Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Multinuclear solid-state NMR spectroscopy of a paramagnetic layered double hydroxide

Shinsuke Ishihara,* Kenzo Deguchi, Hiroaki Sato, Masatoshi Takegawa, Eisaku Nii, Shinobu Ohki, Kenjiro Hashi, Masataka Tansho, Tadashi Shimizu, Katsuhiko Ariga, Jan Labuta, Pathik Sahoo, Yusuke Yamauchi, Jonathan P. Hill, Nobuo Iyi, and Ryo Sasai*

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1. Materials

Nickel (II) nitrate hexahydrate, magnesium nitrate hexahydrate, aluminum nitrate nonahydrate, sodium chloride, acetic acid, sodium acetate, urea, sodium nitrate, sodium sulfate (Wako Pure Chemical Industries, Ltd.), and hexamethylenetetramine (Kanto Chemical Co. Inc.) were all used as received without further purification.

2. Hydrothermal synthesis of LDHs

A solution of $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 6H_2O$, and urea with appropriate concentrations of each compound in water (30 mL) was sealed in a Teflon®-lined pressure vessel (Table 1). Hydrothermal treatment was carried out by placing the pressure vessel in a dry oven for a given time at the appropriate temperature, followed by cooling of the vessel under ambient conditions. CO_3^{2-}-Ni/Al(*n*)LDHs synthesized by the hydrothermal treatment were filtered and rinsed several times with water, then dried at room temperature under reduced pressure.

According to a procedure reported by N. Iyi,[S1] CO_3^{2-}-Mg/Al(2)LDH was synthesized by treating a mixed aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (100 mmol/dm^3), $Al(NO_3)_3 \cdot 9H_2O$ (50 mmol/dm^3), and hexamethylenetetramine (175 mmol/dm^3) under hydrothermal conditions (413 K for 24 h). CO_3^{2}-Mg/Al(2)LDH synthesized by hydrothermal treatment was filtered and rinsed several times with water then dried at room temperature under reduced pressure.

Table S1. Synthesis conditions for each CO_3^{2-}-LDH

LDH	M^{II}/M^{III}	$[Ni(NO_3)_2]$ (mmol/dm^3)	$[Mg(NO_3)_2]$ (mmol/dm^3)	$[Al(NO_3)_3]$ (mmol/dm^3)	[Urea] (mmol/dm^3)	[HMT][a] (mmol/dm^3)	*T* (K)	*t* (h)
Ni/Al(2)LDH	2	100.0	–	50.0	330.0	–	453	72
Ni/Al(3)LDH	3	112.5	–	37.5	335.3	–	503	72
Ni/Al(4)LDH	4	120.0	–	30.0	327.3	–	503	72
Mg/Al(2)LDH	2	–	100.0	50.0	–	175.0	413	24

a: hexamethylenetetramine ($C_6H_{12}N_4$)

3. Characterization of LDHs

X-ray diffraction (XRD) measurements of the LDHs were carried out on a powder X-ray diffractometer using Mn-filtered Fe*K*α radiation (30 kV, 15 mA: MiniFlex II, RIGAKU). Infrared spectra of prepared LDHs were measured by using the KBr pellet method (FT-IR 6100, JASCO). SEM images were obtained usng a Hitachi S-4800 scanning electron microscope operating at an accelerating voltage of 10 kV.

The compositions of the LDHs were determined as follows: (1) the contents of Mg, Ni, and Al were determined by using inductively coupled plasma-atomic electron spectroscopy (ICP-AES: Optima-2000, Perkin-Elmer), after fully dissolving LDH powder in 0.1 mol/dm^3 of nitric acid; (2) water content in LDHs was calculated from weight loss estimated by thermogravimetry-differential thermal analysis (TG-DTA: ThermoPlus TG8120, RIGAKU). (3) The amount of carbonate anions incorporated in LDH interlayer was evaluated by a CHN corder (Yanaco Co., Japan). (4) The amount of chloride, nitrate, and sulfate anions incorporated in LDH interlayer was determined by ion-chromatography (Shimadzu Co., Japan).

Synchrotron-radiation X-ray diffraction (SXRD) measurements of LDHs were performed at BL02B2 in SPring-8 using the large Debye-Scherrer camera with an imaging plate.[S2] The sample powder with homogeneous granularity was sealed in a borosilicate capillary of 0.3 mm internal diameter. The wavelength of X-rays used was 0.78 Å. From preliminary SXRD measurements of the LDH powders, all samples were sufficiently high quality powders for fine crystal structure analysis.

