

## Host-Guest Electron Transfer between Intercalated Co(II)-Tetraphenylporphine Tetrasulfonate and Mg-Fe(III) Layered Double Hydroxides

Tetsuya Shichi,<sup>†</sup> Zhiwei Tong,<sup>†</sup> Shu Hirai,<sup>†</sup> and Katsuhiko Takagi<sup>\*†,††</sup>

<sup>†</sup>Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603  
<sup>††</sup>CREST, Japan Science and Technology (JST)

(Received May 13, 2002; CL-020411)

An electron transfer between Fe(III) of Mg-Fe(III) LDH (Layered Double Hydroxide) and Co(II)TPPS (cobalt(II)-tetraphenylporphine tetrasulfonate) as the guest was investigated. With a low coverage of the guest, the electron transfer occurred during the adsorption process to form an intercalation hybrid. On the other hand, light irradiation (>400 nm) of the hybrid powder resulted in a reverse electron transfer to Co(II)TPPS/Mg-Fe(III) LDH. Structural changes in the laminating hybrid were observed to take place concurrently with the electron transfers.

Layered double hydroxides (LDH) have been widely studied as the host materials for photofunctional organic compounds, as they have the ability to incorporate various anionic species in their interlayers to yield unique molecular assemblies. When photochemically reactive molecules are intercalated, for example, regio- and/or stereospecific photoproducts can be developed.<sup>1</sup> In the case of dye molecules, the organized aggregates are able to exhibit unique photophysical properties.<sup>2</sup> Thus far, such inorganic layer compounds have been utilized as a “template” controlling the reaction pathways. In the present study, the photoinduced electron transfer reaction between the host layers and their guest molecules was undertaken to study the photoinduced charge separation in the LDH containing a transition metal (Mg-Fe(III) LDH) and the anionic metalloporphine complex (Co(II)TPPS).

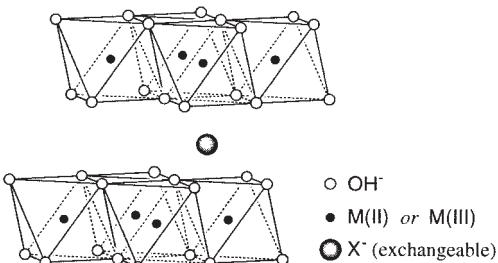


Figure 1. General structure of LDH ( $[M(II)_{1-n}M(III)_n(OH)_2]X_n$ ).

Mg-Fe(III) LDH ( $[Mg_{0.75}Fe(III)_{0.25}(OH)_2]Cl_{0.25} \cdot 4H_2O$ ) was synthesized by a coprecipitation method.<sup>3,4</sup> An aqueous solution of  $MgCl_2 \cdot 6H_2O$  (0.75 mol·dm<sup>-3</sup>) and  $FeCl_3 \cdot 9H_2O$  (0.25 mol·dm<sup>-3</sup>) was titrated by a 2 mol·dm<sup>-3</sup>  $CO_2$ -free NaOH solution until it reached pH = 8 with stirring for 18 h at 65 °C. The light brown precipitate was then filtered, washed and dried in vacuo. The chemical structure of the LDH is depicted in Figure 1, in which the octahedral units of  $Mg(OH)_2$  and  $Fe(OH)_2^+$  are seen to be fused to form a sheet where the apparent cationic charges due to the trivalent Fe(III) are neutralized by the intercalated anions ( $X^-$ ). Co(II)TPPS was obtained by the procedures described in previous literature and

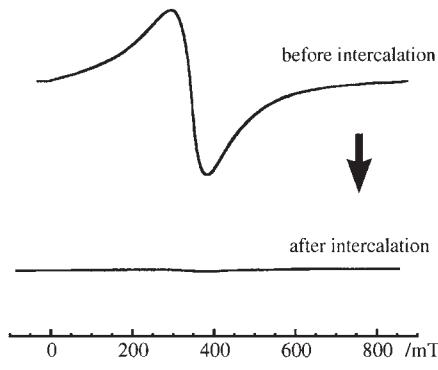


Figure 2. ESR spectra of Mg-Fe(III) LDH before and after intercalation of Co(II)TPPS.

the intercalation was also carried out accordingly.<sup>6,7</sup> In a flask to protect against scattering light, 1.0 g of Mg-Fe(III) LDH was suspended in 25 ml distilled water, and added to an aqueous alkaline solution of Co(II)TPPS, and then stirred for 18 h at 70 °C resulting in a 5% coverage of CoTPPS in the LDH. The suspension of the intercalated compound was filtered, washed, and dried in vacuo. The resulting samples were irradiated by a 300 W medium pressure Hg lamp through a filter (transparent for light >400 nm) and analyzed by ESR, UV-vis spectra and powder XRD analyses.

