

Intercalation of Azo Compounds into Layered Aluminium Dihydrogentriphosphate and a Layered Double Hydroxide

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Abstract. The inner surfaces of inorganic layered compounds such as aluminium dihydrogentriphosphate (ADHP) and layered double hydroxide (LDH) were modified by azo compounds. Upon intercalation of 4-phenylazoaniline and 4,4'-azodianiline into ADHP, the interlayer spacing increased from 6.4 to 21.5 Å and 20.6 Å, respectively. The intensity of IR peaks due to P—OH of ADHP and amino groups of guests decreased by the thermal treatment of the intercalates. The interlayer spacings also decreased to 16.9 Å and 16.7 Å, respectively, indicating a dehydration reaction between P—OH and amino groups. The LDH inner surface was modified by the reaction with *trans-p*-phenylazobenzoylchloride (PAB-Cl). Upon surface modification, the interlayer spacing increased from 7.6 Å to about 27 Å. The absorption of this surface-modified LDH near 410 nm increased upon irradiation with UV light and decreased upon irradiation with visible light, indicating the occurrence of *trans-cis* isomerization of PAB-Cl between the layers.

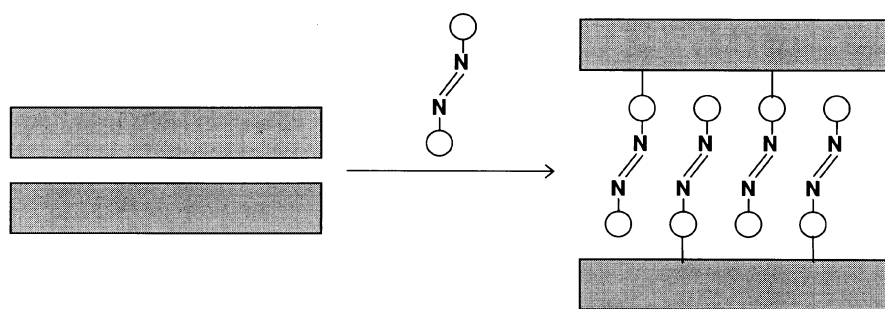
Key words: intercalation, azo compound, surface modification, aluminium dihydrogentriphosphate, layered double hydroxide.

1. Introduction

Chemical surface modifications of inorganic compounds have been extensively studied in order to change their chemical or physical properties in a controlled way [1, 2]. The inner surface of inorganic layered compounds have also been modified by organic compounds [3, 4]. One of the best known layered compounds is zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$ [5]. Zirconium phosphonate surfaces modified by organic compounds are highly resistant to acid and are thermally stable even at 300–400 °C [3]. A variety of surface modified phosphonates have been prepared by the reaction of metal phosphonates with organic compounds [6].

We have already reported that the inner surface of the zinc/aluminium layered double hydroxide (Zn/Al LDH) is modified chemically by the reaction of water treated Zn/Al LDHs with organic oxychlorides [7]. The LDHs are anion exchangeable clays [8–12]. In the present study we have prepared two classes

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Scheme 1.

of surface modified layered compounds. The inner surfaces of layered aluminium dihydrogenphosphate (ADHP) and the Zn/Al LDH were modified by azo compounds as shown in Scheme I. ADHP is a layered compound of composition $H_2M(III)P_3O_{10} \cdot 2H_2O$, where $M(III) = Al, Ga, V, Cr, Mn, \text{ or } Fe$ [13–15]. ADHP can intercalate weak bases such as alkylamines and aniline [16] because it has highly acidic hydroxyl groups with a pK_a of 1.5 [17].

Azobenzenes are characterized by reversible transformations from the stable *trans* form to the less stable *cis* form on irradiation with UV light, which is accompanied by changes in the absorption spectrum [18]. Various azobenzene derivatives have been used as dopants for conventional polymers to form polymer composites, and to change polymer properties [19]. However, surface modification of inorganic layered compounds by azo compounds has been reported only rarely. In this study we have prepared new organic – inorganic hybrid compounds in which the inner surfaces of layered ADHP and LDH are modified by azo compounds. In addition, the absorption spectra of a surface modified Zn/Al LDH film were recorded before and after UV light irradiation

2. Experimental

2.1. SAMPLE PREPARATION

ADHP, $AlH_2P_3O_{10} \cdot 2H_2O$, was prepared by heating phosphoric acid (3 mol) and aluminium hydroxide (1 mol) in a porcelain crucible. A white powder was obtained from the viscous liquid. The powder was heated at 300 °C for 20 h. After washing with distilled water, the powder was dried at 70 °C for 5 h. We could not avoid the production of $Al_4(P_4O_{12})_3$ whose peak was observed at $2\theta = 20.4^\circ$ [20–22]. $Al_4(P_4O_{12})_3$ is stable and does not react with organic compounds.

