Hybridization of Ni–Cr, Cu–Cr, and Zn–Cr layered double hydroxides with polyoxometalates and their catalytic behavior

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Cr-based layered double hydroxides (LDHs) containing Ni, Zn, or Cu as the divalent cation were prepared with a divalent-to-trivalent cation molar ratio of 3. Then, LDH hybrids intercalated with polyanions ($[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (PMoO) or $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ (HWO)) were prepared by ion exchange and hydrothermal processes. The shift of the diffraction line indicating interlayer space in the X-ray diffraction patterns confirmed the intercalation in the LDH. The fraction of PMoO and HWO anions incorporated was 30–70 or 60–90% of ion exchange capacity, respectively, by charge compensation for Cr^{3+} . In the conversion of styrene by epoxidation and oxidation, the hybrid of the LDH composed of Zn and Cr with PMoO showed the maximum catalytic activity, with 70% conversion. For the LDH composed of Ni and Cr, hybridization with a polyanion enhanced the catalytic behavior by a synergistic effect resulting from the basicity of the LDH phase.

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1. Introduction

The general formula for layered double hydroxides (LDHs) is $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][(\text{A}^{n-})_{x/n}] \cdot m\text{H}_2\text{O}$, where M^{2+} is a divalent cation (e.g., Mg^{2+} , Ca^{2+} , and Ni^{2+}), M^{3+} is a trivalent cation (e.g., Al^{3+} , Fe^{3+} , and Cr^{3+}), and A^{n-} is an intercalated anion (e.g., CO_3^{2-} , Cl^- , and NO_3^-) in the interlayer space. These species can form a positively charged hydroxide layer having the same structure as brucite $[\text{Mg}(\text{OH})_2]$, with anions incorporated in the interlayer space for charge compensation. From the brucite structure, the LDH may be topotactically converted to a metal oxide or hydroxide phase by removal of the incorporated anions.^{1,2)} Since LDHs show anion exchange competence, which has been investigated in detail,^{3,4)} their application for the removal of toxic anions (e.g., arsenide ion and fluoride ion)^{5,6)} and as drug delivery systems⁷⁾ has been investigated. Moreover, LDHs have soft chemical properties such as exfoliation and intercalation,^{8,9)} which can result in the formation of a porous structure.^{9,10)} In addition, LDHs exhibit a wide variety of chemical compositions and properties because of the combination of diverse metal cations or anions. In particular, hydroxide layers containing transition metals may exhibit adsorptive or catalytic properties due to the presence of d-electrons. For example, Chen et al. reported that Zn–Cr LDH can be used in photocatalysis.¹¹⁾ Liang et al. reported the use of Ni–Co LDH nanosheets as a catalyst for oxygen evolution.¹²⁾

A polyoxometalate is a polynuclear oxyacid anion containing V^{5+} , Nb^{5+} , Mo^{6+} , W^{6+} , and other similar metal ions. Polyoxometalates display a variety of structures, including Keggin, Paratungstate, and Dawson structures. This class of compounds has been mainly studied for application as homogeneous catalysts in organic conversion reactions.¹³⁾

Intercalation of LDHs with a functional anion can provide functional materials called hybrids. Our group has previously

reported the intercalation of large molecules to an LDH including Ni and Co to form hybrids with catalytic ability. The hybrid including Ni showed moderate catalytic activity for the conversion of alcohols to ketones.¹⁴⁾ In this study, LDH containing some transition metal (Cr, Ni or Cu, and Zn) hybrids were prepared by the intercalation of polyanions for catalytic applications. The prepared catalyst was examined for the epoxidation of alkenes, and a synergistic effect on catalytic activity was expected because of the presence of a polyanion nearby the transition metals in the hydroxide layer of the LDH.

2. Experimental procedures

2.1 Preparation of Cr-based LDH containing Ni, Zn or Cu

The Cr-based LDH was prepared with an $\text{M}^{2+}/\text{Cr}^{3+}$ (M^{2+} : Ni^{2+} , Zn^{2+} or Cu^{2+}) molar ratio of 3 by a hydrothermal reaction. Divalent metal nitrates, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (10.0 mmol), were mixed with a trivalent metal nitrate, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (3.33 mmol) in 40 mL distilled water. After adjusting the pH to 7, 10, or 12 ± 0.2 using NaOH and HNO_3 for each divalent cation, the solutions were hydrothermally treated at 120°C for 72 h in respective polytetrafluoroethylene (PTFE)-lined autoclave. The obtained material was filtered, washed with distilled water and ethanol, then dried at 50°C for 24 h. The LDH materials were designated as 3Ni1Cr– CO_3^{2-} , 3Zn1Cr– CO_3^{2-} , and 3Cu1Cr– CO_3^{2-} with the numbers indicating the composition ratio of the cation and the anion.