The ESR spectra of Mg-Fe(III) LDH and Co(II)TPPS intercalated LDH (CoTPPS/Mg-Fe LDH) are shown in Figure 2. Before intercalation, Mg-Fe(III) LDH showed a broad singlet signal (2 mT) assigned to Fe(III). However, the strong and broad ESR signal disappeared with the intercalation of Co(II)TPPS, indicating a reduction of the Fe(III) into Fe(II) ions within the LDH layers. Indeed, the accompanying one-electron oxidation of Co(II)TPPS could be evidenced by the diffuse reflectance UV

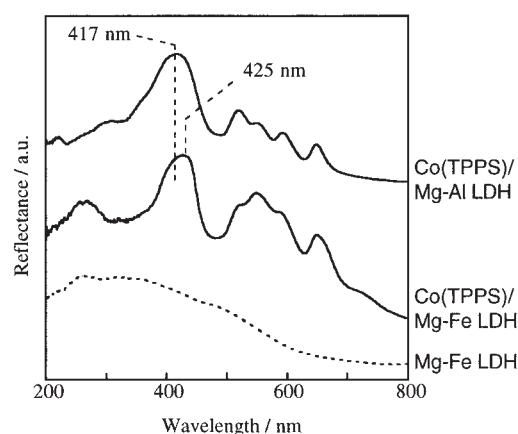


Figure 3. Diffuse reflectance UV-vis spectra of CoTPPS/Mg-Al LDH (upper line), CoTPPS/Mg-Fe LDH (middle line), and Mg-Fe LDH (lower dotted line).

spectra. Figure 3 shows the UV spectra of CoTPPS intercalated in Mg–Fe LDHs in comparison with a Co(II)TPPS hybrid incorporated with a typical Mg–Al(III) LDH clay. Co(II)TPPS intercalated in Mg–Al LDH showed a broad Soret band peak at 417 nm, almost the same as for the diluted aqueous Co(II)TPPS solution. In contrast, the Soret band of CoTPPS in the interlayers of Mg–Fe LDH shifted to longer wavelength regions with a maximum at 425 nm. Such a red shift strongly suggests the oxidation of Co(II)TPPS to Co(III)TPPS. That is, an electron transfer between the LDH host layers and the guest porphine molecules could be observed at the stage of intercalation;  $\text{Fe(III)} + \text{Co(II)} \rightarrow \text{Fe(II)} + \text{Co(III)}$ .

Upon irradiation of the resulting Co(III)TPPS/Mg–Fe(II) LDH hybrid, initially formed by a forward electron transfer during intercalation, with light longer than 400 nm, a back electron transfer could be seen to take place. The ESR spectra were also seen to change again by visible light irradiation, as shown in Figure 4. The broad and strong signal of the Fe(III) ions, having disappeared during the intercalation process, appeared again, and could be retained for 4 h. The UV-vis absorption spectra of Co(III)TPPS were seen to decrease by irradiation (Figure 5), showing a decomposition of the CoTPPS;  $\text{Fe(II)} + \text{Co(III)} \rightarrow \text{Fe(III)} + \text{Co(II)}$ .

Figure 6 shows the powder XRD patterns of the intercalation compounds. The diffraction peaks due to the (00h) basal spacings can be observed in the Cl/Mg–Fe(III) LDH without Co(II)TPPS (a), however, they disappeared after intercalation of Co(II)TPPS (b). The Fe(III) ions, i.e., the anion-exchange sites of the LDH layers, were reduced to Fe(II) during the intercalation process. As a result,

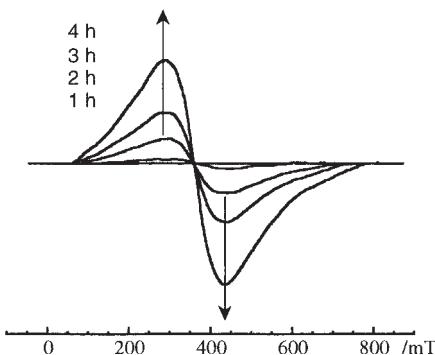


Figure 4. Changes in the ESR spectra of CoTPPS/Mg–Fe LDH accompanied by photoirradiation ( $\lambda > 400$  nm).