The Zn/Al LDH was prepared by the reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with $Al(NO_3)_3 \cdot 9H_2O$ in a Na_2CO_3 solution, whose pH was adjusted to ca. 10 with NaOH solution, under a nitrogen atmosphere. The Zn/Al ratio was 0.75/0.25. After filtering, the product was washed several times and dried at 80 °C for 48 h. The obtained carbonate LDH was calcined at 500 °C for 3 h to prepare the Zn/Al oxide

[23]. The water-treated Zn/Al LDH was prepared by the reaction of the Zn/Al oxide in degassed neutral water with stirring under a nitrogen atmosphere [7].

2.2. SURFACE MODIFICATION OF ADHP AND THE LDH

Excess amounts of organic amines such as 4-phenylazoaniline and 4,4'-azodianiline were treated with ADHP in an organic solvent (toluene, acetonitrile or methanol) at ambient temperature to 60 °C and/or under ultrasonic treatment (300 W, 20 kHz) for 24–140 h. Intercalation compounds were obtained and the interlayer spacings of ADHP increased. By thermal treatment of the intercalation compounds from room temperature to temperatures between 200 and 300 °C, the inner surface of the ADHP was modified by the organic compound.

The carbonate Zn/Al LDH did not react with organic oxychloride. The powdered, water-treated Zn/Al LDH was allowed to react with *trans-p*-phenylazobenzoylchloride (PAB-Cl) in acetonitrile for 5 h. The product was filtered and washed with acetonitrile and ether to remove unreacted and physisorbed PAB-Cl. The LDH film was prepared by drawing a glass slide out of a 1% aqueous suspension of the LDH. The film of water treated LDH was also treated with PAB-Cl in acetonitrile.

2.3. CHARACTERIZATION AND OPTICAL PROPERTIES OF THE PRODUCTS

Powder X-ray diffraction spectra were recorded on a Rigaku powder diffractometer unit using $\text{CuK}\alpha$ (filtered) radiation at 40 kV and 20 mA. Thermal analyses (TG/DTA) were carried out on a SEIKO SSC5000 thermal analysis instrument using a heating rate of 10 °C/min in flowing nitrogen. IR measurements of the samples dispersed in KBr disks were performed using a Horiba FT-200 spectrometer.

UV irradiation was carried out using a 400 W high pressure mercury lamp. Visible light irradiation was carried out using a 500 W xenon lamp. Cut-off filters were used, if necessary. Absorption spectra were recorded using a Shimadzu UV-2200A spectrophotometer.

3. Results and Discussion

3.1. INTERCALATION OF AZO COMPOUNDS INTO ADHP

The interlayer spacing of ADHP dihydrate is 8.0 Å [14] as shown in Figure 1(a). The thickness of the ADHP layer is 6.4 Å, therefore, the interlayer spacing increased to 8.0 Å upon hydration. We have already confirmed that the interlayer spacing of ADHP increased to 19.5, 20.0 and 14.4 Å by the intercalation of aniline, *o*-phenylenediamine and *p*-phenylenediamine, respectively [14]. The interlayer spacings indicate the presence of monolayer or bilayer structures between the layers of ADHP [16], depending on the kind of organic compound studied. However 4-phenylazoaniline did not react with ADHP in a solution of toluene and acetonitrile,

Table I. Intercalation of weak bases such as 4-phenylazoaniline and 4,4'-azodianiline into ADHP and their thermal treatment at 250 and 300 °C.

Weak base	Interlayer spacing (Å)	Interlayer expansion (Å)	Interlayer spacing after thermal treatment (Å)
4-Phenylazoaniline	21.5 (0.91) ^a	15.1	250 °C: 16.9 (0.72) ^b
4,4'-Azodianiline	20.6 (0.51) ^a	14.2	300 °C: 16.7 (0.49) ^b
Aniline	19.5	13.1	250 °C: 11.4
<i>o</i> -Phenylenediamine	20.0	13.6	250 °C: 11.5
<i>p</i> -Phenylenediamine	14.4	8.0	250 °C: 14.3

^a Guest/host ratio of intercalation compounds calculated by elemental analyses.

^b Guest/host ratio of intercalation compounds after thermal treatment.

even under ultrasonic irradiation. 4-Phenylazoaniline was intercalated into ADHP by reaction in methanol for 72 h. The interlayer spacing of ADHP increased to 21.5 Å, as shown in Figure 1(b). The guest/host ratio of the product calculated from the elemental analysis was 0.91, as shown in Table I. Since the length of 4-phenylazoaniline is 13–14 Å, a monolayer structure between the layers is suggested.

