

Supporting Information for

The Role of Mg Doping in Manipulating the Adsorption Mechanisms of CaAl-Layered Double Hydroxide: Investigating the Effects of Calcination Temperature and Borate Concentration Changes

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Test S1. Preparation of LDHs and calcined LDHs

Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), boric acid (H_3BO_3), sodium nitrate (NaNO_3) and sodium hydroxide (NaOH) were obtained from Sinopharm Chemical Reagent Co. Ltd. All chemicals are of analytical reagent and used without purification.

Hydrothermal coprecipitation methods were used for the synthesis of CaAl-LDH and Mg^{2+} -doped CaAl-LDH. For CaAl-LDH, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.36 g) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.86 g) (molar ratio Ca:Al = 2:1) were added to 50 mL of 0.50 mol/L NaNO_3 . Adjust the pH to 12.0 by 2 mol/L NaOH . Then, the resulting slurry was transferred into a Teflon vessel and then sealed with a metal shell, placed in a constant-temperature oven at 100°C for 36 h. The cooled slurry was separated by centrifugation at 9000 rpm for 5 min., then washed using deionized water and ethanol to neutralize them, and dried in 50°C oven. The resulting product was called as CaAl-LDH. CaMgAl-LDH was prepared in the same method. The only difference was that the mixed solution containing Mg^{2+} ions with the molar ratio of Ca:Mg:Al = 1.6:0.4:1.0.

Test S2. Characterization

The crystalline phase of the nanoparticles was determined using a D8 Advance X-ray diffractometer (XRD) (Bruker, Germany) employing Cu K α radiation with scanning speed of 2° min⁻¹ and scanning step of 0.02°. The accelerating voltage and applied current were 30 kV and 20 mA, respectively. The morphologies of adsorbents and solid residues after reaction were observed using a JSM-5510LV scanning electron microscope (SEM) (JEOL, Japan). Thermo-gravimetric analysis (TG-DSC, 2000SA, Billerica, Massachusetts, USA) was performed from room temperature to 1000°C at a heating rate of 10°C/min. Brunauer-Emmett-Teller (BET) surface area measurements were performed with an ASAP-2460 device (Micromeritics, USA). Fourier transform infrared (FTIR) spectra were recorded on a JASCO FTIR spectrometer (FT/IR-670 Plus, Japan).

Extended X-ray absorption fine structure (EXAFS) spectra of the Ca K-edge were collected on BL06 at the Kyushu Synchrotron Light Research Center (SAGA-LS, Tosu, Japan). The spectra of the samples were collected using a silica drift in fluorescence mode. The photon energy was scanned in the range of 3.7-5.6 keV for the Ca K-edge. The samples were mixed with boron nitride (BN) and pressed into pellets. All of the spectra were averaged and normalized using IFFEFIT software version 1.2.11 [1].

- [1] B. Ravel, M. Newville, ATHENA , ARTEMIS , HEPHAESTUS : data analysis for X-ray absorption spectroscopy using IFEFFIT, (2005) 537–541. <https://doi.org/10.1107/S0909049505012719>.

