Functionalization of layered double hydroxides coating films fabricated via aqueous solution reaction for sol-gel derived films

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Abstract: Layered double hydroxides (LDHs) are inorganic materials consisting of the hydroxide layers formed with at least two metallic elements and anions between the layers. In this study, we have investigated the functionalization of LDH coating films by modification of both sol-gel and aqueous solution processes. A binary oxide system, Al₂O₃-TiO₂, was used for the precursor gel films. Judging from XRD and SEM measurements, LDH crystals were generated for the wide range of gel composition. Therefore, the composite structure with Zn-Al LDH and TiO₂ was obtained by simple process. The reconstruction process, heat treatment and following incubation in aqueous solution, can achieve the intercalation of functional molecules in LDH layers and crystallization of TiO₂ for these composite coatings.

Keywords: Hydrotalcite, Sol-gel method, Aqueous solution process, thin film, LDH

1. INTRODUCTION
Studies on layered double hydroxides(LDHs), known as hydrotalcite-like anionic clays materials, have been conducted over the past several decades since they have many possibilities of the applications for anion exchangers, catalysts, and the immobilization hosts of functional molecules by intercalation into the layers [1-6]. LDHs consist of positively charged brucite-like layers, where a fraction of the divalent cations is replaced by trivalent cations. The positively-charged layers are separated by the charge-balancing anions and water molecules [7]. LDHs have been mainly synthesized as powders and there is only little example for coating film on the substrate [8,9]. Development of the synthetic process of LDH coatings, especially the binder-free process, is expected for the applications of LDHs for optical and electric devices. Recently, Yamaguchi and co-workers have succeeded in the direct immobilization of Zn-Al LDH on substrates by treating Al₂O₃-ZnO amorphous thin films with hot water. We have also developed the direct synthesis technique of LDH coatings which involves aqueous solution reaction of sol-gel derived Al₂O₃ thin films. However, the size of LDH crystals formed in these systems is large enough to cause scattering in the visible light region, and the LDH films is almost opaque. Control of the composition of base gel films should give transparent LDH films, which is favorable to evaluate optical properties of LDH coatings. In present paper, a binary oxide system, Al₂O₃-TiO₂, was employed for the precursor gel films. The effects of the composition of Al₂O₃-TiO₂ on the LDH formation by the reaction with aqueous solutions of zinc acetate were investigated in detail.

2. EXPERIMENTAL SECTION
Al₂O₃-TiO₂ gel films were prepared from aluminum tri-sec-butoxide(Al-(O-sec-Bu)₃), titanium tetrabutoxide (TiO-(nC₄H₉)₄) according to the following procedure. Al-(O-sec-Bu)₃, ethylacetoacetate (EAcAc) and isopropyl alcohol (i-PrOH) were mixed and stirring at room temperature for 1 h. A mixture of Ti(O-nC₄H₉)₄ and ethanol was added to the solution and the resultant mixture was stirring at room temperature for 1 h. Then a mixture of water and i-PrOH was then added dropwise to the solution for hydrolysis and the solution was stirring for 1 h. Molar ratios of Ti versus Al were chosen to be 0:1, 1:5, 1:1 and 5:1. Coating was carried out on glass substrate by dipping with a withdrawing speed of 3 mm/s. The obtained Al₂O₃-TiO₂ gel films were then immersed in aqueous solutions of zinc acetate (1.5×10⁻² M) at 97 °C for 10 min and dried overnight at 50 °C. The reconstruction of LDH was carried out by heat-treatment of the films at 400 °C for 30 min, and subsequent immersion of the films in distilled water at room temperature for 1 h.

Fig. 1. XRD patterns of Al₂O₃-TiO₂ gel films immersed in a zinc acetate aqueous solution. The ratios of Al and Ti in the gel films were 1:0, 1:5, 1:1 and 5:1.
temperature for 30 min.

The surface of coated films were examined by scanning electron microscopy(SEM, Hitachi S-3000N). X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT2100 X-ray diffractometer with Cu Kα radiation. Optical transmission spectra were measured by a JASCO V-570 UV-visible spectrophotometer.