In the reaction of 4,4'-azodianiline with ADHP in methanol for 140 h, the interlayer spacing increased to 20.6 Å. The guest/host ratio of the intercalation compound was 0.51. The interlayer spacing of the 4,4'-azodianiline intercalate is less than that of the 4-phenylazoaniline intercalate. The size of 4,4'-azodianiline is larger than 4-phenylazoaniline, and it was therefore suggested that strong interaction occurred between two NH₂ groups and P—OH.

We have also confirmed that pyridine could not be intercalated into ADHP, even with the use of ultrasound. The pK_b of pyridine is 8.75 [24] and the basicity of pyridine is greater than that of aniline. The structure of FeH₂P₃O₁₀·H₂O [13] was similar to that of ADHP. It was considered that P—OH was concealed in the plane of the ADHP layer, and therefore pyridine could not interact with P—OH, although the amino group of aniline could.

3.2. THERMAL TREATMENT OF ADHP INTERCALATES

TG analysis of ADHP dihydrate (Figure 2a) shows that water within the interlayer evolves from 70 to 150 °C. The weight loss of 4-phenylazoaniline alone starts near 150 °C and reaches 100%. The weight loss of a 4-phenylazoaniline intercalation compound up to 100 °C reaches 10%, which corresponded to evolution of water. However, the weight loss from 150 °C to 200 °C is small, and the second weight loss begins at 250 °C. The weight loss from 250 °C to 300 °C is not large, and the weight of the intercalation compound was gradually lost at over 300 °C. This also indicates the presence of a strong interaction between ADHP and 4-phenylazoaniline. After

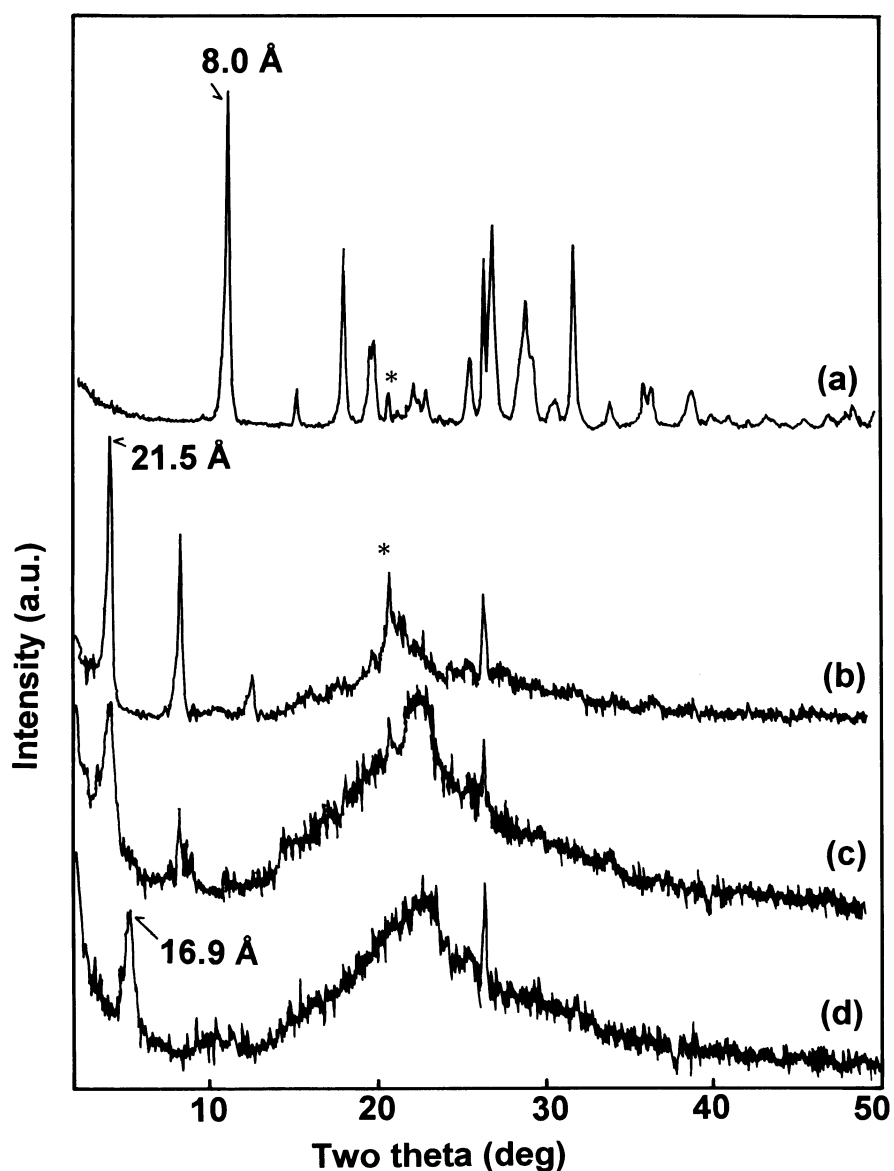


Figure 1. XRD patterns of (a) ADHP, (b) aminoazobenzene intercalated into ADHP, (c) the product after thermal treatment of (b) at 200 °C and (d) the product after thermal treatment of (b) at 250 °C. * Peak is for $Al_4(P_4O_{12})_3$.