The SXRD diffraction patterns obtained of LDHs were analyzed by MEM/Rietveld methods.[S3] Here, R-3m, which has been reported as the space group for CO_3^{2-}-Mg/Al(2)LDH crystal systems in the literature[S4], was adopted as the initial space group for determining the fine crystal structure of each LDH.

Table S2. Composition formula of the synthesized LDHs.

	LDH	M^{II}	M^{III}	Composition formula
(a)	CO_3^{2-}-Ni/Al(2)LDH	Ni	Al	$[Ni_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.16}\bullet 0.43H_2O$
(b)	CO_3^{2-}-Ni/Al(3)LDH			$[Ni_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.13}\bullet 0.44H_2O$
(c)	CO_3^{2-}-Ni/Al(4)LDH			$[Ni_{0.8}Al_{0.2}(OH)_2](CO_3)_{0.1}\bullet 0.25H_2O$
(d)	CO_3^{2-}-Mg/Al(2)LDH	Mg		$[Mg_{0.67}Al_{0.34}(OH)_2](CO_3)_{0.17}\bullet 0.41H_2O$

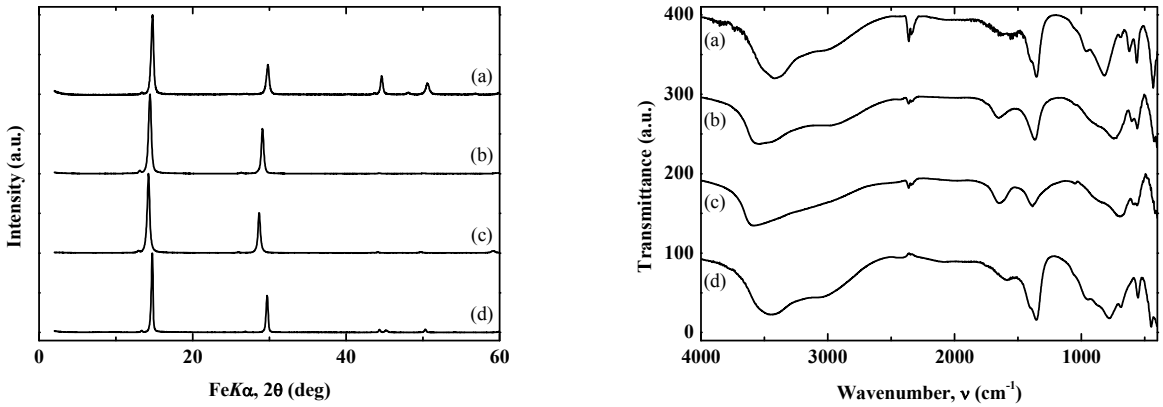

Figure S1. XRD profiles (Left) and IR spectra (right) of LDHs.

4. Solid-state NMR spectroscopy

High-resolution solid-state NMR experiments were carried out at 500.2, 125.7, and 130.3 MHz for ^{1}H, ^{13}C and ^{27}Al, respectively, using a JEOL ECA500 spectrometer. This instrument is equipped with a high power amplifier for proton decoupling and a CP/MAS (cross polarization/ magic angle spinning) probe. Samples were packed as powders in a ZrO rotor (∅ = 4 mm). Sample temperature was 300 ± 3 K. ^{1}H-NMR spectra were externally referenced to the proton signal of tetramethylsilane (TMS) at 0 ppm. ^{13}C-NMR spectra were externally referenced to the methyl carbon signal of hexamethylbenzene (17.4 ppm relative to TMS). ^{27}Al-NMR Spectra were externally referenced to the aluminium signal of $AlCl_3$ at 0 ppm.

