Formation of cobalt clusters in Layered Double Hydroxide

Hitoshi INOKAWA¹,², Koji OKAMOTÓ², Aishah Binti MAHPUDZ¹, Yoshiro OHGI³, Ryuichi TOMOSHIGE¹,² and Katsuki KUSAKABE¹,²

¹Division of Applied Chemistry, Graduate School of Engineering, Sojo University, 4–22–1 Ikeda, Nishi-ku, Kumamoto 860–0082, Japan
²Department of Nanoscience, Faculty of Engineering, Sojo University, 4–22–1 Ikeda, Nishi-ku, Kumamoto 860–0082, Japan
³Kumamoto Industrial Research Institute, 3–11–38 Higashimachi, Higashi-ku, Kumamoto 862–0901, Japan

Cobalt metal clusters were synthesized in interlayers of Layered Double Hydroxide (LDH) composed of magnesium and aluminum. Chelate type complex, which is Co-citrate, was used as a precursor of the cluster and intercalated into the interlayer of LDH by ion exchange method. A structural characterization using XRD, IR, TEM-STEM-EELS and nitrogen adsorption/desorption isotherm revealed that Co-citrate was successfully inserted and reduced in the interlayer. Co clusters smaller than 5 nm were formed and catalyzed a hydrolysis reaction of sodium borohydride, resulting in hydrogen generation.

Key-words : Catalyst, Metal cluster, Nano particle, Layered Double Hydroxide, Hydrogen Energy

1. Introduction

Layered Double Hydroxides (LDHs) are composed of positively charged nanosheets and balancing anions in the interlayer, and have been widely investigated for their structural and/or functional applications.¹⁻³ One area of structural applications is the intercalation of organic or inorganic materials into the LDHs' interlayer.⁴⁻¹⁰ In particular, when a large material is intercalated, the guest material can expand the interlayer as a pillar.⁹,¹¹ Most of the previous investigations on the pillaring with inorganic materials are relevant to oxide pillars, particularly polyoxometalates (POMs).⁷⁻⁹ Alternatively, another challenge is to create pillars with metal nanoparticles/clusters. Anions including noble metals can be intercalated into the interlayer of LDHs. Kameshima et al. reported that Pt nanoparticles can be formed via the intercalation of [PtCl₄]²⁻ into MgAl-LDH and calcination at an air temperature of 500°C.¹² However, the reports regarding the metal pillars are very few and the kinds of elements composing the pillars are also limited. Because metal nanoparticles of transition metals such as Fe, Co, and Ni have been widely used for catalytic reactions,⁴,₁³,₁⁴ it can be considered that diversifying the elements of pillars will contribute to the future development of catalysis.

In this study, we investigate a new synthesis process of metal clusters in interlayers of MgAl-LDH without transforming the crystal structure of the LDH. Because cobalt is normally a cation in aqueous solutions, it cannot be inserted into the interlayer of LDH by a conventional ion exchange process. After forming an anionic chelate complex, such as Co(II)-citrate, the Co containing complex can be intercalated into the LDH interlayers. We report the synthesis process of the metallic cobalt clusters in the interlayer of MgAl-LDH and the structural characterization results. Because cobalt is a promising catalyst for hydrolysis reaction of sodium borohydride [NaBH₄, as shown in Eq. (1)],¹⁴⁻²² resulting in H₂ generation, catalytic performance of the synthesized Co cluster is also reported.

NaBH₄ + 2H₂O → H₂ + NaBO₂  

2. Experimental section

2.1 Materials

All chemicals were purchased from companies and used without any purification. A list of the chemicals are shown as follows: sodium nitrate (NaNO₃, 99.0 %, Kanto Chemical CO., INC., Japan), magnesium nitrate hexahydrate [Mg(NO₃)₂·6H₂O, 99.0 %, Kanto Chemical CO., INC., Japan], aluminum nitrate nonahydrate [Al(NO₃)₃·9H₂O, 98.0 %, Kanto Chemical CO., INC., Japan], cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O, 98.0 %, Kanto Chemical CO., INC., Japan], sodium hydroxide (NaOH, 97.0 %, Kanto Chemical CO., INC., Japan), citric acid (C₆H₈O₇·H₂O, 99.5 %, Kanto Chemical CO., INC., Japan) and sodium borohydride (NaBH₄, 98.0 %, Kanto Chemical CO., INC., Japan).

