

Synthesis and UV Shielding Properties of Layered Double Hydroxide/2-Hydroxy-4-Methoxy-Benzophenone-5-Sulfonic Acid

Qing-Lin He, Shu Yin and Tsugio Sato

IMRAM, Tohoku University, Sendai 980-8577, Japan

Fax: 81-22-217-5597, e-mail: tsusato@tagen.tohoku.ac.jp

Typical organic UV ray absorbent, 2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid (HMBSA) was incorporated in the interlayer of a layered double hydroxide, $\text{Zn}_2\text{Al}(\text{OH})_6\text{X}$ ($\text{Zn}_2\text{Al-LDH/X}$; X: interlayer anion) and the UV shielding properties of resulting nanocomposites were investigated. The $\text{Zn}_2\text{Al-LDH/HMBSA}$ nanocomposites were prepared by ion exchange method using $\text{Zn}_2\text{Al}(\text{OH})_6\text{NO}_3$ as a precursor. The interlayer space of $\text{Zn}_2\text{Al-LDH/HMBSA}$ was 1.57 nm. $\text{Zn}_2\text{Al-LDH/HMBSA}$ showed excellent UV ray absorption capacity and transparency in the visible light region, although the UV ray absorption ability of $\text{Zn}_2\text{Al-LDH/NO}_3$ was modest. In comparison with unsupported HMBSA, $\text{Zn}_2\text{Al-LDH/HMBSA}$ showed slight red shift in the UV-absorption spectrum and higher UV-shielding ability. HMBSA promoted the air oxidation of castor oil, but the oxidation was greatly decreased by incorporating it in the interlayer of $\text{Zn}_2\text{Al-LDH}$. The coating of $\text{Zn}_2\text{Al-LDH/HMBSA}$ powders with amorphous silica was effective to depress the deintercalation of HMBSA by the anion exchange reaction with carbonate ion.

Key words: Intercalation. Organic UV absorber, 2-Hydroxy-4-methoxy-benzophenone-5-sulfonic acid, Photochemical properties, Chemical stability

1. INTRODUCTION

It is well known that ultraviolet (UV) ray contained in sunlight causes several problems such as photodegradation of organic materials and damages to human health, e.g., causing sunburn, suntan, acceleration of aging and cancer [1]. Organic materials such as 4-hydroxy-3-methoxycinnamic acid, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, urocanic acid, 4-hydroxy-3-methoxybenzoic acid and *p*-aminobenzoic acid possess excellent UV ray absorption ability [2] and have been used as sun-care products, 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 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), $[\text{M}^{2+}_x\text{M}^{3+}_y(\text{OH})_z]^{x+y-}\text{A}^{n-}_{x/n}\cdot m\text{H}_2\text{O}$ ($\text{M}^{2+}=\text{Mg}^{2+}, \text{Zn}^{2+}, \text{M}^{3+}=\text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}$, $\text{A}^{n-}=\text{OH}^-, \text{Cl}^-, \text{NO}_3^-, \text{CO}_3^{2-}, \dots$, and $0.20 < x < 0.33$) are practically the only known family of layered solids with positively charged layers and intercalated charge balancing anions which may be replaced with other anions by ion-exchange processes [3-7]. It is expected that the LDHs can incorporate organic UV

absorbents as their anionic forms as shown in Fig. 1, and avoid the direct contact of them and skin. In the present work, a typical organic UV absorbent, 2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid (HMBSA) was intercalated in LDH and the photochemical properties of resulting nanocomposites were investigated.

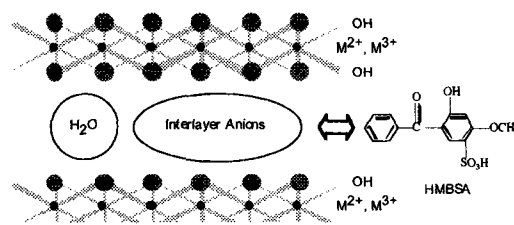


Fig. 1 Schematic illustration of the incorporation of HMBSA in LDH by anion exchange reaction.

2. EXPERIMENTAL

$\text{Zn}_2\text{Al}(\text{OH})_6\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\text{Zn}_2\text{Al-LDH/NO}_3$), precursor was prepared as follows. An aqueous solution of $1.0 \text{ mol} \cdot \text{dm}^{-3}$ NaOH was added dropwise to a 100 cm^3 of aqueous solution containing 0.10 mol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.050 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 was prepared by anion-exchange reaction with Zn₂Al-LDH/NO₃. A 200 cm³ three-necked round-bottom flask equipped with reflux condenser, thermometer, mechanical stirrer, and electric heating mantle was charged with 100 cm³ of boiled water and 0.02 mol of HMBSA. The solution was stirred and pH was adjusted to 9.0 with 0.1 mol·dm⁻³ NaOH aqueous solution. After dissolving HMBSA, 6.0g of Zn₂Al-LDH/NO₃ powder was added to the solution, and kept at 100°C for 18 h with vigorous stirring. The product was filtered out, washed with boiled distilled water and dried at 90 °C for 10 h.

