Electronic Supplementary Material (ESI) for Dalton Transactions.

Surface modification of aqueous miscible organic layered double hydroxides (AMO-LDHs)

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1. General details

1.1 Materials

Triethoxyvinylsilane (TEVS, ≥98%) was purchased from Merck Millipore; Triethoxy(octyl) silane (TEOS, ≥97.5%), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$, AR); Aluminum nitrate nonahydrate ($Al(NO_3)_3){\cdot}9H_2O$, AR); Sodium hydroxide (NaOH, AR); Sodium carbonate (Na_2CO_3, AR); Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, AR), acetone, ethanol (≥99.8%) , (3-glycidyloxypropyl)trimethoxysilane (TMGPS, ≥98%), and Tetrakis(trimethylsilyl)silane (TMS, ≥97%) were purchased from Sigma Aldrich and used as received.

1.2 Characterisation

1.2.1 Powder X-ray diffraction (XRD) data were collected on a PANAnalytical X'Pert Pro diffractometer in reflection mode at 40 kV and 40 mA using Cu Kα radiation (α_1 = 1.54057 Å, α_2 = 1.54433 Å, weighted average = 1.54178 Å).

1.2.2 Thermogravimetric analyses (TGA) was carried out on a Mettler Toledo TGA/DSC 1 system. Samples (10 mg) were heated in an alumina crucible from 25 to 800 °C (at 5 °C min^{-1}) under N_2 flowing at 100 cm^3 min^{-1}.

1.2.3 Specific surface areas and **pore volume** were analysed using the Brunauer–Emmett–Teller (BET) method. The samples were measured from the N_2 adsorption and desorption isotherms at 77 K collected from a Micromeritics TriStar II plus. Before each measurement, LDH samples were first degassed overnight at 110 °C.

1.2.4 Solution ^{1}H NMR Spectroscopy was recorded on a Bruker Avance III HD nanobay NMR spectrometer equipped with a 9.4T magnet at 400 MHz.

1.2.5 Solid-state NMR spectroscopy was recorded on a Varian Chemagnetics CMX Infinity 200 (4.7 T). Samples were packed in 7.5 mm zirconia rotors. A double resonance MAS probe was used for all measurements and a MAS rate of 15 kHz was used for ^{27}Al. ^{27}Al MAS DP-MAS NMR spectra were acquired with a single pulse excitation applied using a short pulse length (0.7 μs). Each spectrum resulted from 2000 scans separated by 1 s delay. ^{13}C CPMAS NMR spectra were measured at a MAS rate of 10 kHz.

1.2.6 Transmission Electron Microscopy (TEM) All TEM images were obtained on a JEOL 2100 microscope with an accelerating voltage of 200 kV. Samples were prepared by dispersing particles in water or ethanol via sonication for 1 hour before casting onto carbon-coated copper grids.

1.3 Moisture measurement

The moisture measurement was tested according to a modified Callahan's method. The water vapour uptake was tested in a sealed box at room temperature (20 °C). The relative humidity of RH99, RH70 and RH60 were generated by saturated solution of KNO_3, NaCl and $Mg(NO_3)_2$, respectively, monitored by electrical moisture meter. The detail measurement procedure is shown as below: in order to have zero baselines for comparison, all samples (around 200 mg) was dehydrated in an oven at 180 °C before moisture adsorption test. After 6 h of heating, the crucible with the sample was caped and cooled in a desiccator under vacuum. Weight a clean and dry vial with cap as *M0*. The dried and cooled sample was transferred into the vial and weight together with the vial and cap as $M1$. The vial containing sample (named as sample vial) without cap is put in the sealed humidity box. At certain interval time, the vial is taken out and closed with the cap immediately. Record the weight of the sample vial with cap as *Mi*. In order to compare samples fairly, the water vapour uptake of all the samples are based on dry basis. The water vapour uptake can be calculated by

$$Moisture\ capacity\ wt\%\ of\ dry\ LDH\ = \frac{Mi - M1}{M1 - M0} \times 100\%$$

