Intercalation of Mercaptocarboxylic Acid into Layered Double Hydroxide Accompanied with Oxidation of Mercapto Group

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The intercalation of mercaptocarboxylic acids into magnesium–aluminum layered double hydroxide (LDH) was accompanied with the oxidation of mercapto groups in aqueous solution as evidenced by ^{13}C solid-state NMR and Raman scattering measurements. The layers of LDH were bridged by two carboxylic groups of the corresponding disulfide, which was formed by the oxidation of mercaptocarboxylic acids.

Recently, organic and inorganic hybrid materials based on layered compounds, such as montmorillonite,[1] layered phosphate,[2–4] and layered double hydroxide,[5] have been focused the spotlight of attention as new functional materials. Furthermore, layered double hydroxide is a solid base, and has been used as base catalyst for epoxidation of alkenes[6] and Baeyer–Villiger oxidation of ketones.[7] Because of the layer structure, magnesium–aluminum layered double hydroxide (LDH) is expected to be a shape-selective catalyst. We investigated the intercalation reaction of mercaptocarboxylic acid into layered double hydroxide to examine the selective activity of the intercalation compound for transition metals using mercapto group in the interlayer space. On the way, we found that the oxidation of mercaptocarboxylic acids occurred during the intercalation, and the corresponding disulfides were intercalated as reported in this paper.

An aqueous solution of 3-mercaptopropionic acid was stirred with 1 g of magnesium–aluminum layered double hydroxide ($Mg_{0.69}Al_{0.31}(OH)_{2.03}Cl_{0.26}(CO_3)_{0.01}\cdot 0.48H_2O$ abbreviated as LDH-Cl) for 5 h at 60 °C in a closed flask with the atmosphere of air. The final pH of the reaction solution was 8. As shown in Figure 1 XRD pattern of the product showed the expansion of the interlayer distance from 0.78 to 1.41 nm, indicating the intercalation of the mercaptopropionic acid. On the other hand, elemental analysis using Shimadzu NC-80 suggested that the composition of the intercalation compound is $Mg_{0.69}Al_{0.31}(OH)_{2.03}(OOC(CH_2)_2SH)_{0.25}Cl_{0.06})$. From XRD data 3-mercaptopropionic acid molecule is intercalated as bilayer structure. Solid-state NMR (Varian Unity INOVA-500) and Raman scattering (Nicolet FT-RAMAN 960) measurements were performed to characterize the intercalation compound. Table 1 shows ^{13}C NMR chemical shift data of 3-mercaptopropionic acids in aqueous solution and in the interlayer space. Large low-field shift of the C_β carbon combined with mercapto group was observed for the intercalation compound (LDH-3-mercaptopropionic acid). This result is sometimes observed by the oxidation of mercapto groups to form disulfide as evidenced by the data of 3,3′-dithiodipropionic acid. Furthermore, shown in Table 1, the similarity of ^{13}C NMR spectra of LDH-3-mercaptopropionic acid with that of 3,3′-dithiodipropionic acid intercalation compound (LDH-3,3′-dithiodipropionic acid) also supports this fact. In order to confirm the existence of disulfide bond Raman scattering measurement, which is very active for symmetric stretching vibration of the S–S bond, was performed. Figure 2 shows Raman spectra of 3-mercaptopropionic acid and LDH-3-mercaptopropionic acid. For reference, the spectra of 3,3′-dithiodipropionic acid and its intercalation compound were shown as well. After the intercalation of 3-mercaptopropionic acid, the S–H stretching band at 2572 cm^{-1} disappeared completely and the band due to the S–S symmetric stretching was observed at 506 cm^{-1}. Furthermore, the spectrum of LDH-3-mercaptopropionic acid was almost the same as that of LDH-3,3′-dithiodipropionic acid. From these experimental results, thus, the formation of disulfide bond was confirmed in the intercalation of 3-mercaptopropionic acid into LDH.

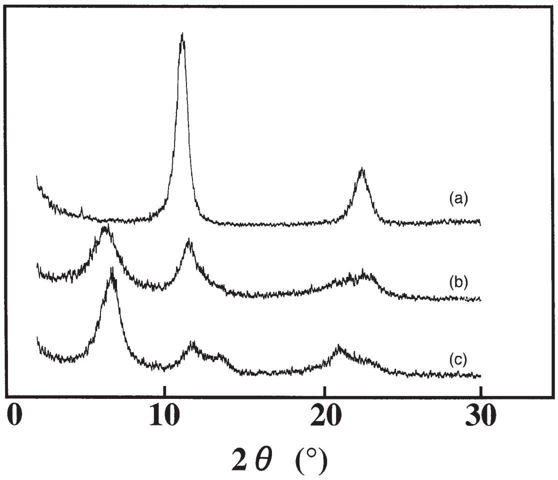

Figure 1. XRD of (a) LDH-Cl (b) LDH-3-mercaptopropionic acid, and (c) LDH-3,3′-dithiodipropionic acid.

