Hybridization of Metal Nanoparticle of ZnAl Layered Double Hydroxide and its Application for Photocatalyst Phenol Degradation

Putri Rizka LESTARI, Takahiro TAKEI*, Sayaka YANAGIDA and Nobuhiro KUMADA

Center for Crystal Science and Technology, University of Yamanashi, 7-32 Miyamae, Kofu 400-8511, Japan

(Manuscript received March 30, 2018; accepted May 15, 2018)

Abstract

ZnAl LDH has been successfully prepared as single phase by urea as precipitant. Anion exchange is conducted for Ag(CN)₂⁻ intercalation. After the LDH has been intercalated by Ag(CN)₂⁻, the anion is reduced into Ag(0) state. The structure of Ag-intercalated LDH was examined by synchrotron XRD. In the sample, the Ag(0) exists at closer position than center between hydroxide layers due to no coordinated H₂O molecules. UV-vis spectra confirm the existence of surface plasmon resonance at around 380 nm. Finally, the LDH has been examined for its photocatalytic activity by phenol degradation in the aqueous solution with Xe light irradiation. The concentration of phenol is continuously decreased during photocatalyst process by the ZnAl/Ag LDH sample. The degradation rate of the sample is much better than those of the pure LDH and unreduced samples. In this case, phenol solution with the concentration of 20 mg/L can be degraded completely for 120 min.

Keywords: Layered Double Hydroxide, Hybridization, Photocatalyst.

1. Introduction

Phenol and phenol derivatives used as raw materials in petrochemical and chemical industries are considered one of the most common organic water pollutants because of its high toxicity, even at low concentrations. Photocatalytic process attracted attention by the scientific community due to possibility using solar light and the simplicity process which degrades the pollutants to their non-toxic forms. The photocatalytic process occurs as follows: when a semiconductor particle absorbs a photon of energy equal to or greater than the band gap energy width, an electron is promoted from the valence band to the conduction band leaving behind an electron vacancy or hole in the valence band. The hole may react with surface-bound H₂O or HO⁻ producing the OH radicals, which are widely accepted to be the primary oxidizing species in the photocatalytic processes.

Layered double hydroxide (LDH) or hydrotalcite-like materials belong to a class of anionic mineral clays, with structures derived from mineral brucite Mg(OH)₂. When a fraction of M²⁺ ions is substituted by a trivalent ion M³⁺, the positive charge generated on the metal hydroxide slab is compensated by the inclusion of anion generating the general formula: M²⁺₁₋ₓM³⁺ₓ(OH)₂(Aⁿ⁻)ₓ/n·mH₂O. Some LDHs have been reported as good alternative for the photodegradation of pollutants organic compound like pesticide, methyl orange, methylene blue. In particular, the layer structure may improve efficiency of photocatalytic reaction by inducing electron transfer and preventing recombination of electrons.

Plasmonic nanoparticles have attracted significant attention in various fields because of their size and shape tunable optical properties. In contrast to smaller molecules, the surface plasmon oscillation of nanoparticles gives rise to both strong absorption and scattering of the incident light.

This paper reports on the preparation of ZnAl LDH, the optimum condition of preparation such as precipitant and amount of precipitant added, pH and temperature will be...
determined. The intercalation of metal, especially Ag nanoparticles (AgNPs), into the interlayer galleries of mother compound using Ag anionic salt had performed and will be discussed. Finally, the final product of ZnAl LDH intercalated by AgNPs is tested for its photocatalyst application.

2. Experiments

2.1 Materials

Aluminum nitrate enneahydrate (Al(NO₃)₃·9H₂O) with purity of 98% (Kanto Kagaku), distilled water, ethanol, sodium hydroxide (NaOH, 97% Kanto Kagaku), urea (CO(NH₂)₂, 98% Kanto Kagaku), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98% Kanto Kagaku), potassium dicyanoargentate (K[Ag(CN)₂], 95% Kanto Kagaku), ultrapure water, Hydrazine (N₂H₄) were used for reduction of silver to prepare the hybrid.