The Zn₂Al-LDH/HMBSA 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 in 30 cm³ of distilled water at room temperature, and then 1 g of Zn₂Al-LDH/HMBSA powder was added. After stirring for 30 min, the product was filtered and dried at 110°C for 10 h.

The elemental analysis with a ICP spectrophotometer (SEIKO, SPS 1200A) under standard conditions indicated that the Zn: Al ratio on each of Zn₂Al LDHs is 2. The content of HMBSA in the Zn₂Al LDHs was obtained with ultraviolet spectrophotometry (SHIMADZU, UV-2450) and thermogravimetry (RIGAKU, TAS200). XRD measurements (SHIMADZU XD-01) were performed using CuKα radiation. The catalytic activity for the oxidation of organic material was determined by the conductometric determination method (Rancimat system [8,9]) using castor oil of cosmetic grade as oxidized material. The sample powder (1 g) was mixed with the castor oil (10 g) and set at 120°C with bubbling 0.5 dm³·min⁻¹ of air, where the air was introduced into distilled water attached to 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. The UV-shielding properties of the samples were evaluated by measuring the transmittance of the film uniformly dispersed by the sample powder with a 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 balls of 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.

3. RESULTS & DISCUSSION

The content of HMBSA in Zn₂Al-LDHs was determined as 42.0 wt% and the molar ratio of HMBSA/Zn₂Al(OH)₆ was 0.70, indicating that HMBSA exists as mixture of HMBSA²⁻ and HMBSA⁻. The powder X-ray diffraction pattern of the Zn₂Al-LDH/HMBSA is shown in Fig. 2 together with that of Zn₂Al-LDH/NO₃. The Zn₂Al-LDH/NO₃ showed sharp diffraction pattern, indicating a well-developed layer structure with the interlayer spacing of 0.88 nm. In the case of Zn₂Al-LDH/HMBSA obtained by replacing interlayer nitrate ions in Zn₂Al-LDH/NO₃ by anion-exchange reaction, the basal spacing was greatly expanded to 2.05 nm. The anion sizes and interlayer space, *d*₀₀₃ of LDHs are summarized in Table I. The observed interlayer space of Zn₂Al-LDH/NO₃, 0.88 nm was in good agreement with the sum of the thickness of ionic NO₃⁻ (0.39 nm) and that of brucite-like layer (0.48 nm). On the other hand, the interlayer distance of LDH/HMBSA (2.05 nm) was much larger than that expected (1.64 nm). Therefore, it was suspected that HMBSA ions were located in a line by turning SO₃ group on the contrary by turns and opposing the fields of aromatic ring mutually by π-π interaction as shown in Figs. 3 and 4.

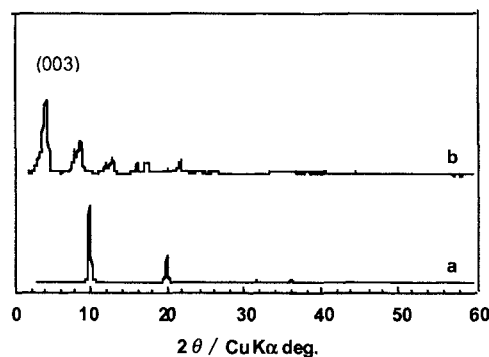


Fig. 2 X-ray diffraction patterns of (a) Zn₂Al-LDH/NO₃ and (b) Zn₂Al-LDH/HMBSA

Table I Anion sizes and interlayer spaces, *d*₀₀₃ of Zn₂Al-LDHs

Sample	Anion size ^a (nm)	<i>d</i> ₀₀₃ (nm)	
		Expected	Found
Zn ₂ Al-LDH/NO ₃	0.39	0.87	0.88
Zn ₂ Al-LDH/HMBSA	1.23	1.71	2.05

^a Assumptions: host LDH layer thickness is 0.48 nm, van der Waals radius of O and H are 0.14 and 0.12 nm, respectively and HMBSA turns SO₃ group perpendicularly to LDH layer.

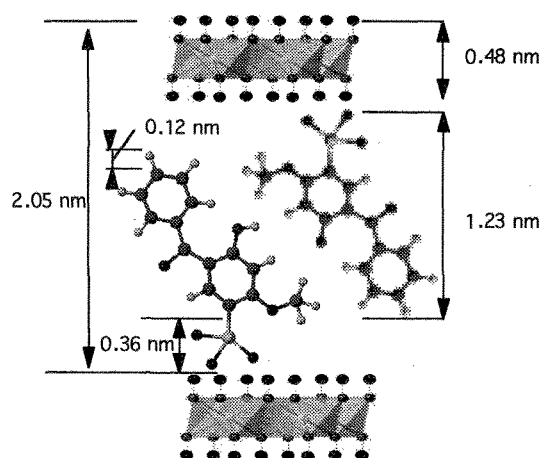


Fig. 3 Schematic representation of $\text{Zn}_2\text{Al-LDH/HMBSA}$.

