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Several organic ultraviolet (UV) - absorbents such as 4-hydroxy-3-methoxybenzoic acid (HMBA), 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (HMBSA), 4-hydroxy-3-methoxycinnamic acid (HMCA), 4,4’-diaminostilbene-2,2’-disulfonic acid (DASDSA), p-aminobenzoic acid (PABA) and urocanic acid (UA) were intercalated into Zn2Al layered double hydroxides (Zn2Al-LDHs) by anion-exchange and/or co-precipitation and the photochemical properties of the nanocomposites materials obtained were investigated. The UV ray absorption ability of the organic UV absorbents increased and their catalytic activity for the air oxidation of castor oil greatly decreased when they were intercalated into the interlayer spaces of the Zn2Al-LDHs.

(Received Dec. 5, 2002)  
(Accepted Jan. 17, 2003)

Key words : Ultraviolet absorbents, Layered double hydroxide, Intercalation, Oxidation catalytic activity

1 Introduction

Ultraviolet (UV) ray contained in sunlight is known as carcinogen for inducing skin cancer[1]~[3]. In order to avoid the healthy damage by the UV ray, various organic UV ray absorbents have been used as sunscreen material. However, it is suspected that organic UV ray absorbents may pose a safety problem when they are used at high concentration, since they tend to be absorbed in the body through the skin. One of solution to this problem may be the incorporation of organic materials in nanospaces of inorganic materials to avoid direct contact of organic molecules and skin. Layered double hydroxides (LDHs) of the general formula [MIIxMIIIX(OH)2]x+ [An-x/nix]x-mH2O consist of cationic hydrotalcite-like layers and exchangeable interlayer anions[4]~[8]. The unique anion exchange capability of LDHs meets the requirement of inorganic matrices for encapsulating organic UV ray absorbents with negative charge in aqueous media. When negatively charged organic UV ray absorbents are incorporated between hydroxide layers, not only avoiding direct contact of them and skin, but also stabilization of them due to electrostatic interactions and hydrogen bonding between cationic hydrotalcite-like layers and anionic organic molecules are expected.

In this work we attempted to intercalate UV absorbing molecules such as 4-hydroxy-3-methoxybenzoic acid (HMBA), 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (HMBSA), 4-hydroxy-3-methoxycinnamic acid (HMCA), 4,4’-diaminostilbene-2,2’-disulfonic acid (DASDSA) and p-aminobenzoic acid (PABA) and urocanic acid (UA), in their anionic forms, into Zn2Al-LDHs by anion-exchange and/or coprecipitation reaction and the photochemical properties of the nanocomposites obtained were investigated.

2 Experimental

2-1 Synthesis

The Zn-Al LDHs containing organic UV absorbing anions were prepared by anion-exchange or coprecipitation. Distilled and deionized water was used in all preparations. The water was boiled immediately before use and all synthesis experiments were carried out under a stream of N2 in order to minimize carbonate contamination. Zn2Al(OH)6NO3·2H2O (Zn2Al-LDH/NO3) precursor was prepared as follows. A Zn/Al ratio...
2 was chosen since this was known from other studies to give samples of good crystallinity. An aqueous solution of 1.0 mol·dm⁻³ NaOH was added dropwise to a 100 cm³ of aqueous solution containing 0.10 mol of Zn(NO₃)₂·6H₂O and 0.050 mol of Al(NO₃)₃·9H₂O with vigorous stirring at room temperature until the pH of the reaction system attained 9.0, and then the resulting slurry was crystallized at 95°C for 15 h. The white precipitate was filtered, washed with decarbonated water for several times, and dried at 100°C for 18 h.

The Zn₂Al-LDH/HMBSA and Zn₂Al-LDH/UA were prepared by anion-exchange reaction with Zn₂Al-LDH/NO₃. A 200 cm³ three-necked round-bottom flask equipped reflux condenser, thermometer, mechanical stirrer, and electric heating mantle was charged with 100 cm³ of boiled water and 0.02 mol of HMBSA or UA. The solution was stirred and pH was adjusted to 9.0 with 0.1 mol·dm⁻³ NaOH aqueous solution. After dissolving HMBSA or UA, 6.0 g of Zn₂Al-LDH/NO₃ powder was added to the solution, and kept at 100°C for 18 h with vigorously stirring. The product was filtered out, washed with boiled distilled water and dried at 90°C for 10 h.

