Photocatalytic Degradation of Anionic Dye by Zn-substituted Layered Double Hydroxide in Aqueous Solution

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Preparation of layered double hydroxide (LDH) by substituting Zn in the structure was attempted to create an environmentally friendly photocatalyst with anion adsorption capacities. Zn-Al-substituted LDH with different Zn/Al molar ratios of 2, 3, and 4 were synthesized. The behavior of each synthetic Zn-Al LDH in photo-induced degradation of an anionic dye, sulforhodamine B, in aqueous solution was evaluated by determining the ultraviolet-visible absorption spectra under ultraviolet light irradiation. Zn-Al-substituted LDH showed photocatalytic activity toward sulforhodamine B, and degradation of sulforhodamine B was accelerated without stabilization under ultraviolet irradiation. Furthermore, the results suggested that Zn-Al LDH with a high charge density was more effective for continuous photo-induced degradation of sulforhodamine B in aqueous solution compared with Zn-Al LDH with a low layer charge. Zn-Al-substituted LDH should be useful as efficient photocatalysts for harmful organic anions.

Key words: photocatalyst, photodegradation, layered double hydroxide, anionic dye, sulforhodamine B

1. INTRODUCTION

Recently, photocatalytic reactions have received considerable attention as effective and sustainable techniques for purifying water contaminated with various types of contaminant¹. The photocatalytic properties of various materials are well recognized. During photocatalytic reactions, especially in aqueous solution, decomposition of some contaminants is promoted after an adsorption process on the photocatalyst surface. However, some principal photocatalysts, such as TiO₂, ZnO, and CdS, have poor ion-adsorption properties. If such photocatalysts were to have efficient adsorption performance, then decomposition of contaminants would be accelerated.

Layered double hydroxide (LDH) has anion adsorption properties and quite a high anion exchange capacity². LDH is reported in nature, and it is well known in the form of anionic clays. The general formula of LDH is $[M^{2+}_{1-x}M^{3+}_x(\text{OH})_2][A^{n-}_{x/n} \cdot m\text{H}_2\text{O}]$, where M^{2+} represents a divalent metal such as Mg, Mn, Fe, Co, Ni, Cu, or Zn, M^{3+} represents a trivalent metal such as Al, Cr, Mn, Fe, or Co, x is equal to the $M^{3+}/(M^{2+}+M^{3+})$ molar fraction and generally ranges from 0.17 to 0.33, and A is the interlayer anion with a valence of n . The octahedral hydroxide layers of LDH have a positive charge attributed to an isomorphic substitution of M^{2+} for M^{3+} ; therefore, anions are intercalated into the interlayers of LDH to maintain electroneutrality with water molecules. LDH is also easily synthesized in the laboratory. Because various M^{2+} and M^{3+} can be incorporated in the LDH structure, LDH can have

multiple compositions.

LDH is currently attracting a lot of attention as an environmentally friendly material because of its innocuous composition. The anion adsorption properties of LDH have been well documented in numerous studies, and it is currently utilized for water clarification and soil remediation. It is also noted that LDH has catalytic abilities associated with its solid basicity³ or modifications with various polyacids⁴. However, the photocatalytic properties of LDH itself have not yet been fully elucidated. Patzko et al.⁵ evaluated the photocatalytic properties of Zn-Al LDH with ZnO derived by calcination. Valente et al.⁶ and Mantilla et al.⁷ conducted photocatalytic degradation experiments of phenol and/or 2,4 dichlorophenoxyacetic acid by using Mg-Zn-Al LDH and Zn-Al-Fe LDH, respectively. However, the original synthetic LDH was also calcined before the degradation experiments. These studies have therefore not revealed the photocatalytic properties of untreated LDH. Although Seftel et al.⁸ tested photodegradation of a methyl orange dye by an untreated Zn-Al LDH, these samples included a ZnO phase at the synthesis stage. Therefore, the photocatalytic function of uncalcined LDH has not been clearly investigated in previous research.

Previously, we investigated the properties of synthetic Zn-Al LDH in the photo-induced catalysis of a methyl orange dye⁹. The results of an ultraviolet (UV) irradiation experiment indicated that Zn-Al-substituted LDH had methyl orange photocatalytic activity. The irradiation experiment was performed with a dried

sample of Zn-Al LDH, with adsorbed methyl orange applied in a thin layer on a quartz plate.