LDH hybrids with a polyanion were prepared by ion exchange and hydrothermal processes, as described in the following sections.

2.2 Preparation of LDH hybrid with polyanion by ion exchange

The as-prepared LDH includes CO_3^{2-} as an intercalated anion. Since CO_3^{2-} is typically stable in the interlayer because of its good affinity to the hydroxide layer, decarbonation was carried out following a literature method¹⁵⁾ to obtain LDH with other

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intercalated anions. An acetate buffer solution (0.1 M) was prepared by the addition of acetic acid and sodium acetate in 1:9 ratio, NaCl was added to the solution with concentration of 2.53 mol/L. LDH was added to the acetate buffer solution and the mixture was shaken at 200 rpm for 24 h. The sample was then filtered and washed with ultrapure water by vacuum filtration. The sample, which might include Cl^- , was dried under reduced pressure over dried silica gel and designated as LDH- Cl^- .

LDH- Cl^- was used for the preparation of an LDH hybrid with a polyanion. Polyanions $\alpha\text{-Na}_2\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$ (PMoO) and $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$ (HWO) were used for this purpose. Figure 1 shows a schematic illustration of the PMoO and HWO polyanions prepared using published methods.^{16),17)} These polyanions were dissolved in ultrapure water separately, and LDH- Cl^- was added to these aqueous solutions in a stoichiometric molar ratio. The resulting solutions were then shaken at 40°C and 200 rpm for 4 days. After vacuum filtration and washing with ultrapure water, the samples were dried under reduced pressure over dried silica gel. The samples were designated as 3Ni1Cr-POM.

2.3 Preparation of LDH hybrid with polyanion by hydrothermal process

The hydrothermal process was carried out under the same conditions as those described in section 2.1, except for the addition of the polyanion-included aqueous solution. 20 mL of the polyanion-included aqueous solution prepared with a stoichiometric ratio to LDH was mixed with the solution (20 mL) containing divalent (10.0 mmol) and trivalent (3.33 mmol) metal

nitrate. After adjusting the pH to 7 ± 0.2 by the addition of NaOH and HNO_3 , the solution was hydrothermally treated at 120°C for 72 h in a PTFE-lined autoclave. The obtained material was filtered, washed with distilled water and ethanol, and dried at 50°C for 24 h.

2.4 Characterization

The structures of the prepared LDH and LDH hybrids were determined by X-ray diffraction (XRD; Rigaku, RINT-2000) using monochromated $\text{Cu K}\alpha$ radiation and Fourier-transform infrared spectroscopy (FT-IR; Jasco, FT/IR-4100). The LDH hybrid particles were observed by field-emission scanning electron microscopy (FE-SEM; JEOL, JEM-6500F), and the chemical composition was analyzed by energy-dispersive X-ray spectrometry (EDX; EDAX Japan, EDAX PHOENIX PRO). The amount of water in the interlayer space was measured by thermogravimetry/differential thermal analysis (TG-DTA; Rigaku, TG-8120).

The catalytic properties of the LDH hybrid were evaluated using high-performance liquid chromatography (HPLC; Jasco, LC-2000 PLUS) with an octadecylsilyl column at 40°C. A solution consisting of 50% ultrapure water and 50% acetonitrile (CH_3CN) was used as the mobile phase. The catalytic test was carried out in accordance with a published method.¹⁸⁾ Styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, 1.0 mmol) was added to 6 mL CH_3CN containing 6 mmol of aqueous hydrogen peroxide (H_2O_2). Then, the solution was heated at 60°C and LDH hybrid (0.02 g) was added to the solution. The reaction was monitored at 60 min intervals by injecting a styrene solution 10-fold diluted with acetonitrile into the HPLC system.