The Zn₂Al-LDH/HMBA, Zn₂Al-LDH/HMCA, Zn₂Al-LDH/DASDSA and Zn₂Al-LDH/PABA were prepared by co-precipitation reaction. After dissolving 0.025 mol of HMBA, HMCA, DASDSA, or PABA into 200 cm³ of NaOH aqueous solution (0.4 mol·dm⁻³) at room temperature, 200 cm³ of mixed nitrate solution containing 0.050 mol of Zn(NO₃)₂·6H₂O and 0.025 mol of Al(NO₃)₃·9H₂O, was added dropwise to the vigorously stirred organic UV absorbent-NaOH mixed solution at room temperature over a period of 60 min, and the pH of reaction system was maintained at 8.0-9.0 by the simultaneous addition of 1.0 mol·dm⁻³ NaOH solution. The resulting slurry was crystallized at 70°C for 15 h. The product was isolated by centrifugal separation, washed with hot distilled water, and dried at 70°C for 18 h.

The Zn₂Al-LDH/HMBSA and Zn₂Al-LDH/HMCA coated with amorphous silica was prepared as follows. After dissolving the predetermined quantity of Na₂SiO₃ in 20 cm³ of distilled water at 100°C, 12 mol·dm⁻³ HCl solution was dropped to precipitate amorphous SiO₂. The precipitate was filtered, washed with distilled water and dispersed again in 30 cm³ of distilled water at room temperature, and then 1 g of Zn₂Al-LDH/HMBSA or Zn₂Al-LDH/HMCA powder was added. After stirring for 30 min, the product was filtered and dried at 110°C for 10 h.

2.2 Characterization methods
The crystalline phase was determined by X-ray powder diffraction analysis (SHIMADZU, XD-01) with CuKα radiation. Elemental analysis of Zn and Al was performed by inductively coupled plasma atomic emission spectroscopy (SEIKO, SPS 1200A) after dissolving the samples with HCl solutions. The contents of organic UV absorbents were determined by UV absorption spectrophotometry (SHIMADZU, UV-2450) after dissolving the samples with HCl-ethanol mixed solutions and TG/DTA measurements (RIGAKU, TAS 200).

The UV shielding properties of the samples were evaluated by measuring the transmittance spectra of the thin film uniformly dispersed the sample powders with an UV-Vis spectrophotometer (SHIMADZU, UV-2450), where 2 g of sample, 4 g of nitrocellulose of industrial grade, 10 g of ethyl acetate and 9 g of butyl acetate were mixed uniformly using paint shaker and 100 g of zirconia ball with 2.7 mm in diameter for 40 h. The dispersion mixture was applied onto a quartz glass plate with an applicator. Thickness of the film was 12.5 μm.

The catalytic activity for the oxidation of organic material was determined by the conductometric determination method (Rancimat System⁹) using castor oil of cosmetic grade as oxidized material. The sample powder (1 g) was mixed with 10 g of castor oil and set at 120°C with bubbling 0.2 dm³·min⁻¹ of air, where the air was introduced into distilled water attached the electric conductivity measurement cell. The oxidation catalytic activity was evaluated by measuring the increase in the conductivity of distilled water by trapping volatile molecules formed by the oxidation of castor oil on heating.

3 Results and Discussion
The powder X-ray patterns for the samples are shown in Fig. 1. The pristine Zn₂Al-LDH/NO₃ had a well developed layer structure with the basal spacing (d₀₀₃) of 0.88 nm (Fig. 1a), which was in agreement with sum of the thickness of ionic NO₃⁻ (0.39 nm) and that of brucite-like layer itself (0.48 nm)¹⁰. In the case of Zn₂Al-LDH/HMBSA and Zn₂Al-LDH/UA (Fig. 1b and c), which were obtained by replacing interlayer nitrate ions in Zn₂Al-LDH/NO₃ by anion-exchange reaction, the basal spacing are greatly expanded as 2.05 and 1.99 nm, respectively. The
The results for chemical analysis, anion sizes calculated, and interlayer spaces of LDHs expected from the anion size and determined, are summarized in Table 1. As expected, the Zn/Al ratios in all samples were close to 2, which is the value of the starting solution. The molar ratio of organic UV absorber/Zn$_2$Al(OH)$_6$ changed from 0.35 to 1.0 depending on the species of organic molecule intercalated. The interlayer distances of LDH/HMBSA and LDH/DASDSA were in good agreement with sum of the thickness of brucite-like layer and size of organic molecules turning the functional groups perpendicularly to LDHs layers as shown in Fig. 2 d and e. On the other hand, the interlayer distances of LDH/HMBSA, LDH/UA, LDH/HMBA and LDH/PABA were much larger than those expected. Therefore, it was suspected that HMBSA, UA, HMBA and PABA ions were located in a line by turning the functional group on the contrary by turns and opposing the fields of aromatic ring mutually by π-π interaction as shown in Figs. 2 c-f and 3.