This study focused on the photodegradation of anionic dye by synthetic Zn-Al LDH particles dispersed in aqueous solution under UV light irradiation. The aim was to examine the photocatalytic activity of uncalcined LDH.

2. EXPERIMENTAL

To minimize the influence of carbon dioxide, synthesis and adsorption experiments were performed under a nitrogen atmosphere and with degassed distilled water. Use of glassware was completely avoided to prevent contamination with silicate ions.

2.1 Synthesis of Zn-Al LDH

Zn-Al-substituted LDH with different Zn/Al molar ratios of 2 (Zn₂-Al LDH), 3 (Zn₃-Al LDH), or 4 (Zn₄-Al LDH), and with chloride anions, was synthesized as follows. An aqueous solution of 200 mL containing ZnCl₂ and AlCl₃ · 6H₂O with a total metal ion concentration of 0.5 mol/L and with a Zn/Al molar ratio of 2, 3, or 4 was continuously added to 50 mL of distilled water in a polypropylene reactor, with vigorous stirring, at room temperature. During co-precipitation in the reactor, the pH was maintained at a constant value of 8 by the simultaneous addition of 1 mol/L NaOH solution. The total volume of the resulting suspension was adjusted to 500 mL with distilled water. Then, the suspension was stirred for 24 h at room temperature to avoid the generation of a ZnO phase. The solid products obtained were filtered and then washed with distilled water, then dried for 48 h with a vacuum freeze drier.

Synthesized materials were characterized as follows. The XRD patterns of the products were determined by using a powder diffractometer (Ultima IV, Rigaku) with graphite monochromatized CuK α radiation (λ = 0.1541 nm) at 40 kV and 30 mA in the 2° to 70° range with a scanning rate of 1°/min. The Zn/Al molar ratios of each synthesized LDH were determined as follows. Precisely 20.0 mg of synthesized LDH was melted with Na₂CO₃ and H₃BO₃ in a platinum crucible. The product was dissolved in HCl solution, and the solution obtained was analyzed for Zn and Al concentrations by using ICP-AES (IRIS Advantage, Nippon Jarrell-Ash).

2.2 Adsorption of anionic dye

Sulfurhodamine B (SRB; C₂₇H₂₉N₂NaO₇S₂ [formula weight: 580.65], Fig. 1) was used as an anionic dye adsorbate. Batch experiments for SRB adsorption onto the Zn-Al LDH were performed. SRB aqueous solution with an initial concentration of 10.0 μ mol/L (pH adjusted to 10 by addition of 0.1 mol/L NaOH) solution was mixed with each Zn-Al LDH in a 40-mL polypropylene centrifuge tube. The concentration of LDH solid was adjusted to 10 mg/L.

Each suspension was dispersed in an ultrasonic bath for 2 min and then placed in a shaker for 24 h at room temperature. The adsorption experiments were conducted under light shielding. The suspensions were then used for the following UV light irradiation experiments.

2.3 UV light irradiation

Fig. 1 Structural formula of sulfurhodamine B.

The suspensions of Zn-Al LDH with adsorbed SRB molecules were transferred to a quartz cell which had a 10-mm light path. They were then irradiated under UV light from an ultrahigh pressure mercury lamp (USH-250SC, Ushio Optical Modulex) for the desired length of time (≤ 300 min). The photodegradation rate of SRB was monitored with an UV-Vis spectrometer (UV-2450, Shimadzu) in the wavelength range of 400 to 700 nm.

3. RESULTS AND DISCUSSION

3.1 Synthesized Zn-Al-substituted LDH

The XRD profiles of synthesized Zn-Al LDH were consistent with that of Zn-Al LDH including chloride ions in the interlayer¹⁰. Zn-Al-substituted LDH phases with different Zn/Al molar ratios were successfully synthesized by the co-precipitation reaction. There were no crystalline byproducts such as ZnO, zinc hydroxide, or aluminum hydroxide in each resultant profile. The d_{003} and d_{006} values of Zn₂-Al LDH were 0.78 nm and 0.39 nm respectively. The d_{003} spacing is equivalent to the thickness of a unit layer. For the pattern obtained for Zn₃-Al LDH, the d_{003} and d_{006} values were the same as those of Zn₂-Al LDH. The profile of Zn₄-Al LDH had d_{003} and d_{006} values of 0.79 nm and 0.39 nm, respectively.