thermal treatment of the 4-phenylazoaniline intercalation compound at 200 °C, there was a slight change in interlayer spacing, as shown in Figure 1(c). The presence of the P–OH group was confirmed from an IR spectrum. The interlayer spacing decreased to 16.9 Å after thermal treatment of the intercalate at 250 °C. The

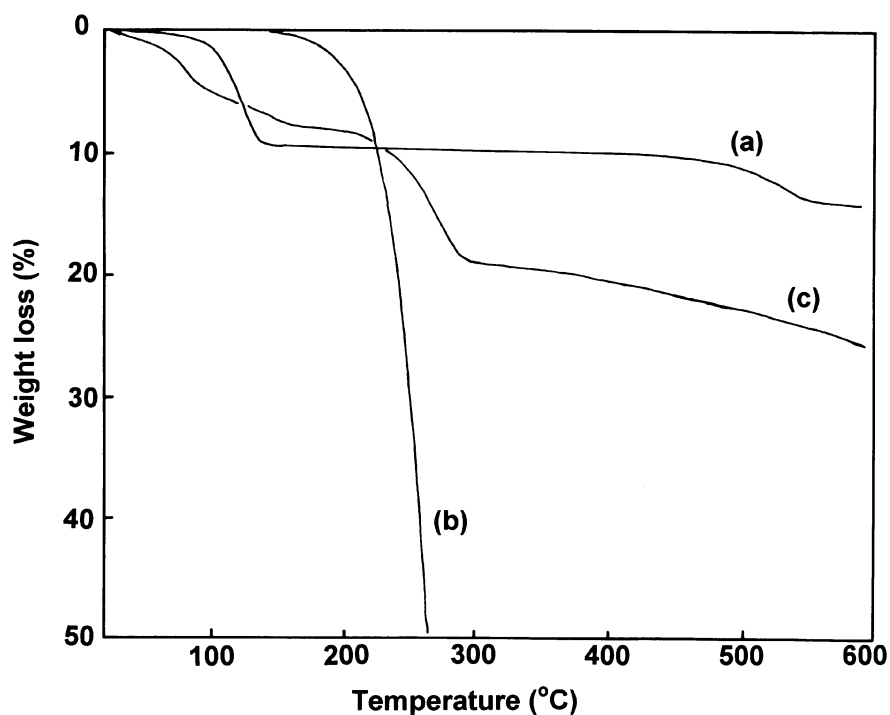


Figure 2. Thermal analysis of (a) ADHP, (b) aminoazobenzene, (c) aminoazobenzene intercalated into ADHP.

guest/host ratio of the 4-phenylazoaniline intercalation compound decreased from 0.91 to 0.72 by thermal treatment at 250 °C, indicating that a small amount of 4-phenylazoaniline was lost. In this study, we have confirmed the similar weight losses and decreases of interlayer spacings in the cases of the aniline, *o*-phenylenediamine, and *p*-phenylenediamine intercalates. In all cases, the absorption peak around 2600 cm^{-1} in the IR spectra disappeared upon intercalation, indicating that a dehydration reaction between P—OH and the amino groups occurred, producing P—N bonds as shown in Figure 3.

A similar dehydration reaction was observed in the case of the 4,4'-azodianiline intercalation compound after thermal treatment at 285–300 °C. The interlayer spacing decreased from 20.6 to 16.7 Å upon thermal treatment. The guest/host ratio of the 4,4'-azodianiline intercalation compound after thermal treatment at 300 °C was 0.49. The value was almost the same as that before thermal treatment, indicating that 4,4'-azodianiline was stable to thermal treatment at 300 °C.

We could not obtain good quality absorption spectra of these surface-modified ADHP materials because reflection spectra of the pressed powders were not clear, and films could not be prepared.