The UV ray can be divided into three parts by wavelength as UV-A (320–400 nm), UV-B (280–320 nm), and UV-C (200–280 nm). Since UV-C and most of UV-B are absorbed by ozone layer in the upper atmosphere, the UV ray in the sunlight which reaches on the ground is mainly UV-A (90–99%), and UV-B is also contained slightly (1–10%). Therefore, the UV shielding materials are expected to absorb UV-ray less than 400 nm wavelength. In order to evaluate UV shielding ability of the Zn$_2$Al-LDH/organic UV absorbent nanocomposites obtained, the UV-Vis transmittance spectra of the samples were determined and the results are shown in

Table 1  Chemical compositions, anion sizes and interlayer spaces, $d_{003}$ of Zn$_2$Al-LDHs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic ratio of Zn/Al</th>
<th>Anion intercalated</th>
<th>Anion size /nm$^3$</th>
<th>$d_{003}$/nm</th>
<th>Expected</th>
<th>Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH/NO$_3$</td>
<td>2.03</td>
<td>17.3</td>
<td>1.00</td>
<td>0.39</td>
<td>0.87</td>
<td>0.87</td>
</tr>
<tr>
<td>LDH/HMBSA</td>
<td>1.99</td>
<td>42.0</td>
<td>0.70</td>
<td>1.16</td>
<td>1.64</td>
<td>2.05</td>
</tr>
<tr>
<td>LDH/UA</td>
<td>2.02</td>
<td>28.2</td>
<td>1.00</td>
<td>0.96</td>
<td>1.44</td>
<td>1.99</td>
</tr>
<tr>
<td>LDH/HMBA</td>
<td>2.12</td>
<td>23.8</td>
<td>0.76</td>
<td>0.87</td>
<td>1.35</td>
<td>1.49</td>
</tr>
<tr>
<td>LDH/HMCA</td>
<td>1.93</td>
<td>21.3</td>
<td>0.50</td>
<td>1.05</td>
<td>1.53</td>
<td>1.55</td>
</tr>
<tr>
<td>LDH/DASDSA</td>
<td>1.98</td>
<td>30.0</td>
<td>0.35</td>
<td>1.03</td>
<td>1.51</td>
<td>1.51</td>
</tr>
<tr>
<td>LDH/PABA</td>
<td>2.08</td>
<td>32.9</td>
<td>1.00</td>
<td>0.90</td>
<td>1.38</td>
<td>1.55</td>
</tr>
</tbody>
</table>

$a$ Assumptions: LDH layer thickness is 0.48 nm, van der Waals radius of O and H are 0.14 and 0.12 nm, respectively and anions turn the functional groups perpendicularly to LDHs layers.

Fig. 4. It is seen that the UV shielding ability of Zn$_2$Al-LDH/NO$_3$ was poor (Fig. 4a), however, all Zn$_2$Al-LDH/organic UV absorbing molecule nanocomposites showed excellent UV-shielding ability and transparency in the visible light region. Especially, the Zn$_2$Al-LDH/HMBSA, Zn$_2$Al-LDH/HMCA and Zn$_2$Al-LDH/DASDSA resulted in excellent UV shielding capacity in UV–A region. In order to inspect the effect of host-guest interaction, the UV shielding ability of a mixed-compound containing 30.0 mass% DASDSA and 70.0 mass% Zn$_2$Al-LDH/NO$_3$

Fig. 2 Schematic representation of the Zn$_2$Al–LDH/organic UV-absorbing molecule nanocomposites.

Fig. 3 Estimated configuration of organic UV absorbing molecules in the interlayer by π–π interaction.

Fig. 4 UV–Vis transmittance spectra of thin films of a: Zn$_2$Al–LDH/NO$_3$, b: Zn$_2$Al–LDH/PABA, c: Zn$_2$Al–LDH/UA, d: Zn$_2$Al–LDH/HMBA, e: Zn$_2$Al–LDH/HMBSA, f: Zn$_2$Al–LDH/HMCA, g: Zn$_2$Al–LDH/DASDSA.
was compared with that of Zn$_2$Al-LDH/DASDSA which contained 30.0 mass% DASDSA in the interlayer (See Table 1). As shown in Fig. 5, the UV shielding ability of Zn$_2$Al-LDH/DASDSA was superior to that of DASDSA and Zn$_2$Al-LDH/NO$_3$ mixture. The excellent UV shielding ability of Zn$_2$Al-LDH/DASDSA is considered because DASDSA in the interlayer was highly dissociated to ion. Similar results were also obtained with other organic UV absorbents. On the other hand, the absorption peak of the Zn$_2$Al-LDH/DASDSA was slightly red shifted from 334.0 nm of DASDSA and Zn$_2$Al-LDH/NO$_3$ mixture to 341.0 nm. The red-shift in the spectrum might be due to the guest-host interaction, i.e., the low symmetry ligand distortions in the spatially restricted environment of galleries\(^{11,12}\).