2.2 Methods

During the preparation process, two kinds of experiments were used to synthesize ZnAl LDH. In these processes, the used precipitants were NaOH and urea. In the case of NaOH, Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were dissolved in 50mL distilled water with the ratio of 3:1. NaOH solution with concentration of 5 M was added into the Zn-Al solution until the pH solution reached to 9, then the flask’s cap were all closed and the temperature was increased up to 80 °C. The mixture was continuously stirred and kept under the reflux condition for 48 h. After 48 h, the process was stopped. The resulting precipitant then was filtered and washed three times by deionized water and once by ethanol. Finally, it was dried at 50°C for 24 h.

In the case of urea (CO(NH₂)₂), into the Zn-Al mixed solution, urea solution were added at several molar ratio (Zn:Al:urea molar ratio = 3:1:2, 3:1:3 and 3:1:4) The solution was refluxed with stirring for 48 h at 80 °C. The resulting precipitant was filtered and washed 3 times by distilled water and once by ethanol. The powder was dried at 50 °C for over a night.

Anion exchange to Cl⁻ for the ZnAl LDH was performed since the prepared ZnAl LDH may contain CO₃²⁻ as an anion presence in the interlayer galleries of LDH. The process is necessary to perform due to the stability of CO₃²⁻ in the LDH material. Into 250 mL solution containing NaCl, CH₃COONa and CH₃COOH, 2.5 mg LDH sample was added. The mixture then was shaken at room temperature for 48 h. The precipitant was filter and washed three times by ultrapure water and once by ethanol. The samples were dried in vacuum oven in room temperature for overnight.

Intercalation of Ag(CN)₂⁻ by direct anion exchange was performed as follows. Several amount of molar ratio (LDH:Ag molar ratio = 1:2, 1:3 and 1:4) of K[Ag(CN)₂] was dissolved in 25mL ultrapure water. After completely dissolved, 0.5 g of LDH which has been anion-exchanged by Cl anion is added into the solution. The mixture was then shaken at 200 rpm at room temperature for 48h. The resulting precipitant was collected by suction filtration. During filtration, the samples were washed three times by ultrapure water and once by ethanol. The samples were then dried in vacuum oven at room temperature for overnight.

Reduction process was conducted by addition of 0.25 g ZnAl LDH/Ag(CN)₂ sample into 25mL of ultrapure water, and then 1.5 mL hydrazine solution was added into the mixture. The mixture was kept in continuous stirring at 200 rpm at room temperature for 48 h. The resultant sample was filtered by vacuum filtration. During the filtration process, the collected samples was washed three times by ultrapure water and once by ethanol. The ZnAl LDH/Ag then was dried in vacuum oven for 24 h at room temperature.

2.3 Characterization

The structure of LDH samples were characterized by powder X-ray diffraction (XRD) using rigaku RINT 2000 with Cu-Kα radiation (λ = 1.5406 Å), FTIR (JASCO FT/IR-4100), XPS Shimadzu (Axis-ultra-DLD), UV-Vis Spectrophotometer (JASCO V-550). The crystal structure was also examined by synchrotron X-ray Diffraction (SXRD) in BL02B2 (SPring-8) with λ = 0.799379 Å.

2.4 Photocatalysis Experiment

Photocatalytic phenol degradation was evaluated by high performance liquid chromatography (HPLC with C18 column). For considering practical application, 300W Xe lamp (PE 300BF, Excellitas Tech.) was used as the irradiation source. In the beginning, 20 mg/L phenol solution was prepared using ultrapure water, then the LDH sample was dispersed into the phenol solution at concentration of 3 g/L. The solution stirred at dark condition for 60 minutes to achieve balance of phenol. After 60 minutes stirring, the solution was irradiated using 300W Xe lamp. While irradiation, 0.5 mL of the solution was extracted from the solution at 30, 60, 90, 120, 150, 180, 210 and 240 min on the elapsed time.

3. Results and Discussion

Figure 1 shows XRD patterns of prepared ZnAl LDH by NaOH or urea with different amount. These patterns explain that ZnAl LDH has been successfully prepared by NaOH and urea as precipitants. The XRD patterns of all materials showed the characteristic reflection of the planes (003) (006) (012) (015) and (018) which are characteristic of typical ZnAl layered double hydroxide (LDH).