The Zn/Al molar ratios in the synthesized Zn-Al LDH solid phases were calculated to be 1.94, 2.88, and 3.77, corresponding to Zn₂-Al, Zn₃-Al, and Zn₄-Al LDH, respectively. These values were approximately consistent with the compositions of mixed metal solutions prepared in LDH synthesis processes.

3.2 Photodegradation of SRB

The photodegradation of SRB by Zn-Al LDH suspensions transferred to a quartz cell was monitored from the UV-Vis absorption spectra (Fig. 2). Initially, aqueous solutions of SRB only and SRB with Zn-Al LDH showed a clear absorption peak at 565 nm and a shoulder at about 530 nm. The absorbances of SRB without LDH and with Zn-Al LDH were the same when the solutions were left in the dark. These result suggests that Zn-Al LDH had no intrinsic catalytic activity without UV irradiation.

In the case of SRB without LDH (Fig. 2a), the reduction in absorption spectra was obviously slow during UV irradiation. In contrast, the reductions in absorbance of SRB with each Zn-Al LDH were faster than that of SRB without LDH (Fig. 2b, 2c, and 2d). During photodegradation of SRB, the peaks attributed to

Fig. 2 Changes in UV-Vis absorption spectra during UV irradiation of (a) SRB without LDH, (b) SRB with $\text{Zn}_2\text{-Al}$ LDH dispersed particles, (c) SRB with $\text{Zn}_3\text{-Al}$ LDH, and (d) SRB with $\text{Zn}_4\text{-Al}$ LDH.

SRB were slightly shifted toward shorter wavelengths (blue shift).

We examined the wavelength shift of SRB without LDH and with $\text{Zn}_2\text{-Al}$ LDH as a function of irradiation time (Fig. 3). The blue shift in SRB with $\text{Zn}_2\text{-Al}$ LDH was large compared with that of SRB without LDH. This was likely caused by the photo-induced catalytic degradation of SRB by Zn-Al LDH. This hypsochromic shift indicated the occurrence of de-ethylation during the oxidation of SRB. These results were consistent with that of previous research, which was performed in a TiO_2 dispersion system¹¹⁻¹⁴.

We summarized the relative degradation rates of SRB without LDH and with each Zn-Al LDH under UV irradiation (Fig. 4). The degradation rates were determined from reductions in the absorbance of SRB at 565 nm. After 300 min of UV irradiation, the absorbance of SRB without LDH at 565 nm had dropped by 30%. In contrast, the absorption peaks of SRB with each Zn-Al LDH had been reduced by more than half after 300 min of UV irradiation. Furthermore, Zn-Al LDH with a high charge density (e.g. $\text{Zn}_2\text{-Al}$ LDH) was more effective for continuous photo-induced degradation of SRB in aqueous solution compared with Zn-Al LDH with a low layer charge.

Therefore, Zn-Al-substituted LDH had photocatalytic activity for SRB anions in aqueous solution. Zn-Al LDH displayed performance sufficient for SRB decomposition and decolorization. Even though the

Fig. 3 Wavelength shifts of (a) SRB without LDH and (b) SRB with $\text{Zn}_2\text{-Al}$ LDH as a function of UV irradiation time.

organic compounds were intercalated into Zn-Al LDH interlayers, degradation was accelerated without stabilization under UV irradiation.

4. CONCLUSION

Zn-Al-substituted LDH phases were successfully synthesized without any byproducts. The results of UV

irradiation experiments indicated that Zn-Al-substituted LDH had photocatalytic activity toward SRB in aqueous solution, and Zn-Al LDH with a high charge density was the most effective for continuous photo-induced degradation.

Zn-Al LDH has an extremely high anion adsorption capacity and relatively large reactive surfaces, and it is easily synthesized. Additionally, Zn-Al LDH is more stable than ZnO in aqueous solutions owing to the formation of a solid solution with Al. Therefore, Zn-Al-substituted LDH could be utilized as an efficient photocatalyst for the degradation of harmful organic anions in various environments.

Fig. 4 Relative residual rates of (a) SRB without LDH, (b) SRB with Zn₂-Al LDH, (c) SRB with Zn₃-Al LDH, and (d) SRB with Zn₄-Al LDH as a function of UV irradiation time.

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