2 Supplementary characterisation data

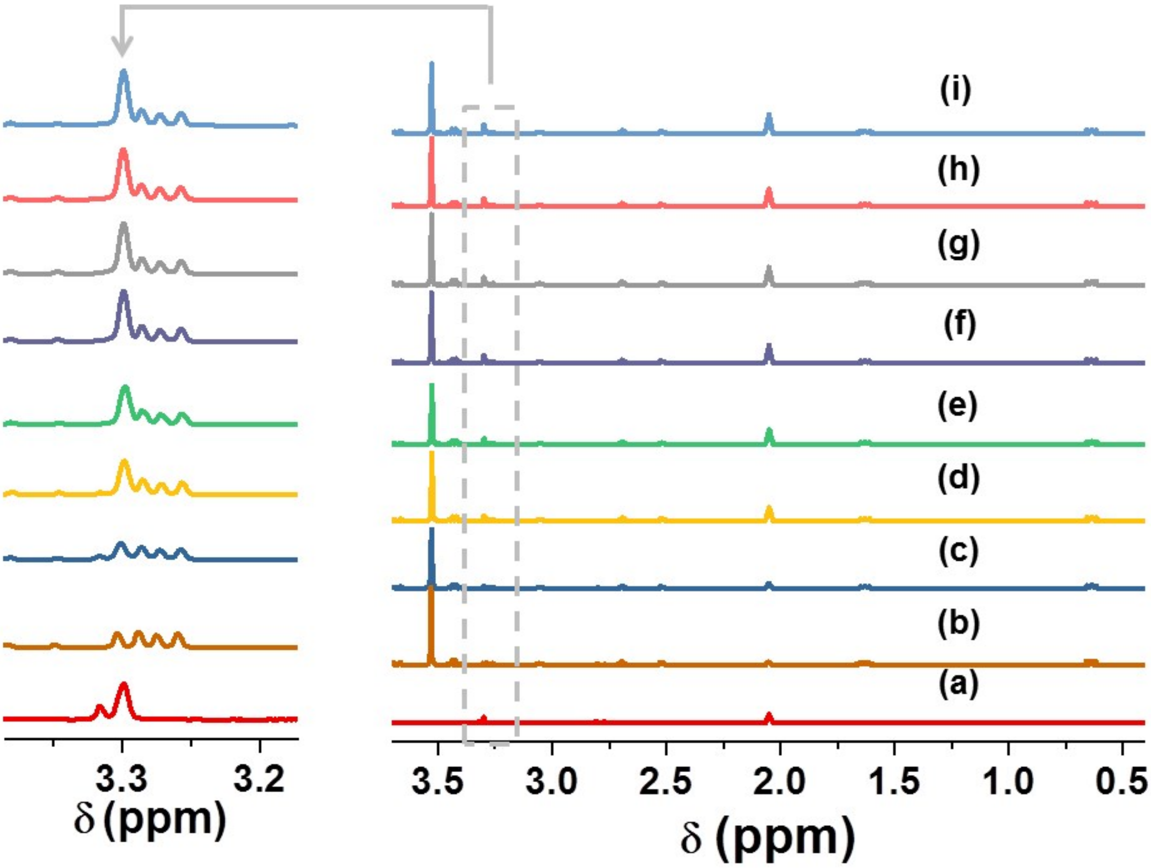


Fig. S1 ^{1}H NMR spectra of (a) methanol, (b) TMGPS, AMO-Zn_2MgAl-CO_3-LDH-TMGPS at (c) RT for 6 h, at 60 °C for (d) 3 h, (e) 10 h, (f) 26 h, (g) 29 h, (h) 35 h and (i) 68 h in acetone-d_6.

