2}) \text{ and the molar ratios of the adsorbed phenol to bpy were ca. 0.2 (Table 2), despite of the variation in the gallery heights of the }[\text{Ni(bpy)}_n]^{2+}\text{-saponites }n=1, 2\text{ and }3 (\text{Table 1). It is thought that the nanopores formed in }[\text{Ni(bpy)}_n]^{2+}\text{-saponites }n=1, 2\text{ and }3\text{ are large ones to interact with bpy effectively, so that phenol adsorbed on }[\text{Ni(bpy)}_n]^{2+}\text{-saponites }n=1, 2\text{ and }3\text{ with the constant proportion of bpy to phenol.

CONCLUSIONS

[\text{Ni(bpy)}_n]^{2+}\text{ and }[\text{Ni(en)}_3]^{2+}\text{-saponites were successfully synthesized by the reactions of }\text{Ni(II)}\text{-saponite with bpy or en. The }[\text{Ni(bpy)}_n]^{2+}\text{-saponites }n=1, 2\text{ and }3\text{ adsorbed phenol from aqueous solution and the isotherms conformed to Langmuir model, indicating strong adsorbent-adsorbate interactions. On the contrary, the adsorption of phenol onto the }
[\text{Ni(en)}_3]^{2+}\text{-saponite did not occur effectively. It was shown that the adsorption of phenol on the }
[\text{Ni(bpy)}_n]^{2+}\text{-saponites }n=1, 2\text{ and }3\text{ from aqueous solution was governed by the }\pi\text{-interactions between phenol and the interlayer pyridine ring by the comparison of the adsorption behavior for the }[\text{Ni(bpy)}_n]^{2+}\text{-saponite }n=1, 2\text{ and }3\text{ system with that for the }
[\text{Ni(en)}_3]^{2+}\text{-saponite system.

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