2.2 Catalyst preparation

An LDH composed of Mg, Al and NO₃⁻ was prepared by a conventional co-precipitation method. A mixed
nitrate salts’ solution of Mg and Al was prepared by dissolving their salts into deionized water. The concentrations of Mg and Al were 0.66 and 0.33 mol/L, respectively. The mixed nitrate salt solution was dropped into 1.25 M sodium nitrate solution at 50 °C. The pH of the solution was maintained at 10 by dropping 2.0 M sodium hydroxide solution. A white precipitation was generated and collected via filtering, washing with deionized water and drying. The whitish powder is labeled as NO3-LDH.

0.6 mmol of cobalt(II) nitrate hexahydrate and 0.6 mmol of citric acid was dissolved in 150 ml of deionized water, resulting in 4.0 mM Co-citrate solution. 1.0 M sodium hydroxide solution was added into the solution in order to adjust its pH to 9. 1.0 g of NO3-LDH was added to the solution and stirred at 50 °C for 12 h. A pink powder, labeled as IonEx(Co)-LDH, was obtained after filtering and washing with deionized water.

1.0 g of IonEx(Co)-LDH was immediately transferred into a sodium borohydride solution, which was prepared by dissolving 5.0 g of NaBH4 into 50 ml of deionized water, at 50 °C in order to reduce Co species to metal. Hydrogen was generated via exothermic reaction during the reduction process, resulting in the increasing temperature of the suspension. After a while, the gas generation resulted in vigorous bubbling and ended. A black powder labeled as Co-LDH was obtained after filtering, washing with deionized water, and drying at 60 °C overnight. All synthesis processes, which are precipitation of NO3-LDH, ion exchange process to intercalate Co-citrate complex and the reduction process of IonEx(Co)-LDH, were carried out with nitrogen flushing in the flasks in order to avoid contamination of CO2 from the ambient air. The deionized water was degassed by an aspirator in order to remove CO2 from the water before its use.

2.3 Structural characterization

The crystal structure was characterized by X-ray Diffraction (XRD; Smartlab, Rigaku, Japan). Anions in LDH were characterized by Attenuated Total Reflection Infrared Spectroscopy (IR; Spectrum 100 FT-IR Spectrometer, PerkinElmer, U.S.A.). The microstructure, which is the shape and size of clusters in nanometer scale, was observed by Transmission Electron Microscope (TEM; Titan Themis200, FEI, U.S.A.) equipped with Electron Energy Loss Spectroscopy (EELS; Gatan, U.S.A.). For the TEM observation and the EELS analysis, Co-LDH obtained by a reduction of Co(NO3)2 by NaBH4 solution was collected by a vacuum condition in order to remove adsorbates from the samples before starting N2 adsorption measurement. In order to estimate Co content in the samples, Co-LDH was dissolved into nitric acid, and the concentration of Co in the acidic solution was analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; iCAP6600 series, Thermo Fisher Scientific, U.S.A.).

2.4 Catalytic performance examination

A catalyst of 100 mg was added into 10 g of an aqueous solution in a flask containing 5 mass% sodium borohydride and 5 mass% sodium hydroxide. The flask was placed in a water bath at 25 °C. The amount of generated hydrogen was measured by water replacement method.22,23) The catalytic activity of cobalt metal powder, which was purchased from the Nilaco Corporation (Japan), was also measured as a reference under the same situation. A blank experiment, that is only sodium borohydride and sodium hydroxide aqueous solution without catalyst, was performed as well.

3. Results and discussion

3.1 Structural characterization

A typical XRD pattern of LDHs was obtained as shown in Fig. 1(a). Peaks at 10 and 20° were assigned to (0 0 3) and (0 0 6) of MgAl-LDH with nitrate anion, respectively, according to a reference.24 After the ion exchange process with the Co-citrate solution, the peak of (0 0 3) shifted to

![Fig. 1. XRD patterns of (a) NO3-LDH, (b) IonEx(Co)-LDH, (c) Co-LDH and (d) reference pattern of Mg0.67Al0.33(OH)2-(CO3)0.165(H2O)0.48 with PDF#01-089-5434.](image-url)
a lower angle, meaning that basal spacing of the LDH had expanded from 8.94 to 12.24 Å. This peak shifting indicates successful intercalation of Co-citrate anion into the interlayer of LDH. After the reduction with sodium borohydride, XRD pattern of Co-LDH was corresponding to one of MgAl-LDH with carbonate anion in the interlayer as shown in Fig. 1(d). If Co clusters were formed in the interlayer of LDH and the distance of the layers was expanded, peaks assigned to (0 0 l), e.g. (0 0 3) and (0 0 6), must have shifted to a lower angle on the Fig. 1(c). However, we could not confirm the shift of the peaks derived from basal spacing.