As observed by XRD pattern, LDH prepared by NaOH could not attain single phase pattern. Several peaks corresponding to ZnO has been observed as showed in Fig. 1. Consequently, the peaks occurring at 31.6, 34.4 and 36.2 in 2θ are the peaks attributed to ZnO. On the other hand, by using urea, the LDH peaks can be observed as a single phase. The basal reflection attribute to 003 plane was appeared at 11.5 in 2θ. The peak shift which observed from the patterns results from the difference of...
anion presence in the LDH material. NO$_3^-$ anion and water molecule had intercalated during the preparation by NaOH. On the other hand, HCO$_3^-$ anion had produced by urea since urea tends to form HCO$_3^-$ or CO$_3^{2-}$ anion by self-decomposition. In the case of urea, during the synthesis process, the pH of the solution tended to increase and became more basic. Because the pH of all samples after 48 h heated are about 6, the anion mostly intercalated in the interlayer is HCO$_3^-$. From this consideration, LDH by NaOH may have NO$_3^-$ and by urea has HCO$_3^-$ within the interlayer space.

After the anion exchange, the characteristic reflections of the LDH (003) (006) (012) (015) and (018) are still able to be maintained as it showed in Fig. 2. In terms of position 2θ, notable peak shift could not be observed. Peak shift is generally one of the indicator if the anion successfully exchanged. The shift which directly attributes to interlayer size changes may be able to be observed if Ag(CN)$_2^-$ is present in the interlayer space. However, the molecular shape of Ag(CN)$_2^-$ is linear and thin. Therefore, intercalated LDH with Ag(CN)$_2^-$ may be difficult to distinguish.

At a glance, for ion exchanged samples and reduced samples, we pay attention to the increase of intensity ratio of (012) or (003). Such relative strong intensity of (012) or (003) may indicate deviation of electron within the interlayer space by intercalation of other species. Therefore, we analyze the structure of the reduced sample by SXRD in SPring-8. Figure 3 shows SXRD pattern of 1:2 ZnAl LDH/Ag analyzed by RietanFP and schematic illustration of the unit cell refined by the Rietveld process. In the process, Ag(CN)$_2^-$ was presumed to be reduced to Ag(0) and CO$_3^{2-}$ was to be intercalated for charge compensation. By this analysis $R_{wp}$ and $R_e$ values are 4.56% and 1.24%, respectively. From the analysis, Ag exists slightly close position to the hydroxide layer. As showed in the figure, the refined results can be a collateral evidence for existence of Ag within the interlayer space. The ratio of Ag on ZnAl LDH phase is estimated to around 0.14 molar ratio. Consequently, chemical formula can be expressed as Zn$_{0.75}$Al$_{0.25}$(OH)$_2$(CO$_3$)$_{0.13}$Ag$_{0.14}$·0.47H$_2$O for the reduced sample. By the Rietveld refinement, we confirmed that 3 phases included in the sample are LDH, Ag and ZnO. Each phase was present in molar ratio 90%, 6% and 4% respectively.

The FTIR spectra of ZnAl LDH was showed in Fig. 4. All the prepared samples exhibit a broad vibration at 3300-3600 cm$^{-1}$ attributed to the stretching vibration of OH groups belong to water molecule and hydroxyl group in the interlayer gallery. The vibration bands at 1366 cm$^{-1}$ appearing in ZnAl LDH, ZnAl LDH/Ag(CN)$_2$ and ZnAl LDH/Ag can be assigned to $v_3$ stretching of the HCO$_3^-$ and CO$_3^{2-}$ anion of the interlayer in a symmetric environment. In the case of ZnAl LDH/Ag(CN)$_2$, the vibration of C-N can be observed at 2183 cm$^{-1}$. The presence of C-N can be regarded as one of the evidence that Ag(CN)$_2^-$ has been hybridized into LDH sample. After the reduction
The absorption at around 380 nm may indicate the existence of Ag nanoparticle, known as a surface plasmon resonance (SPR) caused by the collective oscillation when silver nanoparticle was excited by specific light wavelength. Meanwhile other LDH materials show absorption at less than 330 nm. The absorption around 300 nm may imply the absorption of CN group. The lowest absorption is belonging to ZnAl LDH/Cl which has none Ag intercalated in the structure. In this spectrum, the absorption band emerges at 300 nm which have been reported in the other literature showing ZnAl LDH and its hybrids.