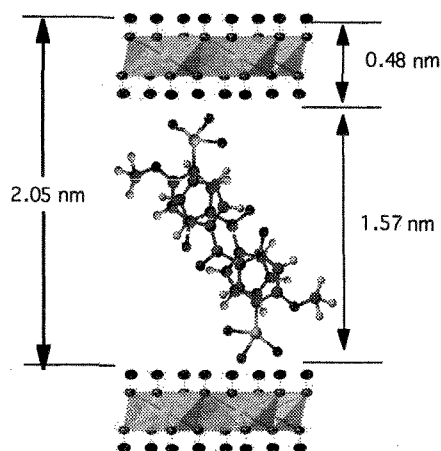


Fig. 4 Estimated configuration of HMBSA in the interlayer by π - π interaction of aromatic groups.

UV-Vis transmittance spectra of (a) $\text{Zn}_2\text{Al-LDH/NO}_3$, (b) $\text{Zn}_2\text{Al-LDH/HMBSA}$ intercalating 42 wt% HMBSA and (c) mixture of 42 wt% HMBSA and 58 wt% $\text{Zn}_2\text{Al-LDH/NO}_3$ are shown in Fig. 5. The UV absorption ability of $\text{Zn}_2\text{Al-LDH/NO}_3$ was modest, however, $\text{Zn}_2\text{Al-LDH/HMBSA}$ showed excellent UV shielding ability ($\lambda < 400$ nm) and high transparency in the visible light region ($\lambda > 400$ nm). It is notable that the UV shielding ability of $\text{Zn}_2\text{Al-LDH/HMBSA}$ was superior to that of HMBSA and $\text{Zn}_2\text{Al-LDH/NO}_3$ mixture. The excellent UV shielding ability of $\text{Zn}_2\text{Al-LDH/HMBSA}$ nanocomposite is considered because HMBSA in the interlayer was highly dissociated to ion. In

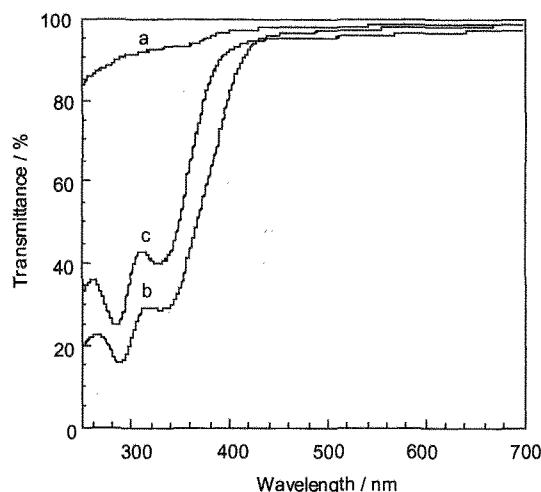


Fig. 5 UV-Vis transmittance spectra of thin films of (a) $\text{Zn}_2\text{Al-LDH/NO}_3$, (b) $\text{Zn}_2\text{Al-LDH/HMBSA}$ and (c) mixture of 42 wt% HMBSA and 48 wt% $\text{Zn}_2\text{Al-LDH/NO}_3$.

addition, the spectrum of $\text{Zn}_2\text{Al-LDH/HMBSA}$ was similar to that of unsupported HMBSA except for slight red shift. 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 [10,11].

It is well known that some organic materials promote the air oxidation of other organic material. The air oxidation of castor oil in the presence of (a) $\text{Zn}_2\text{Al-LDH/HMBSA}$, (b) unsupported HMBSA and (c) without additive (Blank) was investigated using the Ranchimat test apparatus at 120°C . The results are shown in Fig. 6. Unsupported HMBSA greatly promoted the air oxidation of castor oil. On the other hand, when HMBSA molecules were intercalated into Zn_2Al hydroxide layers, as expected, the oxidation was depressed substantially, so far as to be lower than the blank reaction without additive. These results indicated that the host material, the Zn_2Al hydroxide layer, has a capacity to restrain the oxidation catalytic activity of HMBSA.