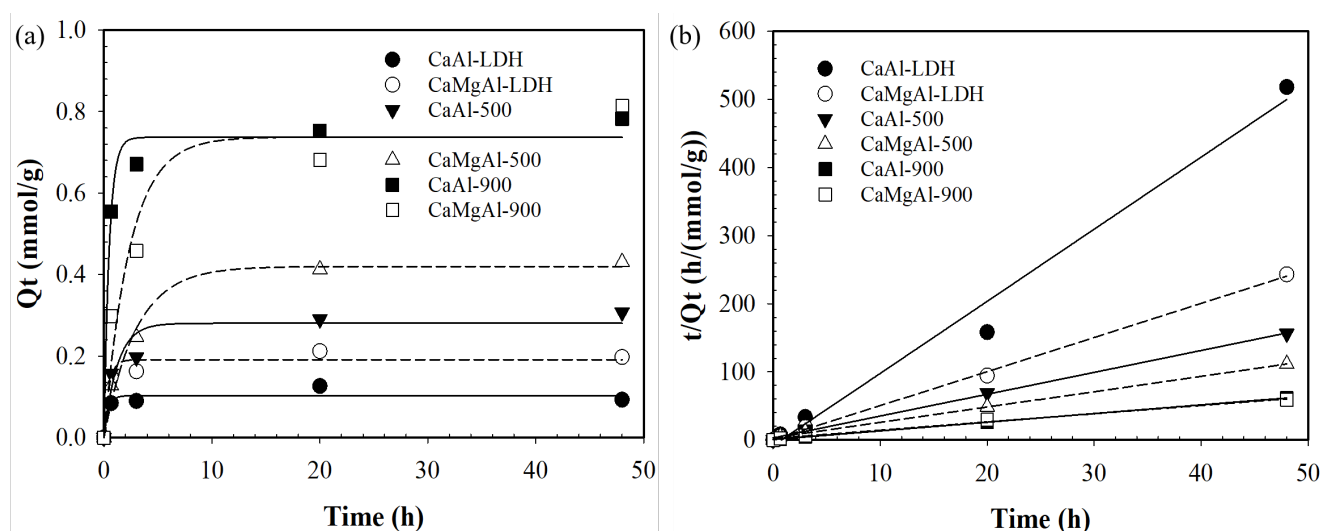


Figure S1. Adsorption kinetics of borate by CaAl-LDH and CaMgAl-LDH with different calcination temperatures. (a) Pseudo-first-order kinetic mode (b) Pseudo-second-order kinetic mode.

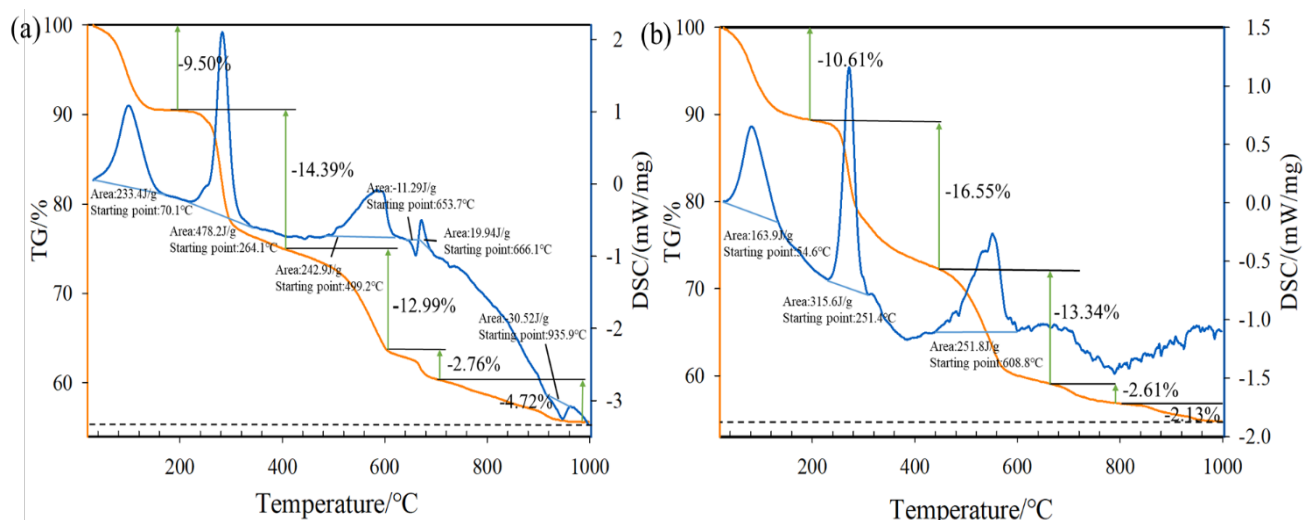


Figure S2. TG/DSC results of (a) CaAl-LDH and (b) CaMgAl-LDH. Reaction temperature is from room temperature to 1000°C.