Intercalation and decomposition of Co-citrate was investigated by IR as shown in Fig. 2. The IR spectrum of NO$_3$-LDH [Fig. 2(a)] shows a large peak at 1347 cm$^{-1}$ assigned to NO$_3^-$

After the ion exchange process, the peak of NO$_3^-$ decreased and another peak assigned to COO$^-$ appeared at 1564 cm$^{-1}$, as shown in Fig. 2(b). This change on IR spectra suggests that NO$_3^-$ was exchanged with Co-citrate complex. After the reduction process, the peak of COO$^-$ disappeared, as shown in Fig. 2(c), and a peak assigned to CO$_3^{2-}$ was observed at 1360 cm$^{-1}$. Carbonate anion can be generated by the decomposition of citrate during the reduction process. Regarding the successful reduction of Co species, we found that IonEx(Co)-LDH must be immediately transferred into the sodium borohydride solution after collection from the Co-citrate aqueous solution. The exposure time of IonEx(Co)-LDH to the ambient air should be as short as possible. According to our IR results (not shown in Fig. 2), Co-citrate was not decomposed by the reduction treatment after drying the IonEx(Co)-LDH in the air.

TEM observation revealed that Co clusters were formed as shown in Fig. 3 with blackish contrast [shown by the white arrows in Fig. 3(a)]. The size of the clusters seems to be mainly 2–4 nm in diameter, but even smaller particles were also found. High-Resolution (HR) TEM of Co cluster with diameter of 2.5 nm showed bright and dark stripe image corresponding to the lattice spacing. Fast Fourier Transformation (FFT) image of the Co cluster [Fig. 3(c)] revealed that the d spacing of the stripe was estimated 0.205 nm, which are corresponding to (0 0 2) of hexagonal cobalt with d$_{002}$ = 0.202 nm or (1 1 1) of cubic cobalt with d$_{111}$ = 0.205 nm.

In order to confirm the chemical state of the cobalt clusters, EELS profile of the cobalt cluster in Fig. 3(b) was compared with those of reference materials, which were Co metal powder, CoO, Co$_3$O$_4$ and Co(OH)$_2$, as shown in Fig. 4. Energy Loss Near Edge Structure (ELNES) shows L$_3$ and L$_2$ edges at 779 and 794 eV, respectively. The L$_3$ and L$_2$ edges are corresponding to excitation of electrons from 2p$_{3/2}$ to 3d and from 2p$_{1/2}$ to 3d, and the ratio of L$_3$ and L$_2$ (L$_3$/L$_2$) is related to chemical state of the element. After subtraction of background from the EELS spectra, the ratios of L$_3$/L$_2$ of the Co-LDH and reference materials were calculated from integrated intensities of L$_3$ and L$_2$. The L$_3$/L$_2$ ratios of Co-LDH, Co metal powder (Co$^0$), CoO (Co$^{2+}$), Co$_3$O$_4$ (Co$^{2+}$ and Co$^{3+}$)
were 1.23, 1.29, 2.11, 1.72 and 1.63, respectively. The L3/L2 ratio of metallic Co was significantly lower than those of divalent or trivalent Co ions, and the value was quite close to that of Co-LDH. Xin et al. reported that metallic Co has lower L3/L2 value than CoO.26) According to a report by Wang et al., the L3/L2 ratio of Co3O4 was lower than CoO. 27) The L3/L2 ratios of reference materials obtained in this study are in good agreement with the trend of L3/L2 ratios reported by other scientists. In addition to the ELNES analysis, Extended electron Energy Loss Fine Structure (EELFS) was also analyzed by comparing shapes of EELS spectra among the Co-LDH and reference materials at higher energy loss range than L2 edge. Their spectra showed different behavior from 805 to 900 eV as shown in Fig. 4. In the above range, the EELS profile of Co cluster in Co-LDH [Fig. 4(a), shown as black] was flat and quite similar to one of Co metal powder [Fig. 4(c), shown as red], whereas other materials, CoO, Co3O4 and Co(OH)2, has broad peaks. The both ELNES and EELFS strongly suggest that chemical state of the Co species in Co-LDH is metallic state. This is consistent with the results of HR-TEM [Fig. 3(b)] and FFT [Fig. 3(c)]. From the above results, it can be demonstrated that Co-citrate in the LDH interlayer was reduced to metallic Co cluster. SEM-EDS revealed that the atomic ratio of Co-LDH was Mg:Al:Co = 4.5:2.1:1. Because the Co-citrate complex is a mono valent anion, it is calculated that about 48% of anion sites were occupied with Co-citrate after the ion exchange process. From the result of ICP-AES analysis, it is calculated that the Co content of Co-LDH is 4.6 mass %.