3. Results and discussion

3.1 Preparation of Cr-based LDH containing Ni, Zn, or Cu and its decarbonation

Figure 2(a) shows the XRD patterns of Cr-based LDH containing Ni, Zn, or Cu as the divalent cation prepared at pH 7, 10, and 12. The XRD patterns confirmed that 3Ni1Cr could be prepared at pH 7, 10, and 12. 3Zn1Cr LDH showed relatively good crystallinity at pH 7 and 10, although ZnO and Cr_2O_3

Fig. 2. XRD patterns of (a) Cr-based LDHs containing Ni, Zn, or Cu at pH 7, 10, and 12, and (b) LDHs at pH 7 before and after decarbonation.

Fig. 3. XRD patterns of LDH hybrid with polyanion by (a) ion exchange and (b) hydrothermal process.

Fig. 4. FT-IR spectra of LDH-polyanion hybrid with (a) PMoO and (b) HWO.

emerged as impurity phases at pH 10 and 12. In the case of 3Cu1Cr, LDH and $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$ were present as the impurity phase at pH 7, and the CuO phase appeared as an impurity at pH 10 and higher. In this study, the LDH sample prepared at pH 7 without metal oxide impurity phases was used for decarbonation. Figure 2(b) shows the XRD patterns of the samples before and after decarbonation. After decarbonation of LDH-CO_3^{2-} , the (003) peak for 3Zn1Cr and 3Cu1Cr LDHs, which indicated interlayer spacing d , shifted from ~ 0.9 to 0.8 nm, possibly because of the ion exchange of CO_3^{2-} by Cl^- . After decarbonation, the yield of LDH decreased to around 70–30 mass % due to the weak acidity of the buffer solution. In the case of 3Cu1Cr, the impurity phase vanished. In the FT-IR spectra for all the samples [Figs. 4(a) and 4(b) in the next section], the absorptions derived from CO_3^{2-} or NO_3^- (around 1375 cm^{-1}) disappeared upon decarbonation. These results confirmed that the originally intercalated ions were successfully exchanged by Cl^- .

3.2 LDH hybrid with polyanion prepared by ion exchange and hydrothermal process

Figure 3 shows XRD patterns of the LDH hybrid with polyanions obtained by the (a) ion exchange and (b) hydrothermal processes. In the ion exchange process, the interlayer spacings of

3Ni1Cr-PMoO and 3Zn1Cr-PMoO increased to around 1 nm. For the other samples, particularly those with HWO, the diffraction line indicating interlayer spacing did not seem to shift and the diffraction peaks broadened. In the hydrothermal process, the interlayer spacings of 3Ni1Cr-HWO and 3Zn1Cr-HWO increased to around 1.2 nm. The other samples, especially those containing PMoO, showed changes in their diffraction patterns, indicating that the LDH phases disappeared upon hydrothermal treatment. The XRD profile showed no peaks for 3Zn1Cr-PMoO and 3Ni1Cr-PMoO, and 3Cu1Cr-PMoO included some impurities of $\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$, CuO, Cu_2O , and $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$ polymorph phases. These results indicated that the optimum process for intercalation into the interlayer space of the LDH phases depended on the polyanion used: ion exchange for PMoO and hydrothermal treatment for HWO. The XRD patterns of the hybrids included broad peaks due to their low crystallinity. However, upon incorporating complexes with high molecular weight and electron density into the interlayer of the LDH, the intensity of the (003) diffraction peak tended to decrease. The (006) diffraction peak appeared at $2\theta \approx 18^\circ$ for 3Zn1Cr-PMoO, 3Ni1Cr-HWO, and 3Zn1Cr-HWO, suggesting that the layered structure was retained after intercalation of the polyanion. Based on these results, the samples produced by ion exchange and hydrothermal