It is suspected that the anions incorporated in LDHs are deintercalated by the anion exchange reaction with carbonate ion since the selectivity of ion exchange of carbonate ion is quite high. The deintercalation of HMBSA from $\text{Zn}_2\text{Al-LDH/HMBSA}$ may be depressed by forming a protection film on the surface of the powder. The amounts of the elution of HMBSA from $\text{Zn}_2\text{Al-LDH/HMBSA}$ coated with various amounts of amorphous silica were determined in 0.01

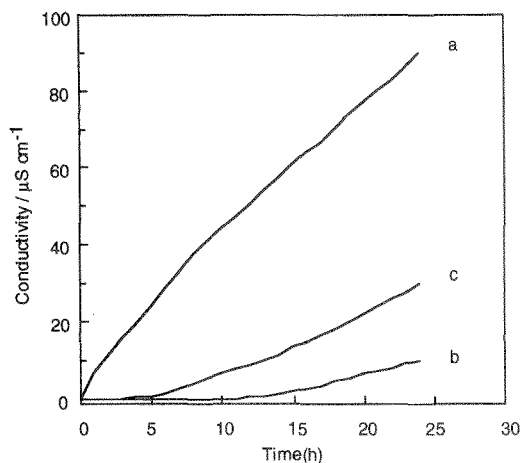


Fig. 6 Evaluation of the air oxidation of castor oil at 120°C in the presence of (a) HMBSA, (b) Zn₂Al-LDH/HMBSA and (c) Blank (without additive) by the Rancimat test.

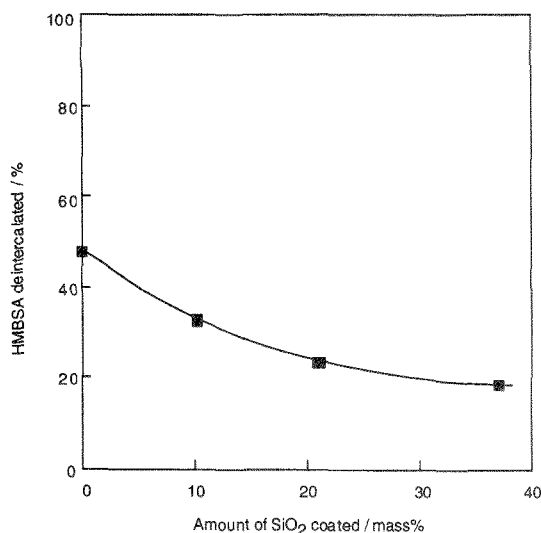


Fig. 7 Dissolution of HMCA from Zn₂Al-LDH/HMCA in 0.01 mol·dm⁻³ Na₂CO₃ solutions at 50°C for 5 h as a function of the amounts of coated amorphous silica.

mol·dm⁻³ Na₂CO₃ aqueous solution. The agglomerated particle sizes of Zn₂Al-LDH/HMBSA before and after silica coating were 84 and 92 nm, respectively, indicating that the agglomeration of particles during silica coating did not go on so much. As seen in Fig. 7, the elution of HMBSA was effectively depressed by increasing the amount of coated silica.

4. CONCLUSIONS

A typical organic UV absorber, HMBSA in its anionic

form, could be intercalated in the layers of the Zn₂Al-LDH by ion exchange reaction with Zn₂Al-LDH/NO₃. The HMBSA molecules incorporated showed much more excellent UV absorption ability than unsupported HMBSA. HMBSA promoted the air oxidation of castor oil, but the oxidation catalytic activity was greatly decreased by incorporating HMBSA in LDH layer. When Zn₂Al-LDH/HMBSA was coated with amorphous silica, the chemical elution of HMBSA by the anion exchange reaction with carbonate ion could be effectively depressed.

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REFERENCES

- [1] S. Asano, *Hyomenkagaku*, **15**, 473-478 (1994).
- [2] H. Masaki, *Fragrance J.*, **26**, 65-73 (1998).
- [3] R. Allman, *Chimia*, **24**, 99-108 (1970).
- [4] S. Miyata, *Clays Clay Miner.*, **23**, 369-375 (1975).
- [5] T. Sato, K. Kato, T. Endo and M. Shimada, *React. Solids*, **2**, 253-260 (1986).
- [6] T. Sato, T. Wakabayashi, T. Endo and M. Shimada, *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 89-92 (1986).
- [7] T. Sato and A. Okuwaki, *Solid State Ionics*, **45**, 43-48 (1991).
- [8] J. Frank, J. V. Greil and R. Freaso, *Food Technol.*, **36**, 71-76 (1982).
- [9] M. W. Laubi and P. A. Bruttel, *J. Am. Oil Chem. Soc.*, **63**, 792-795 (1986).
- [10] T. Bakas, A. Moukarika, V. Papaefthymiou and A. Ladavos, *Clays Clay Minerals*, **42**, 634-642 (1994).
- [11] E. P. Giannelis, D. G. Nocera and T. J. Pinnavaia, *Inorg. Chem.*, **26**, 203-205 (1987).

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