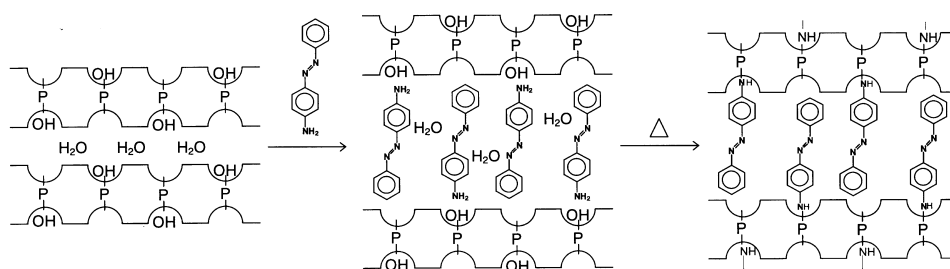


Figure 3. Pictorial representation of the intercalation of aminoazobenzene into ADHP and of surface grafting modification by the dehydration reaction between P—OH and amino groups.

3.3. SURFACE MODIFICATION OF THE LDH BY *trans*-PAB-CL

The interlayer spacing of the water-treated LDH was 7.6 Å. Upon reaction of PAB-Cl with the water-treated LDH in acetonitrile, the interlayer spacing increased to 26.8 Å (Figure 4). *p*-Phenylazobenzoyl carboxylic acid (PAB-COOH) was intercalated into the LDH. The interlayer spacing of the intercalation compound was 19.7 Å. This was clearly different from the interlayer spacing of the reaction product of PAB-Cl with the water-treated LDH. The main IR absorption peaks of the water-treated LDH, PAB-Cl and PAB-COOH were 1360, 1770 and 1680 cm^{-1} , respectively, as shown in Figure 5. The main IR peaks of the PAB-COOH intercalation compound were 1535 and 1394 cm^{-1} , which are typical absorptions of carboxylate anions. The IR peaks of the reaction product of the water treated LDH with PAB-Cl were 1430 and 1660 cm^{-1} . The values were different from those of the intercalation compound. The IR peaks for the reaction product of $\text{Zn}(\text{OH})_2$ with PAB-Cl were 1560 and 1419 cm^{-1} , which are close to the values of the reaction product of the water-treated LDH with PAB-Cl. From these results, it was considered that the reaction products of PAB-Cl with the water-treated LDHs were not intercalation compounds of carboxylate ions, but rather surface-modified LDH as shown in Figure 6. The presence of an absorption peak around 3400 cm^{-1} indicated that unreacted OH groups remained.

The surface area of one HO—Zn—OH unit is 9.6 Å² [25, 26]. The minimum cross-sectional area of PAB-Cl is 14 Å², indicating that less than 65% of the O—H groups could react with PAB-Cl. The composition of the surface-modified LDH was calculated as $\text{Zn}_{0.75}\text{Al}_{0.25}(\text{OH}^-)_{0.25}(\text{OH})_{0.76}(\text{PAB})_{1.24}$ or $\text{Zn}_{0.75}\text{Al}_{0.25}(\text{Cl}^-)_{0.25}(\text{OH})_{0.70}(\text{PAB})_{1.30}$ from elemental analysis, indicating that 62–65% of the O—H groups were modified by PAB-Cl. The value was near to the calculated maximum value.

3.4. OPTICAL PROPERTIES OF THE SURFACE-MODIFIED LDH

The surface-modified LDH film was prepared by the reaction of PAB-Cl with the water-treated LDH film. The absorption spectrum of the surface-modified LDH