N2 adsorption/desorption isotherms of NO3-LDH, IonEx(Co)-LDH and Co-LDH are compared in Fig. 5. Surface areas were calculated by the Brunauer–Emmett–Teller method and pore volumes are shown in Table 1. The results clearly show that formation of Co clusters results in a drastic increase of pore volumes and surface areas. In particular, Co-LDH [Fig. 5(c)] showed higher N2 adsorption than other samples at low relative pressure, indicating that Co-LDH has micropores with diameters smaller than 2 nm. However, t-plot of the Co-LDH at low pressure range [Fig. 6(a)] revealed that surface area of the micropores was only 3.3 m2/g and one of external surface was 51.6 m2/g, suggesting that formation of micropores was limited. On the other hand, BJH plot obtained from the desorption profile of Co-LDH suggests the formation of mesopores with diameters of 2–3 nm. In addition, the isotherm of Co-LDH [Fig. 5(c)] has an H3 type hysteresis, suggesting existence of slit type pores. The behavior of the isotherms is similar to that of LDH pillared with POM reported by Kwon.9) If the clusters made LDH layers regularly integrate with a uniform distance of 2–4 nm, a peak assigned to basal spacing of (0 0 3) could appear at 2–5° on the XRD pattern. However, the peak of (0 0 3) due to the expanded interlayer was not observed on the XRD profile of Co-LDH as shown in Fig. 1(c). From the above results, it can be hypothesized that the Co clusters were formed in the interlayer of the LDH and the layers were partially delaminated and stacked irregularly, resulting in the formation of slit type mesopores as shown in Scheme 1.

### Table 1. Comparison of specific surface areas and pore volumes

| Sample          | Specific Surface Area (m2/g) | Pore Volume (cm3/g) |
|-----------------|-----------------------------|--------------------|
| Co-LDH          | 54.9                        | 0.105              |
| IonEx(Co)-LDH   | 26.5                        | 0.046              |
| NO3-LDH         | 7.2                         | 0.016              |

3.2 Catalytic performance

Hydrogen was generated from both Co-LDH and cobalt metal powder as a zero-order reaction, as shown in Fig. 7. On the other hand, no hydrogen was generated at all from the sodium borohydride solution without any catalyst. The generation rate of Co clusters was much higher than that of cobalt metal powders. Co-LDH generated H2 at 1186 ml min⁻¹ g⁻¹ Co, whereas Co metal powder generated only
The improvement of the activity is considered to be caused by great dispersion and high surface area of the Co clusters. According to the reports by other scientists, CoCl₂, which is one of the promising catalysts for hydrolysis reaction of NaBH₄, generated H₂ at 3.5–4.9 L min⁻¹ g⁻¹ Co at around 25 °C.²⁸⁻³⁰) The relatively lower activity of Co-LDH might be due to carbonate anion in the interlayer, which is strongly adsorbed in the interlayer and could disturb accessibility of BH₄⁻ anion to the Co clusters. From the total amount of generated H₂ over Co-LDH, it is calculated that about 188 mol of NaBH₄ can react with water over 1 mol of Co. Although turn over number (TON) of this catalyst cannot be estimated from our results because the catalyst was not deactivated, TON of Co-LDH must be much higher than 1. Therefore, it was demonstrated that Co clusters in Co-LDH catalyzed the hydrolysis reaction of sodium borohydride. Both catalysts required an induction time to initiate H₂ generation from the point of adding the catalyst into the sodium borohydride solution. The induction time is considered to be due to reduction of the surface of the cobalt particle or cluster.

4. Conclusion

Cobalt clusters were synthesized in interlayers of MgAl-LDH via intercalation of Co-citrate complex and reduction with sodium borohydride. Co-citrate was successfully intercalated into the interlayer of LDH by ion exchange with NO₃⁻. Chemical reduction using sodium borohydride solution at 50 °C resulted in formation of metallic Co clusters smaller than 5 nm. The formation of Co clusters brought a porous structure to the LDH. Because the particle size of Co clusters was not uniform, the reduction condition should be optimized in order to obtain regular integration of layers and clusters. In this study, we suggest a novel method to synthesize metal clusters of transition metal elements in interlayer of LDHs. This method can be applied to other metal species and LDHs.
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