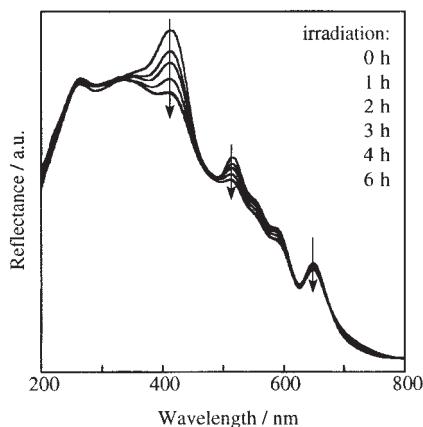


Figure 5. Changes in the absorption spectra of CoTPPS/Mg–Fe LDH by photoirradiation ( $\lambda > 400$  nm).

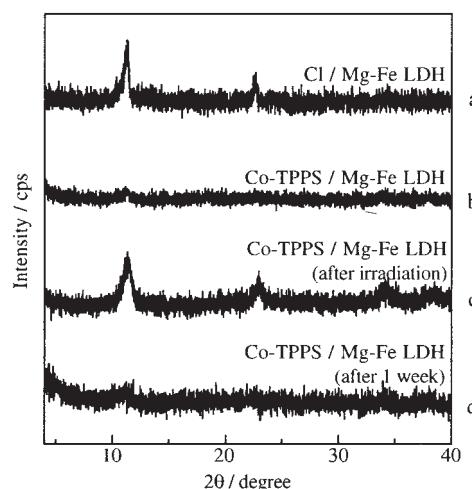


Figure 6. Powder XRD patterns of the CoTPPS/LDH composite: before (a) and after (b) intercalation, after photoirradiation (c), and after one week (d).

the anion-exchange properties in the LDH layers were lost, resulting in the disappearance of the regular laminate structure. The XRD peaks of the basal spacings regenerated by irradiation (c) are due to the reverse electron transfer, which resulted in Fe(III). Moreover, the laminate structure of LDH gradually collapsed within a week's time (d).

Meanwhile, an imbalance in the stoichiometry of the concentrations of the Fe(III) and Co(II) ions could be observed. Such unique redox reactions could be observed only in the case where small amounts of Co(II)TPPS were present in the interlayers, i.e.,  $\text{Co/Fe} < 5\%$ . The redox reactions could, therefore, be reasonably understood by the presence of such other reductants. A great amount of chloride ions still remained unexchanged in the LDH interlayers in the case of low adsorption degrees. Considering the fact that Co(II)TPPS/Mg–Fe LDH with a high intercalation degree did not show such redox reactions, the chloride ions can be considered the most plausible reductant.

In conclusion, anionic porphine, i.e., Co(II)TPPS, could be successfully intercalated into Mg–Fe(III) LDH. The resulting hybrid was then subject to a redox reaction to form Co(III)TPPS/Mg–Fe(II) LDH. A reverse electron transfer was seen to occur by photoirradiation, to yield Co(II)TPPS/Mg–Fe(III) LDH. In this series of redox reactions, a drastic change in the lamellar structure could be observed.

This work was supported by NEDO (New Energy and Industrial Technology Development Organization) and by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan. We would like to express our thanks for their assistance.

#### References

- 1 K. Takagi, T. Shichi, H. Usami, and Y. Sawaki, *J. Am. Chem. Soc.*, **115**, 4339 (1993); T. Shichi, K. Takagi, and Y. Sawaki, *J. Chem. Soc., Chem. Commun.*, **1996**, 2027; T. Shichi, K. Takagi, and Y. Sawaki, *Chem. Lett.*, **1996**, 781; R. Sasaki, N. Shin'ya, T. Shichi, K. Takagi, and K. Gekko, *Langmuir*, **15**, 413 (1999).
- 2 S. Takagi, T. Shimada, T. Yui, and H. Inoue, *Chem. Lett.*, **2001**, 128.
- 3 N. S. Puttaswamy and P. V. Kamath, *J. Mater. Chem.*, **7**, 1941 (1997).
- 4 S. Miyata, *Clays Clay Miner.*, **23**, 369 (1975).
- 5 C. Shi and F. C. Anson, *Inorg. Chem.*, **37**, 1037 (1998).
- 6 W. K. Kuk and Y. D. Huk, *J. Mater. Chem.*, **7**, 1933 (1997).
- 7 I. Y. Park, K. Kuroda, and C. Kato, *Chem. Lett.*, **1989**, 2057.