Table 1. Chemical composition of LDH hybrids with PMoO and HWO

Sample	Chemical composition*
3Ni1Cr-PMoO	$\text{Ni}_{4.5}\text{Cr}_{1.0}(\text{OH})_{11}[\text{PMo}_{12}\text{O}_{40}]_{0.22}\text{Cl}^{-0.34}\cdot 6.4\text{H}_2\text{O}$
3Zn1Cr-PMoO	$\text{Zn}_{3.6}\text{Cr}_{1.0}(\text{OH})_{9.2}[\text{PMo}_{12}\text{O}_{40}]_{0.23}\text{Cl}^{-0.31}\cdot 6.7\text{H}_2\text{O}$
3Cu1Cr-PMoO	$\text{Cu}_{4.3}\text{Cr}_{1.0}(\text{OH})_{10.6}[\text{PMo}_{12}\text{O}_{40}]_{0.11}\text{Cl}^{-0.67}\cdot 3.0\text{H}_2\text{O}$
3Ni1Cr-HWO	$\text{Ni}_{3.8}\text{Cr}_{1.0}(\text{OH})_{9.6}[\text{H}_2\text{W}_{12}\text{O}_{42}]_{0.088}(\text{CO}_3^{2-})_{0.060}\cdot 5.5\text{H}_2\text{O}$
3Zn1Cr-HWO	$\text{Zn}_{3.6}\text{Cr}_{1.0}(\text{OH})_{9.2}[\text{H}_2\text{W}_{12}\text{O}_{42}]_{0.083}(\text{CO}_3^{2-})_{0.085}\cdot 4.8\text{H}_2\text{O}$
3Cu1Cr-HWO	$\text{Cu}_{5.9}\text{Cr}_{1.0}(\text{OH})_{13.8}[\text{H}_2\text{W}_{12}\text{O}_{42}]_{0.064}(\text{CO}_3^{2-})_{0.18}\cdot 3.0\text{H}_2\text{O}$

*Chemical stoichiometric composition, 0.33 for PMoO/Cr and 0.10 for HWO/Cr.

Fig. 5. Schematic illustration of LDH-polyanion hybrid models.

processes were adopted for the PMoO and HWO hybrids, respectively. **Table 1** shows the chemical composition and fraction of the polyanion incorporated into the prepared LDH hybrid. 30–70% of PMoO or 60–90% of HWO could be incorporated by charge compensation for Cr^{3+} . In 3Cu1Cr LDH, polyanions could not be intercalated into the structure but might be adsorbed on the surface of the LDH particles.

Figure 4 shows the FT-IR spectra of the polyanion and LDH-polyanion hybrid. Xu et al. reported that PMoO shows FT-IR absorptions due to the antisymmetric stretching vibrations of P–O, Mo–O, and Mo–O–Mo at 1064, 961, and 867–781 cm^{-1} , respectively.¹⁹ Chaalia reported that HWO shows FT-IR absorptions due to the stretching vibrations of W–O and W–O–W at 940 and 900–600 cm^{-1} , respectively.²⁰ The spectra reported herein clearly included these absorptions, indicating the presence of the polyanions. In Fig. 4(b), the absorption due to the stretching vibration of the carbonate or nitrate anion was observed in the spectra of these LDH hybrids, because no decomposition and ion exchange treatments were performed for these samples.

Figure 5 shows a schematic illustration of the LDH-polyanion hybrid models. For 3Ni1Cr and 3Zn1Cr LDH, PMoO and HWO anions could be intercalated in the interlayer space. These anions might also be adsorbed on the surface of the LDH particles. For 3Cu1Cr LDH, intercalation of polyanions into the interlayer space was difficult, although these anions might be adsorbed on the surface of the LDH particles.

3.3 Catalytic behavior of LDH-polyanion hybrid for epoxidation of alkene

The catalytic behavior of the LDH-polyanion hybrid in the epoxidation of styrene was examined. **Figure 6** shows the concentration changes of styrene and its derivatives in the presence of the LDH-PMoO-type catalyst. The initial concentration (C_0) was 0.167 mol/L, and the blank (black line) showed that the concentration remained nearly constant in the absence of the catalyst. The solid and dotted lines denote the results in the presence of the LDH hybrid and LDH- CO_3^{2-} . The blank test indicated that the

Fig. 6. Comparison of concentration change of (a) styrene, (b) acetophenone, and (c) styrene oxide in the presence of LDH-PMoO-type catalyst.

reaction could not progress in the presence of H_2O_2 alone. When incorporated into the column, the 3Ni1Cr-PMoO and 3Zn1Cr-PMoO catalysts caused a sharp decline in the concentration of styrene, while the concentration of the derivatives, acetophenone, and styrene oxide, increased. For 3Zn1Cr without PMoO, the styrene concentration decreased during the reaction (around 70%), consistent with that obtained for the 3Zn1Cr-PMoO hybrid. Compared to the 3Zn1Cr sample, 3Ni1Cr without PMoO showed low activity for the catalytic conversion.