It is well known that some organic materials promote the air oxidation of other organic materials by forming active oxygen radicals, etc. The air oxidation of castor oil in the presence of Zn$_2$Al-LDH/organic UV absorbent nanocomposites and unsupported organic UV-absorbers were investigated using the Ranchimat test apparatus at 120°C. The results are shows in Fig. 6. Unsupported organic UV absorbents such as HMCA and HMBSA greatly promoted the air oxidation of castor oil. When they were intercalated into the Zn$_2$Al hydroxide layers, as expected, the oxidation was substantially decreased, so far as to be lower than the blank reaction without additives. The results indicated that the host material, the Zn$_2$Al hydroxide layer, has a capacity not only to restrain the oxidation catalytic activity of guest materials, but also to depress the air oxidation of castor oil. Therefore, it is suspected that the Zn$_2$Al hydroxide layer plays as a radical capture agent.

It is well known that the anion incorporated in LDH is easily deintercalated by the anion exchange reaction with carbonate ion since the selectivity of ion exchange of carbonate ion is quite high. The deintercalation of organic UV-absorbing molecules from Zn$_2$Al-LDH layer may be depressed by forming a protection film on the surface. The amounts of the elution of HMBSA and HMCA from Zn$_2$Al-LDH/HMBSA and Zn$_2$Al-LDH/HMCA coated with various amounts of silica were determined in 0.02 mol·dm$^{-3}$ Na$_2$CO$_3$ aqueous solution. As seen in Table 2, the particle size slightly increased by coating with amorphous silica, but the agglomeration of particle during silica coating seems not to go on so

As expected, the elution of the organic molecule was effectively depressed by increasing the amount of coated silica (Fig. 7). It was also found that Zn$_2$Al–LDH/HMBSA showed more excellent stability in carbonate ion solution than Zn$_2$Al–LDH/HMCA. It may be due to the stabilization of HMBSA ion in the interlayer by the π–π interaction between HMBSA molecules.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size /μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH/HMBSA</td>
<td>0.084</td>
</tr>
<tr>
<td>LDH/HMBSA–21.0 mass% SiO$_2$</td>
<td>0.092</td>
</tr>
<tr>
<td>LDH/HMCA</td>
<td>0.069</td>
</tr>
<tr>
<td>LDH/HMCA–26.0 mass% SiO$_2$</td>
<td>0.093</td>
</tr>
</tbody>
</table>

Conclusions

The organic UV–absorbents, HMBA, HMBSA, HMCA, DASDSA, PABA and UA, in their anionic forms, could be intercalated into the layers of the Zn$_2$Al–LDHs by anion-exchange and/ or co-precipitation reaction. The organic anions in the interlayer still maintained their original structures and UV absorption ability. When the organic UV absorbent molecules were intercalated into the layers of the Zn$_2$Al–LDHs, their oxidation catalytic activity for the air oxidation of castor oil greatly decreased, and their UV absorption ability increased further. The deintercalation of organic molecules by the anion exchange reaction with carbonate ion could be depressed by coating the powder surface with amorphous silica.

Acknowledgement

This work was supported by the JSPS Postdoctoral Fellowship for Foreign Researchers in Japan (IDNo. P00312).

References

層状複水酸化物/有機紫外線吸収剤ナノ複合体の合成と光化学特性

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4-ヒドロキシ-3 メトキシ安息香酸(HMBA), 2-ヒドロキシ-7 メトキシベンゾフェノン-5-スルホン酸 (HMBSA), 4-ヒドロキシ-3 メトキシ桂皮酸(HMCA), 4,4'-ジアミノスチレン-2,2'-ジスルホン酸 (DASDSA), p-アミノ安息香酸(PABA), ユロカニン酸(UA)のような種々の有機紫外線吸収剤をイオン交換法あるいは共沈法により亜鉛－アルミニウム層状水酸化物の層間に包接し、得られたナノ複合体の光－化学特性について検討した。有機紫外線吸収剤を層状複水酸化物を層間包接することにより、紫外線吸収特性を向上させ、ヒマシ油の空気酸化に対する触媒活性を著しく低減することができた。