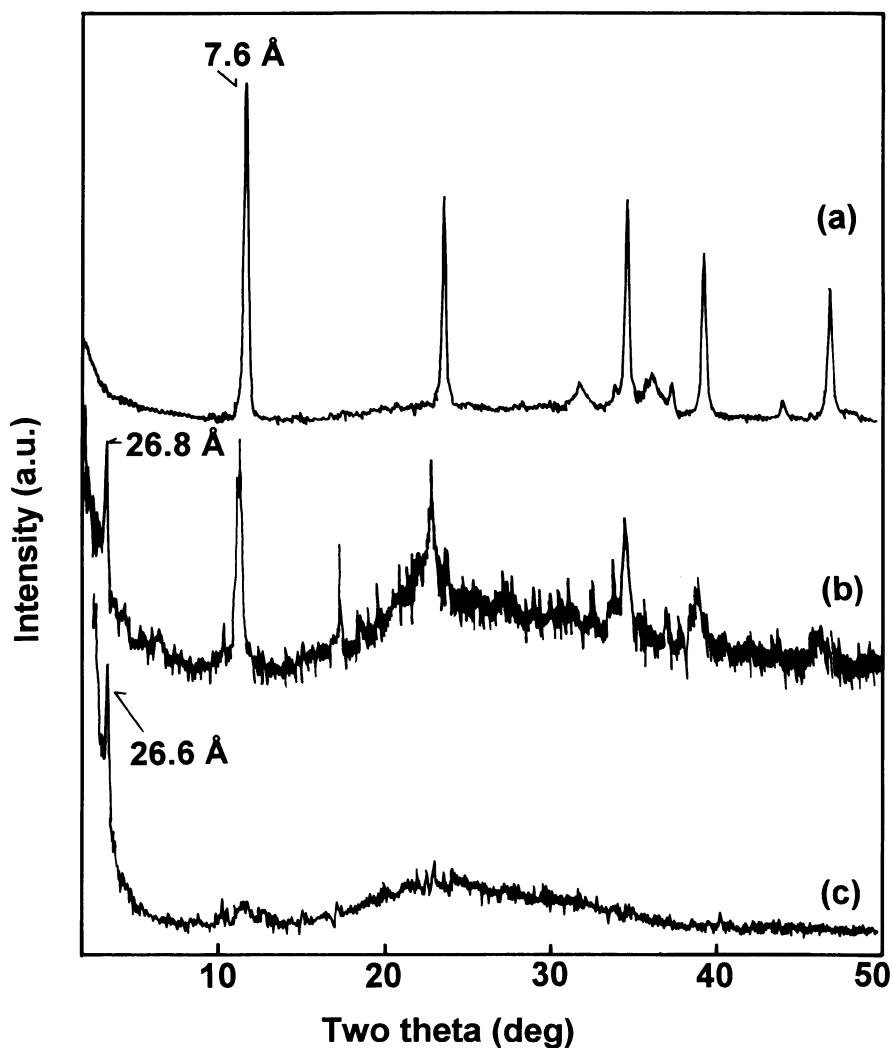


Figure 4. XRD patterns of (a) LDH, (b) the reaction product of PAB-Cl with the LDH powder and (c) the reaction product of PAB-Cl with the LDH thin film.

film was recorded. Two broad absorption peaks were observed at 334 nm and 410 nm. After irradiation with UV light, the absorption near 334 nm decreased in intensity and that near 410 nm increased, as shown in Figure 7. Upon irradiation with visible light, the absorption at 334 nm was stable and the absorption at 410 nm decreased in intensity. Such changes were not observed upon irradiation of either the PAB-Cl film and/or the intercalation compound of PAB-COOH.

We have prepared new organic-inorganic hybrids in which the inner surfaces of layered ADHP and LDH were modified by azo compounds. The reversible absorption change of surface-modified LDH indicates *trans-cis* isomerization of