In Fig. 5b, Tauc plots of LDHs materials by assuming indirect transition were showed. In the case of the plot calculated by direct transition, as the curves have a short linear region, the absorption can be regarded as indirect transition. The estimated energy absorption of ZnAl LDH/Cl, ZnAl LDH/Ag(CN)₂, and ZnAl LDH/Ag are consequently 4.9, 4.0 and 3.1 eV. These energy absorptions imply that the SPR may show the shrinkage of the apparent optical band gap.

The chemical state of Ag was examined by XPS. Figure 6 shows XPS spectra of Ag 3d in ZnAl LDH/Ag(CN)₂ and ZnAl LDH/Ag. In the case of ZnAl LDH/Ag(CN)₂, the binding energy for 3d₅/₂ and 3d₇/₂ appear at 374.8 and 368.9 eV. These energies are attributed to Ag cation, as the Ag carries positive charge in Ag(CN)₂⁻. After reduction process, the peaks have been split into two peaks, which represent the existence of Ag cation and Ag neutral. The Ag 3d₅/₂ binding energy at around 369.2 eV is attributed to Ag cation, and the energy at around 367.8 eV is attributed to Ag neutral. This results support the probability of the successful hybridization process.

Figure 7 described the relationship between the elapsed times and the concentration of phenol by ZnAl LDH/Cl, ZnAl LDH/Ag(CN)₂, and ZnAl LDH/Ag. From the figure, in the dark circumstance, all of the LDH materials almost did not performed photocatalytic activity as the amount of phenol did

Fig. 4 FTIR spectra of prepared LDH, anion exchanged with Cl and followed by anion exchange by different amount of Ag(CN)₂ and reduced by hydrazine.

Fig. 5 (a) UV-Vis absorption spectra of ZnAl LDH/DS, ZnAl LDH/Ag(CN)₂ and ZnAl LDH/Ag; (b) Tauc plot of ZnAl LDH/DS, ZnAl LDH/Ag(CN)₂ and ZnAl LDH/Ag.

Fig. 6 XPS spectra of ZnAl LDH/Ag(CN)₂ and ZnAl LDH/Ag.
not show a significant decrease. Under irradiation, ZnAl LDH/Ag shows the highest photocatalytic activity compared to the other LDH materials. This activity proves the existence of SPR effect during the photocatalytic reaction as follows. The contribution of Ag nanoparticle in the LDH material is a much important factor of the photocatalytic reaction for the sample. The light irradiated filtered with 380 nm short cut filter and the largest energy was around 3.26 eV. Therefore, base material of ZnAl-LDH cannot show the photocatalytic activity because of the larger bandgap estimated from the Tauc plot in Fig. 5. For the hybrid ZnAl LDH/Ag, on the other hand, the light with shorter wavelength of round 390 nm can be absorbed by the SPR. Under irradiation, the plasmon-induced photoexcited electrons of the Ag nanoparticle in the ZnAl LDH/Ag move into the CB of LDH and then the electrons in the CB of LDH can produce superoxide radicals. Not only hole produced by excitation of photoelectron but the superoxide radical can be used for the degradation of phenol. In addition, the presence of Ag nanoparticle that serve as a trapping center to capture electron generated from the irradiation for the effective separation of the photogenerated hole-electron pairs, causing a better photocatalyst reaction.

4. Conclusion

In this work, it has been reported that ZnAl LDH has been successfully prepared by hydrolysis with urea. XRD patterns has confirmed that the single phase of ZnAl LDH has been attained. The hybridization of silver nanoparticle into interlayer galleries of LDH has been attempted. Anion exchange method has been conducted for hybridization of Ag nanoparticle. Tauc-plot inform that the intercalation of Ag nanoparticle leads to the shrinkage of band gap of LDH material. The existence of surface plasmon resonance also can be observed by UV-Vis absorption.

All the LDH samples has been tested for photocatalytic phenol degradation. The results show all the materials performed photocatalyst activity, however, ZnAl LDH/Ag showed the highest performance as the phenol concentration could rapidly decreased. This activity could be an indication that the SPR effect helps the photocatalyst reaction.

Acknowledgement

The Experiments at SPring-8 were performed with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal 2016B1510).

References