

Determination of Carbonate Ion Contents in Layered Double Hydroxides by FTIR Spectrometry

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Experimental Details

Materials

Special grade carboxylic acid and alcohol reagents were obtained from Kanto Chemical Co., Inc., and Nacalai Tesque, Inc., Japan, respectively, and were used as received without further purification. The starting material CO₃-LDH is commercially available (DHT-6: Mg/Al = 3, Kyowa Kagaku Kogyo Co., Ltd.).

Sample characterization

Fourier transform infrared (FTIR) spectra were measured on a JASCO FT/IR-350 Fourier transform infrared spectrometer. Thermogravimetric-differential thermal analysis (TG-DTA) was performed using a Rigaku TG 8120 instrument over a temperature range from room temperature to 800°C with a 10°C min⁻¹ heating rate in air, using α -Al₂O₃ as a standard. The contents of metal elements and carboxylate ions of the LDH samples were analyzed using a Thermo Fisher Scientific iCAP 6300Duo inductively-coupled plasma (ICP) spectrometer and a Dionex DX-100 ion chromatograph by dissolving the samples in dilute H₂SO₄. CHN elemental analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O analyzer.

Determination of CO_3^{2-} content by FTIR spectrometry or chemical composition analyses

Deconvolution results of $\text{CO}_3\text{-LDH}$

Table S1. Separated peak area of the $\nu_3\text{-CO}_3^{2-}$ band of the starting $\text{CO}_3\text{-LDH}$ and calculated statistical values.

Entry	A_i ^a	$A_i - \bar{A}$ ^b	$(A_i - \bar{A})^2$
1	70.316	-11.548	133.367
2	72.800	-9.064	82.164
3	79.964	-1.900	3.612
4	88.145	6.281	39.445
5	102.030	20.166	406.649
6	72.877	-8.987	80.774
7	72.647	-9.217	84.961
8	82.722	0.858	0.735
9	85.526	3.662	13.407
10	86.058	4.194	17.586
11	87.424	5.560	30.909

^a A_i : Peak area of $\nu_3(\text{CO}_3^{2-})$ band of $\text{CO}_3\text{-LDH}$. ^b \bar{A} : Mean value of A_i .

Chemical composition analyses of RCOO-LDHs

Table S2. Compositions of the RCOO-LDHs with different CO_3^{2-} contents and molar ratios of $2(\text{CO}_3^{2-})/\text{Al}$.

RCOO-LDH	Composition ^d	$2(\text{CO}_3^{2-})/\text{Al}$
Formate-LDH (1) ^a	$[\text{Mg}_{0.747}\text{Al}_{0.253}(\text{OH})_2](\text{HCOO})_{0.106}(\text{CO}_3)_{0.074} \cdot 0.146\text{H}_2\text{O}$	0.5827
Formate-LDH (2) ^a	$[\text{Mg}_{0.747}\text{Al}_{0.253}(\text{OH})_2](\text{HCOO})_{0.164}(\text{CO}_3)_{0.044} \cdot 0.150\text{H}_2\text{O}$	0.3512
Formate-LDH (3) ^a	$[\text{Mg}_{0.742}\text{Al}_{0.258}(\text{OH})_2](\text{HCOO})_{0.189}(\text{CO}_3)_{0.034} \cdot 0.130\text{H}_2\text{O}$	0.2680
Acetate-LDH (1) ^b	$[\text{Mg}_{0.742}\text{Al}_{0.258}(\text{OH})_2](\text{CH}_3\text{COO})_{0.102}(\text{CO}_3)_{0.078} \cdot 0.224\text{H}_2\text{O}$	0.6059
Acetate-LDH (2) ^b	$[\text{Mg}_{0.735}\text{Al}_{0.265}(\text{OH})_2](\text{CH}_3\text{COO})_{0.145}(\text{CO}_3)_{0.060} \cdot 0.195\text{H}_2\text{O}$	0.4522
Acetate-LDH (3) ^b	$[\text{Mg}_{0.738}\text{Al}_{0.262}(\text{OH})_2](\text{CH}_3\text{COO})_{0.193}(\text{CO}_3)_{0.034} \cdot 0.161\text{H}_2\text{O}$	0.2616
Acetate-LDH (4) ^b	$[\text{Mg}_{0.727}\text{Al}_{0.273}(\text{OH})_2](\text{CH}_3\text{COO})_{0.207}(\text{CO}_3)_{0.033} \cdot 0.216\text{H}_2\text{O}$	0.2409
Acetate-LDH (5) ^b	$[\text{Mg}_{0.731}\text{Al}_{0.269}(\text{OH})_2](\text{CH}_3\text{COO})_{0.240}(\text{CO}_3)_{0.015} \cdot 0.272\text{H}_2\text{O}$	0.1087
Acetate-LDH (6) ^b	$[\text{Mg}_{0.767}\text{Al}_{0.233}(\text{OH})_2](\text{CH}_3\text{COO})_{0.227}(\text{CO}_3)_{0.003} \cdot 0.696\text{H}_2\text{O}$	0.0254
Propionate-LDH (1) ^c	$[\text{Mg}_{0.761}\text{Al}_{0.239}(\text{OH})_2](\text{C}_2\text{H}_5\text{COO})_{0.035}(\text{CO}_3)_{0.102} \cdot 0.200\text{H}_2\text{O}$	0.8543
Propionate-LDH (2) ^c	$[\text{Mg}_{0.765}\text{Al}_{0.235}(\text{OH})_2](\text{C}_2\text{H}_5\text{COO})_{0.064}(\text{CO}_3)_{0.086} \cdot 0.225\text{H}_2\text{O}$	0.7271
Propionate-LDH (3) ^c	$[\text{Mg}_{0.763}\text{Al}_{0.237}(\text{OH})_2](\text{C}_2\text{H}_5\text{COO})_{0.080}(\text{CO}_3)_{0.079} \cdot 0.275\text{H}_2\text{O}$	0.6609
Propionate-LDH (4) ^c	$[\text{Mg}_{0.732}\text{Al}_{0.268}(\text{OH})_2](\text{C}_2\text{H}_5\text{COO})_{0.178}(\text{CO}_3)_{0.046} \cdot 0.479\text{H}_2\text{O}$	0.3375

^a The samples prepared by formic acid/1-propanol (30°C, 4 h) in different concentrations. ^b The samples prepared by acetic acid/ethanol (50°C, 24 h) in different concentrations. ^c The samples prepared by propionic acid/methanol (70°C, 24 h) in different concentrations. ^d Chemical compositions were obtained from elemental analyses using ICP, CHN analysis, ion chromatography, and TG-DTA.