5. Magnetization measurement

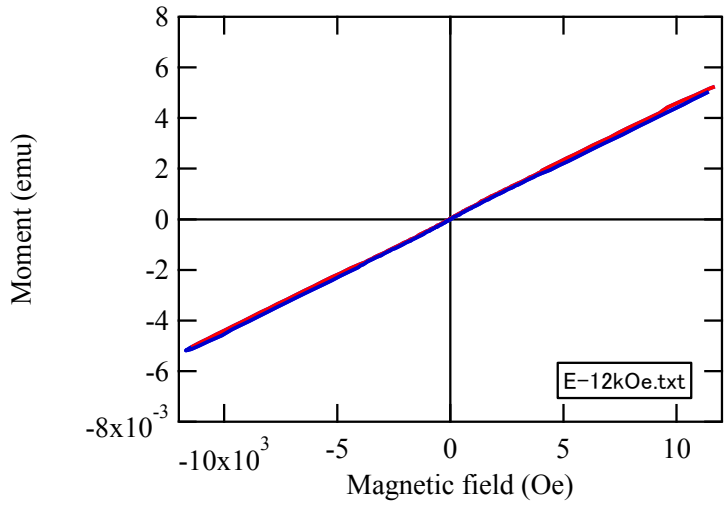

Figure S2. Typical magnetization data for Ni/Al LDHs. Magnetic field (H) dependence of magnetization (M) for Ni/Al(3) was measured at room temperature.

6. Cation distribution model of Ni/Al LDH

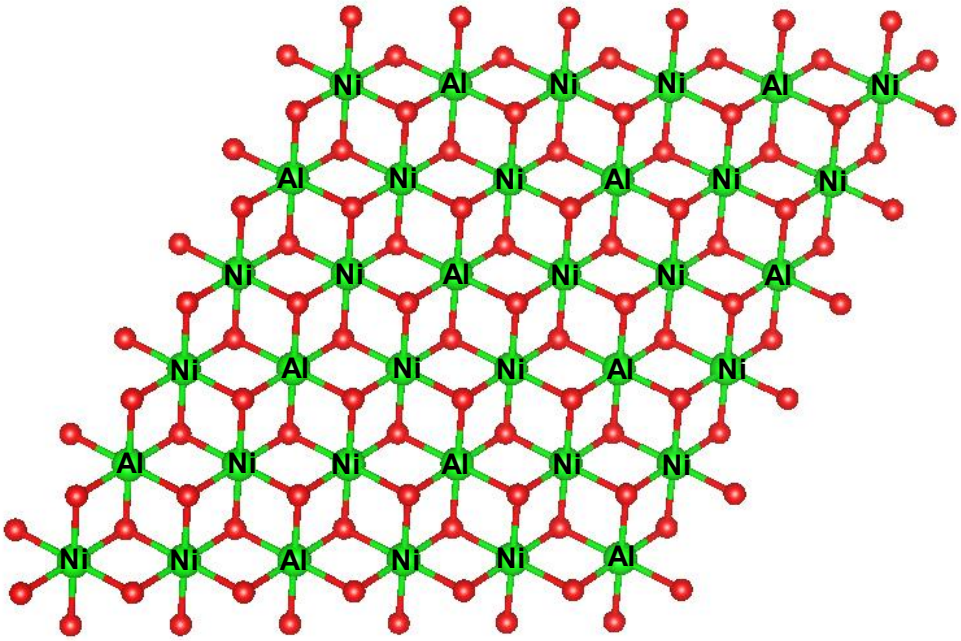

Figure S3. Intralayer cation distribution of Ni/Al(2) LDH when Al-O-Al bond is restricted. Oxygen atoms are denoted by red balls. In cases of Ni/Al(3) LDH and Ni/Al(4) LDH, some of the Al atoms are replaced with Ni atoms although the local environment of Al atoms, which are surrounded by six Ni atoms via oxygen atoms, does not vary.

7. References

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S2. Nishibori, E.; Takata, M.; Kato, K.; Sakata, M.; Kubota, Y.; Aoyagi, S.; Kuroiwa, Y.; Yamakata, M.; Ikeda, N. "The Large Debye-Scherrer Camera Installed at SPring-8 BL02B2 for Charge Density Studies," *Nucl. Instrum. Methods Phys. Res. Sect. A*, **2001**, *467-468*, 1045-1048..

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S4. (a) Belloto, M.; Rebours, B.; Clause, O.; Lynch, J.; Bazin, D.; Elkaim, E. "A Reexamination of Hydrotalcite Crystal Chemistry," *J. Phys. Chem.*, **1996**, *100*, 8527-8534. (b) Radha, A.; Kamath, P. V.; Shivakumara, C. "Order and Disorder among the Layered Double Hydroxides: Combined Rietveld and *DIFFaX* Approach," *Acta. Crystallogr. Sect. B*, **2007**, *63*, 243-250.