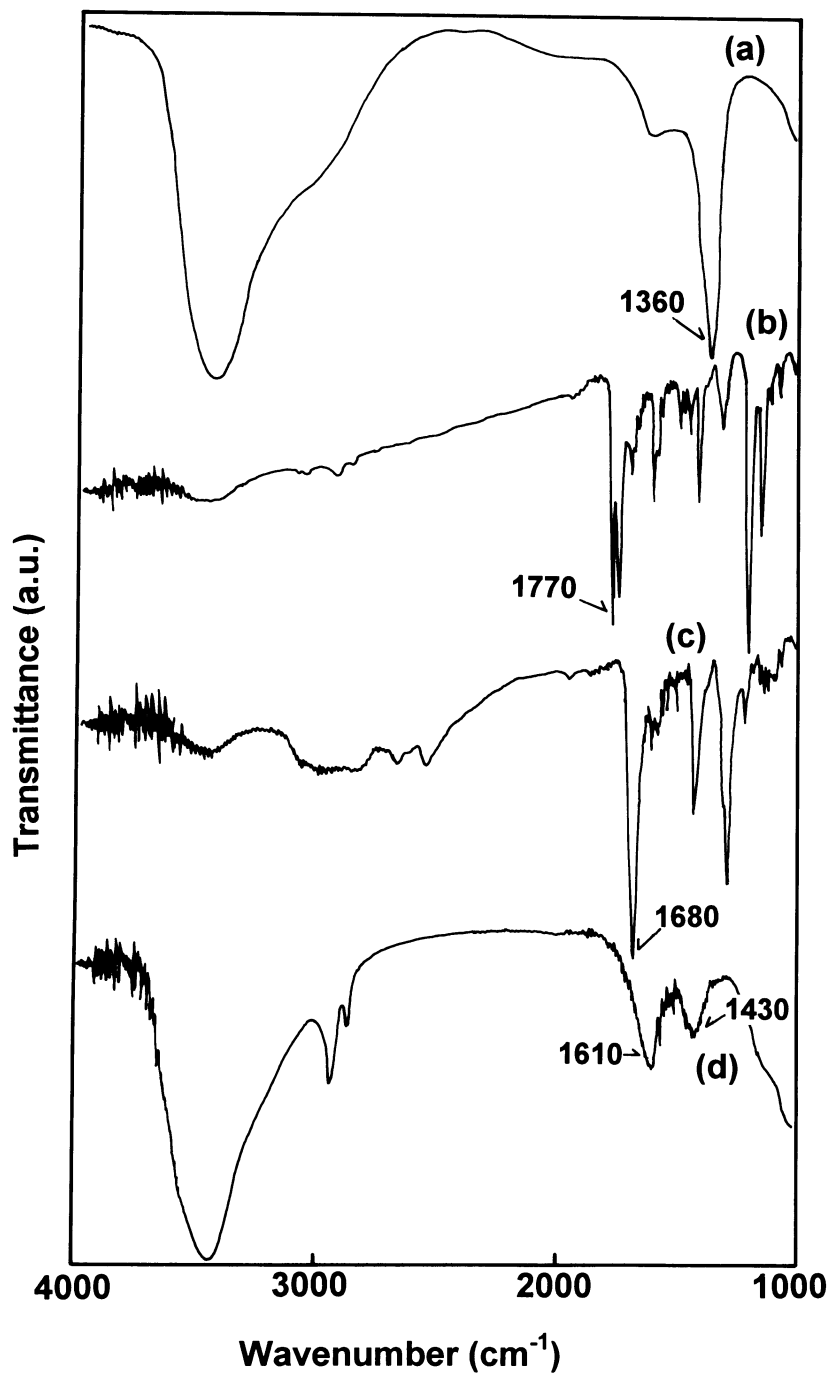


Figure 5. IR spectra of (a) LDH, (b) PAB-Cl, (c) PAB-COOH and (d) the reaction product of PAB-Cl with the LDH thin film.

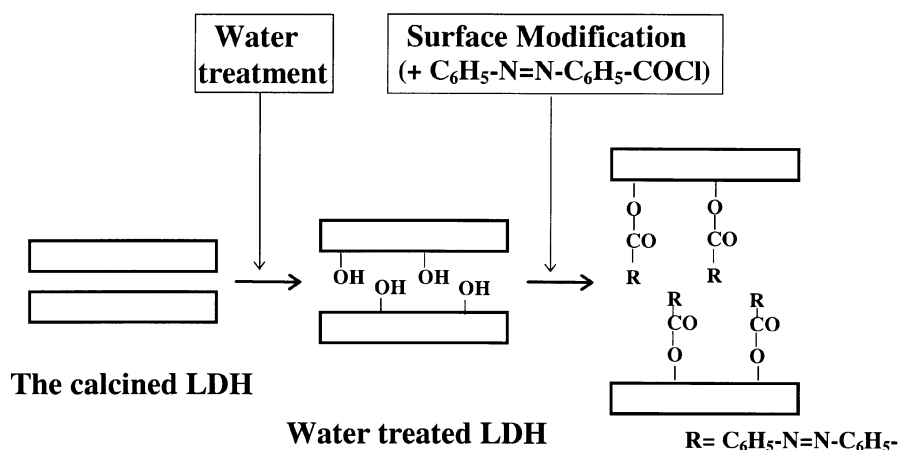


Figure 6. Schematic representation of grafting of the water-treated LDH with organic oxychloride.

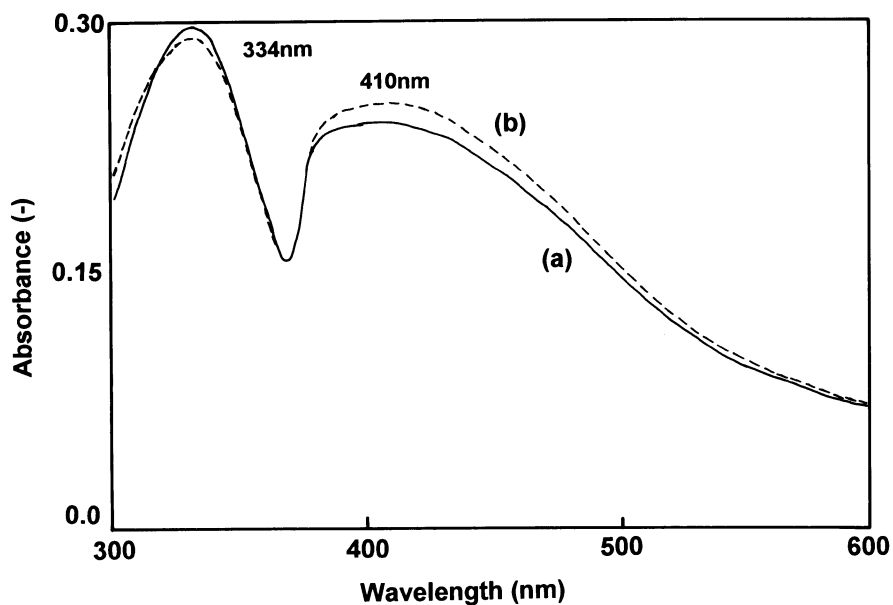


Figure 7. Absorption spectra of (a) the surface modified LDH and (b) the surface modified LDH after UV light irradiation.

the azo compound occurred between the layers. A photomechanical effect has been reported for polymer films with azo-aromatic crosslinks [27]. We have achieved a reversible absorption change, however, no change of XRD patterns was observed after UV and visible light irradiation.