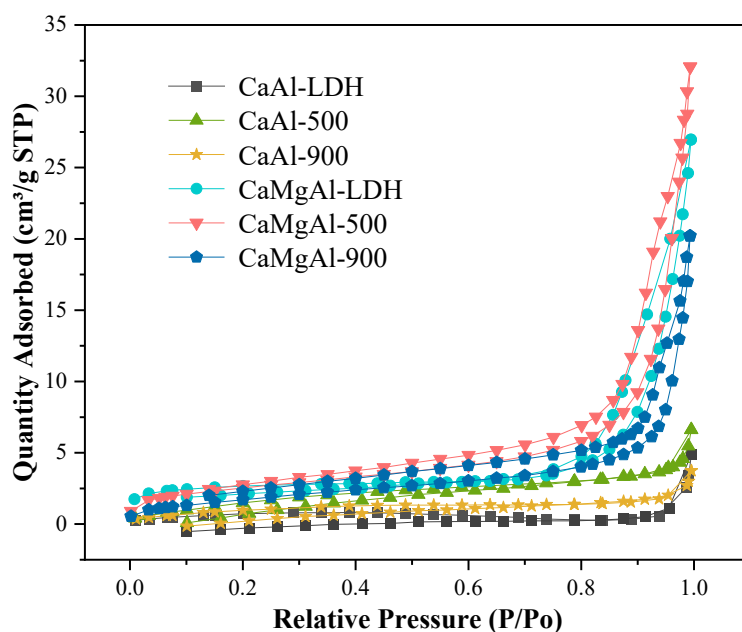


Figure S3. N₂ adsorption-desorption isotherms of all adsorbents.

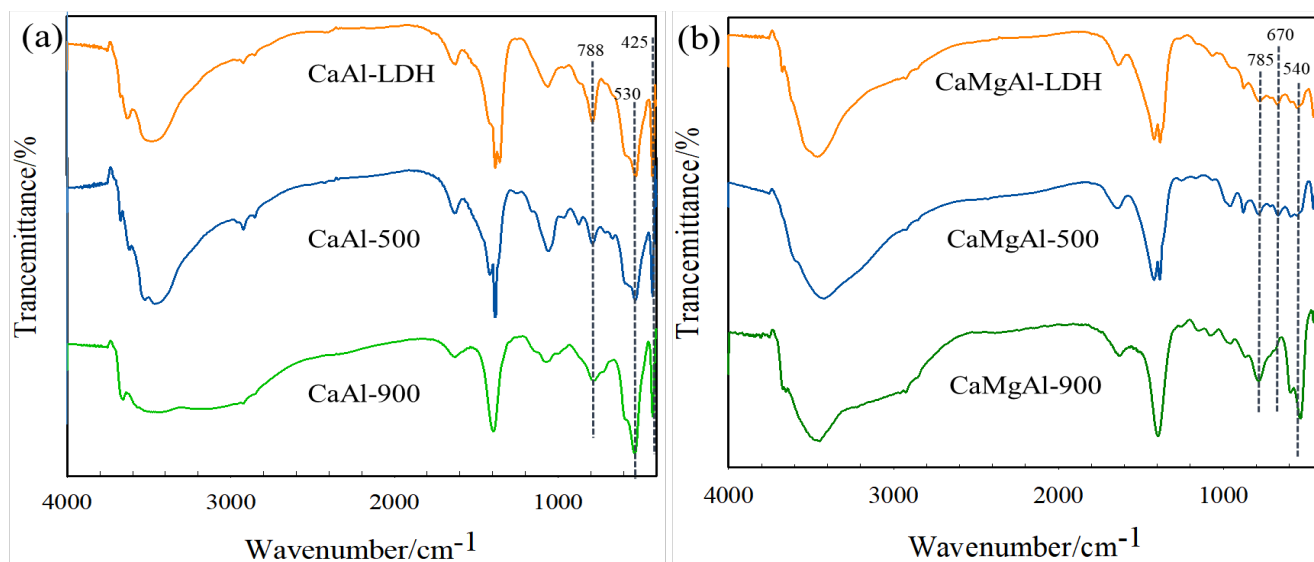


Figure S4. FTIR spectra of solid residues after adsorption of 2.5 mM borate on CaAl-LDH and CaMgAl-LDH with different calcination temperatures.

Table S1. Surface properties of different adsorbents.

Sample	S_{BET} (m^2/g)	t-MA (m^2/g)	t-ESA (m^2/g)	V (cm^3/g)	D_a (nm)	D_b (nm)
CaAl-LDH	2.67	1.35	1.32	0.0075	12.49	11.04
CaAl-500	6.11	0.28	5.83	0.010	5.16	4.56
CaAl-900	3.69	0.56	3.13	0.0057	6.03	4.69
CaMgAl-LDH	9.80	7.86	1.94	0.042	29.22	17.50
CaMgAl-500	7.36	0.21	7.15	0.050	23.17	19.16
CaMgAl-900	6.51	0.06	6.45	0.031	17.92	15.04

Note: S_{BET} is the BET surface area, t-MA is the t-plot Micropore area, t-ESA is the t-Plot external surface area, V is the total pore volume, and D_a and D_d are the Barrett-Joyner-Halenda (BJH) pore size calculated from the adsorption and desorption branches.