Table 1. ^{13}C NMR chemical shifts data of 3-mercaptopropionic acid and 3,3′-dithiodipropionic acid in aqueous solution and intercalated in LDH

	δ/ppm		
	COOH	C_α	C_β
In aqueous solution			
3-mercaptopropionic acid	183.6	44.4	23.3
3,3′-dithiodipropionic acid	183.4	39.4	37.2
Intercalated in LDH			
3-mercaptopropionic acid	180	36	36
3,3′-dithiodipropionic acid	180	36	36

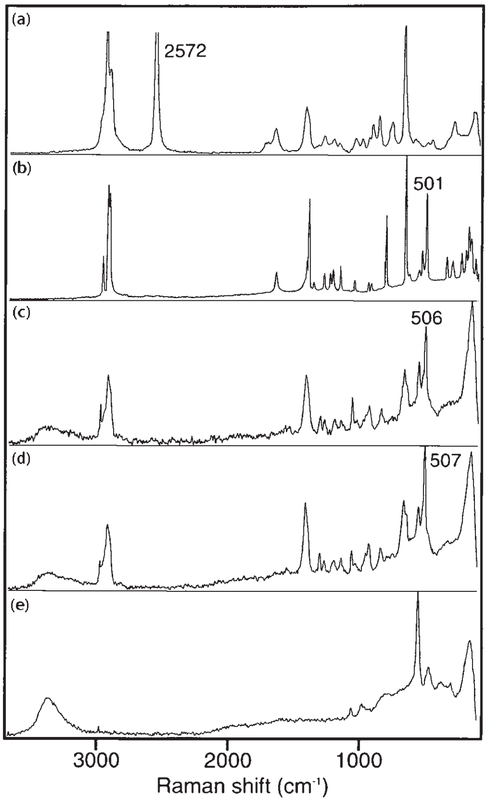

Figure 2. Raman spectra of (a) 3-mercaptopropionic acid, (b) 3,3′-dithiodipropionic acid, (c) LDH-3-mercaptopropionic acid, (d) LDH-3,3′-dithiodipropionic acid and (e) LDH-Cl.

Recently, Hirano et al. reported the rapid oxidation of mercapto group by the calcinated LDH as base catalyst under mild condition.[8] They reported the complete oxidation, but it was realized using the calcinated LDH as catalyst and hexane as solvent under the bubbling of O_2. And there was no progress of the oxidation under the existence of tiny of H_2O. In contrast to this, the oxidation of mercapto group proceeded in aqueous solution without airflow in our experimental condition.

In order to examine exactly the mechanism of this oxidative intercalation reaction, ^{13}C NMR of 3-mercaptopropionic acid in the reaction solution was examined. After the complete intercalation reaction, that is, 5 h at 60 °C, more than 80% of mercaptocarboxylic acid in aqueous reaction solution was not oxidized. However, there was no existence of mercapto group in the interlayer space. These experimental results suggest that the catalytic oxidation of 3-mercaptopropionic acid might not be performed on the solid surface of the LDH-3-mercaptopropionic acid but in the interlayer space as shown in Figure 3. That is why this oxidation proceeded even in aqueous solution. This oxidative intercalation is probably accelerated in the confined space of the interlayer of LDH. In mercaptocarboxylic acid the presence of carboxylic group enables the intercalation reaction easier by ion-exchange mechanism, and the interlayer space in LDH might accelerate the oxidation of mercapto group. Unexpected catalytic reaction in the interlayer space was observed for polyamine intercalated layered zirconium phosphate as well.[3]

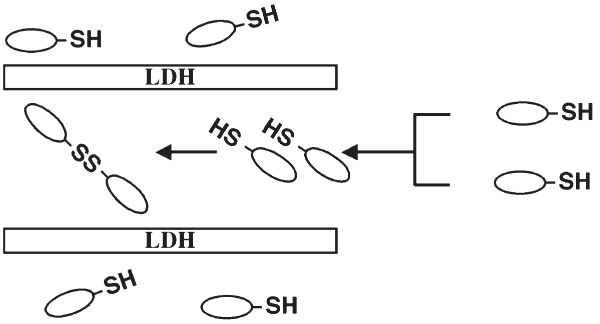

Figure 3. Schematic intercalation mechanism of mercaptocarboxylic acid in LDH.

In order to certify the appropriateness of this oxidative intercalation reaction, the intercalation reactions of various mercaptocarboxylic acids were investigated. Table 2 summarizes the interlayer distances of the intercalation compounds and uptakes of mercaptocarboxylic acid. Although the expansion of the interlayer distance and the uptake were different for these mercaptocarboxylic acids, disulfide formation was confirmed by Raman spectra for all the mercaptocarboxylic acids examined. This oxidative intercalation reaction of mercaptocarboxylic acid into layered double hydroxide was universal.

Table 2. Characteristics of mercaptocarboxylic acids intercalated LDH

Guest compound	d/nm	Uptake/mmol g^{-1}
3-mercaptopropionic acid	1.41	3.0
thiosalicylic acid	1.50	2.8
cysteine	0.79	1.5

In conclusion, the oxidative intercalation of mercaptocarboxylic acid in Mg–Al LDH was evidenced by Raman and solid-state NMR spectra.

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