Figure 7 shows the change in the concentration of styrene and its derivatives in the presence of the LDH-HWO hybrids. Similar results were obtained for LDH-PMoO. The 3Ni1Cr and 3Zn1Cr hybrids caused a decrease in the concentration of styrene. For the 3Zn1Cr sample, pure LDH showed similar catalytic activity. 3Ni1Cr LDH without HWO did not show any catalytic activity, although the LDH hybrid showed good activity.

Table 2 summarizes the styrene conversion activity for each LDH and the corresponding hybrids. In the case of 3Zn1Cr, the LDHs with and without polyanion intercalation showed conversion activity; on the other hand, pure 3Ni1Cr or 3Cu1Cr LDH did not display catalytic activity, but the 3Ni1Cr LDH hybrid showed moderate conversion activity. These results implied that intercalation of a polyanion between the LDH layers was

Fig. 7. Comparison of concentration change of (a) styrene, (b) acetophenone, and (c) styrene oxide in the presence of LDH-HWO-type catalyst.

Table 2. Summary of styrene conversion activity for each LDH and LDH hybrid

Sample	Position of polyanion	Styrene conversion activity		
		LDH-CO ₃ ²⁻	LDH-PMoO	LDH-HWO
3Ni1Cr	Interlayer and surface	×	○	○
3Zn1Cr	Interlayer and surface	○	○	○
3Cu1Cr	Surface	×	×	×

○: high ×: low.

important for the conversion reaction. Liu et al. reported that LDH-POM catalysts showed much higher epoxide selectivity than the corresponding homogeneous Na-POM catalysts, which can be attributed to the beneficial effect of the basic LDH host on the suppression of acid-catalyzed epoxide hydrolysis.²¹⁾ Thus, it was supposed that the host LDH attracts the reactant into the active sites containing the polyanion and exerts a basic effect for the reaction conditions. In our system, the electronegativity values of Cr, Ni, Cu, and Zn are 1.66, 1.91, 1.90, and 1.65, respectively. Since 3Zn1Cr composed of Cr and Zn which had relatively low electronegativity, its hydroxide layer should be more positive than that of the 3Ni1Cr and 3Cu1Cr LDH samples. Therefore, 3Zn1Cr might attract electrons easily during the

reaction, even if the LDH were present in the reactive solution. For 3Ni1Cr and 3Cu1Cr, the LDH itself might not work effectively due to the higher electronegativity of Ni and Cu than that of Zn. However, the intercalation resulted in strong activity because W or Mo in the polyanion, which have higher electronegativity than Ni and Cu, enhanced electron attraction.

4. Conclusions

Cr-based LDHs with Ni, Zn, or Cu as the divalent cation were prepared, and [PMo₁₂O₄₀]³⁻ or [H₂W₁₂O₄₂]¹⁰⁻ was intercalated into the LDH interlayer via an ion exchange or hydrothermal process. The prepared LDH-polyanion hybrids were analyzed by XRD, and their catalytic activity for the epoxidation of an alkene was investigated. The results are as follows.

1. In the case of 3Ni1Cr and 3Zn1Cr LDH, hybrids with the [PMo₁₂O₄₀]³⁻ and [H₂W₁₂O₄₂]¹⁰⁻ anions were successfully prepared by ion exchange and hydrothermal processes, respectively.
2. The polyanions, [PMo₁₂O₄₀]³⁻ and [H₂W₁₂O₄₂]¹⁰⁻, were incorporated into the LDH interlayer space with 30–70 and 60–90% of ion exchange capacity by charge compensation for Cr.
3. 3Zn1Cr-PMoO showed the highest catalytic activity, and ~70% of styrene underwent epoxidation. In the case of the 3Zn1Cr sample, the LDH without the polyanion was catalytically active for the conversion of styrene. In the case of the 3Ni1Cr and 3Cu1Cr samples, the LDH without polyanion showed no catalytic activity, and the 3Ni1Cr-LDH hybrid with the polyanion was catalytically active. These results indicated that the polyanion intercalated within the LDH interlayer works as an active site.

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