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References

1. J.E. Mark, C.Y.-C. Lee, and P.A. Bianconi (Eds.): *Hybrid Organic-Inorganic Composites*, ACS Symp. Ser. 585, American Chemical Society, Washington D.C. (1995).
2. E.F. Vansant, P. Van der Voort, and K.C. Vrancken (Eds.): *Characterization and Chemical Modification of the Silica Surface*, Elsevier, New York (1995).
3. A. Clearfield: in W.M. Warmuth and R. Schöllhorn (Eds.), *Progress in Intercalation Research*, Kluwer Academic Publishers, Dordrecht, (1994), p. 223.
4. D. O'Hare: in D.W. Bruce and D. O'Hare (Eds.), *Inorganic Intercalation Compounds*, John Wiley & Sons, Chichester (1992), p. 165.
5. G. Alberti, U. Costantino, S. Alluli, and N. Tomassini: *J. Inorg. Nucl. Chem.* **40**, 1113 (1978).
6. M.E. Thompson: *Chem. Mat.* **6**, 1168 (1994).
7. H. Morioka, H. Tagaya, M. Karasu, I. Kadokawa, and K. Chiba: *J. Solid State Chem.* **117**, 337 (1995).
8. H. Tagaya, S. Sato, H. Morioka, J. Kadokawa, M. Karasu and K. Chiba: *Chem. Mat.* **5**, 1431 (1993).
9. H. Tagaya, T. Kuwahara, S. Sato, J. Kadokawa, M. Karasu, and K. Chiba: *J. Mat. Chem.* **3**, 317 (1993).
10. H. Tagaya, S. Sato, T. Kuwahara, J. Kadokawa, M. Karasu, and K. Chiba: *J. Mat. Chem.* **4**, 1907 (1994).
11. H. Tagaya, S. Sato, K. Chiba, K. Takahashi, T. Yokoyama, and M. Endo: *Kagaku Kogaku Ronbunshu* **19**, 923 (1993).
12. T. Kuwahara, H. Tagaya, and K. Chiba: *Micropor. Mat.* **4**, 247 (1995).
13. M. Averbuch and J. Guitel: *Acta Crystallogr.* **B33**, 1613 (1977).
14. V. Lyutsko and A. Selevich: *Russ. J. Inorg. Chem.* **30**, 1023 (1985).
15. V. Lyutsko, M. Nikanovich, K. Lapko, and V. Tikavyi: *Russ. J. Inorg. Chem.* **28**, 1105 (1983).
16. H. Tagaya, S. Sato, N. Kuramoto, J. Kadokawa, M. Karasu, and K. Chiba: *J. Incl. Phenom.* **18**, 193 (1994).
17. M. Tshako, Y. Kawamoto, M. Danjo, Y. Baba, M. Murakami, H. Nariai, and I. Motooka: *Nippon Kagaku Kaishi* 944 (1992). *Chem. Abstr.* 118, 32015e.
18. G. Zimmerman, L.-Y. Chow, and U.-J. Paik: *J. Am. Chem. Soc.* **80**, 3528 (1958).
19. S. Xie, A. Natansohn, and P. Rochon: *Chem. Mat.* **5**, 403 (1993).
20. M. Tshako, K. Hasegawa, T. Matsuo, I. Motooka, and M. Kobayashi: *Bull. Chem. Soc. Jpn.* **48**, 1830 (1975).
21. M. Tshako, K. Hasegawa, T. Matsuo, I. Motooka, and M. Kobayashi: *Chem. Lett.* 573 (1973).
22. M. Tshako, I. Motooka, and M. Kobayashi: *Nippon Kagaku Kaishi* 1028 (1974). *Chem. Abstr.* 81, 71956z.
23. T. Kuwahara, O. Onitsuka, H. Tagaya, J. Kadokawa and K. Chiba: *J. Incl. Phenom.* **18**, 59 (1994).
24. H. Tagaya, K. Takeshi, K. Ara, J. Kadokawa, M. Karasu, and K. Chiba: *Mat. Res. Bull.* **30**, 1161 (1995).
25. G.J. Ross and H. Kodama: *Amer. Mineral.* **52**, 1036 (1967).
26. R. Allmann: *Acta Crystallogr.* **B24**, 972 (1968).
27. C.D. Eisenbach: *Polymer* **21**, 1175 (1980).