3. RESULTS AND DISCUSSION

Formation of LDH can be confirmed by XRD measurements. Before the immersion in zinc acetate solutions., the Al₂O₃-TiO₂ gel films were amorphous. On the other hand, two typical peaks were observed after immersion in a zinc acetate aqueous solution at 97 °C for 10 min. Figure 1 shows the XRD patterns of the Al₂O₃-TiO₂ gel films with Al/Ti ratios, immersed in a zinc acetate aqueous solution. The peaks were observed at 12° and 23°, which could be assigned to (003) and (006), respectively. It agrees well with the published values for Zn-Al LDH with carbonate anions[9]. The intensity of the peaks changes with the ratio of Al and Ti of the original gel films. Interestingly, the strongest diffraction peaks were observed in the case of the gel film with the atomic ratio Al/Ti unity. The formation of LDHs from gel films consists with dissolution-reprecipitation process. Therefore, the formation rate of LDHs should depend on the dissolution rate of Al ions from gel films.

Figure 2 shows the optical transmission spectra of Al₂O₃-TiO₂ gel films immersed in a zinc acetate aqueous solution. The ratios of Al and Ti in the gel films were 1:0, 1:5, 1:1 and 5:1. The transmission spectrum of glass substrate without coating is also shown for comparison. The transmittance of the coated substrate decreases with an increase in the ratio of Al because of light scattering by LDH crystals formed on the gel films. It is noteworthy that the transparency of the coating films was improved with increase of the TiO₂ contents. When 85TiO₂-15Al₂O₃/2 gel films was employed as precursor the optical transmittance of LDH coating films is higher than...
80 % in the visible range. Thus, almost transparent LDH coatings were achieved.

Figure 3 shows the surface of Al2O3-TiO2 gel films after immersion in a zinc acetate aqueous solution for 10 min.

The surface morphology due to the immersion is different for each composition of the film. The gel films with Al/Ti ratio of 1:0 (a) and 5:1 (b) show reticulation structure after immersion in zinc acetate solutions. It seems that LDH crystals stand perpendicularly on the substrate. On the other hand, the surface morphology of the films with Al/Ti ratio of 1:1 (c) and 1:5 (d) is different from that of the films with Al/Ti ratio of 1:0 (a) and 5:1 (b). The amount of formed LDH after treatment with zinc acetate solution was small and the LDH crystals deposit parallel to the substrates. These results well-corresponds to the results of XRD measurements. In the case of the gel films with Al/Ti ratio of 1:0 and 5:1, no peaks were found in XRD pattern. It is due to the orientation of LDH crystals on the substrate, and does not indicate that LDHs are not formed in these conditions.

In addition, these results indicate that the transparency of LDH coatings depends on the composition of gel films. The deposition amount, the deposition rate, and the deposition morphology are influenced by the Al/Ti composition and cause difference in the transparency of LDH films.

XRD patterns of LDH coating films after reconstruction process are shown in Figure 4. The ratio of Al and Ti in the gel film was fixed to 1:1. When the film was heated at 400 °C, the typical peaks assigned to LDH crystals were disappeared. It indicates that the LDH crystals decomposed by elimination of the interlamellar anions. After the immersion in the distilled water, the peaks restored. It indicates that the LDH crystals were reconstructed by rehydration. In this system, LDH should be formed as the Zn-Al type and the major component of leftover base films after aqueous solution reaction should consist mainly of TiO2. Therefore, the composite structure with Zn-Al LDH and TiO2 was obtained by simple process. The reconstruction process, heat treatment and following incubation in aqueous solution, can achieve the intercalation of functional molecules in LDH layers and crystallization of TiO2 for these composite coatings.

4. CONCLUSIONS

LDH coating on the substrates has been achieved by aqueous solution treatment of sol-gel derived Al2O3-TiO2 gel films with various Al/Ti ratios. Zn-Al LDHs were successfully deposited on the gel films by immersion of gel films into the zinc acetate solution. The transparency of LDH coatings is controllable by changing the ratio of Al/Ti of precursor gel films. In the case of 85TiO2-15AlO3/2 film, the optical transmittance of obtained LDH coating films was higher than 80% in the visible range. When the obtained LDH film was heated at 400 °C, the LDH crystals decomposed. After the immersion in the distilled water, the LDH crystals were reconstructed by rehydration. Therefore, the composite structure with Zn-Al LDH and TiO2 was obtained by simple process. Direct formation of the composite structure with Zn-Al LDH and TiO2 will expand the application fields of LDH.

REFERENCES