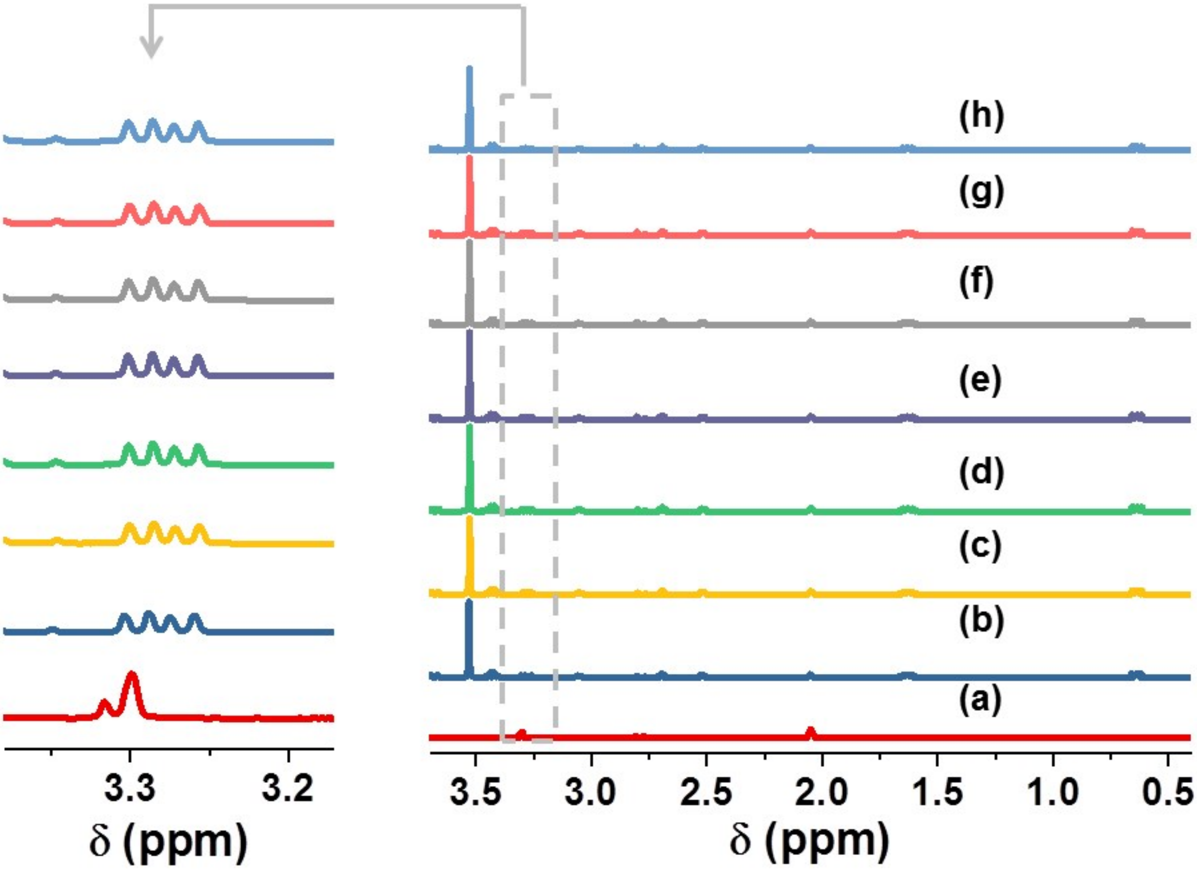


Fig. S2 ^{1}H NMR spectra of (a) methanol, TMGPS at (b) RT and at 60 °C for (c) 3 h, (d) 10 h, (e) 26 h, (f) 29 h, (g) 35 h and (h) 68 h in acetone-d_6.

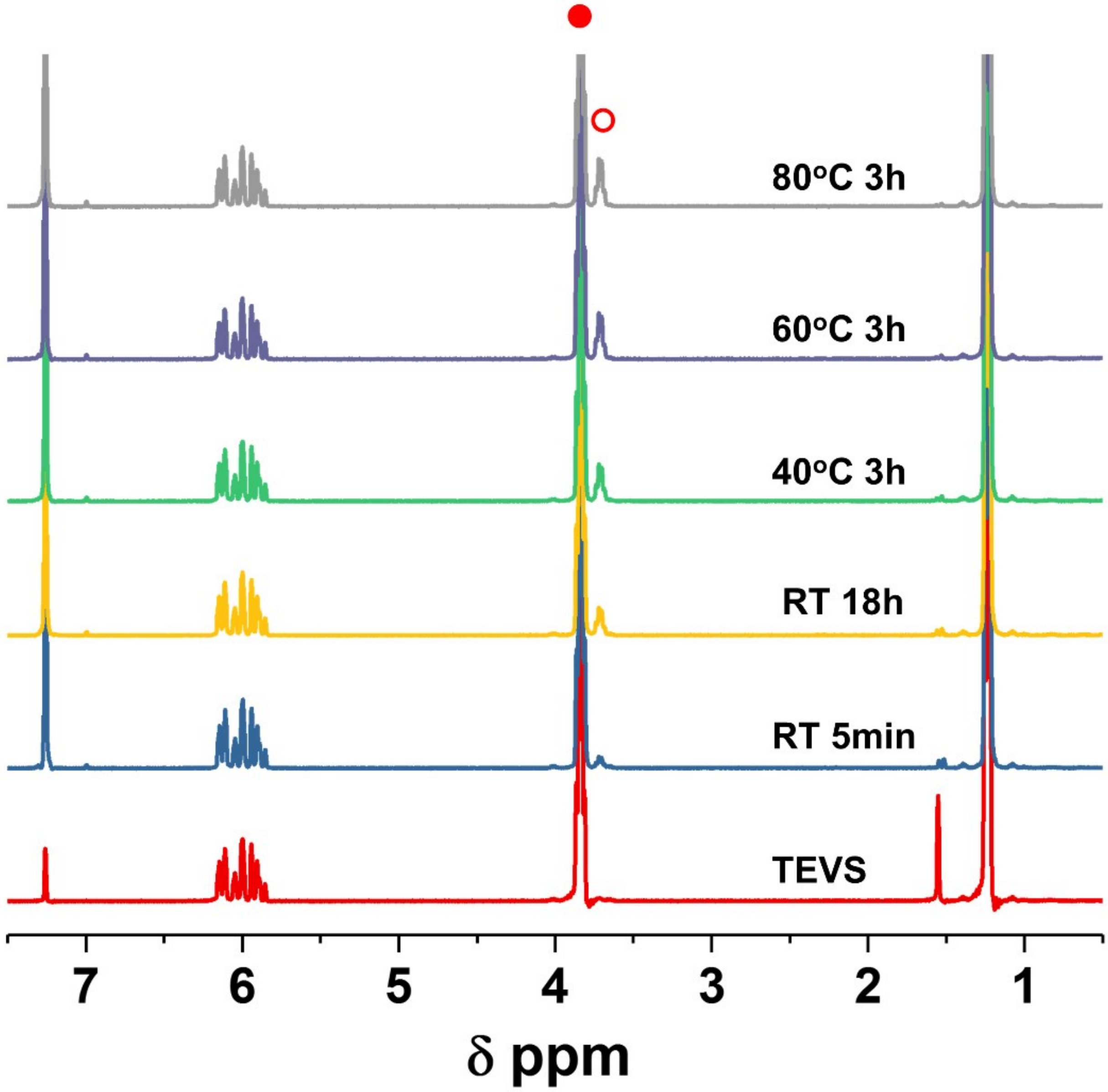
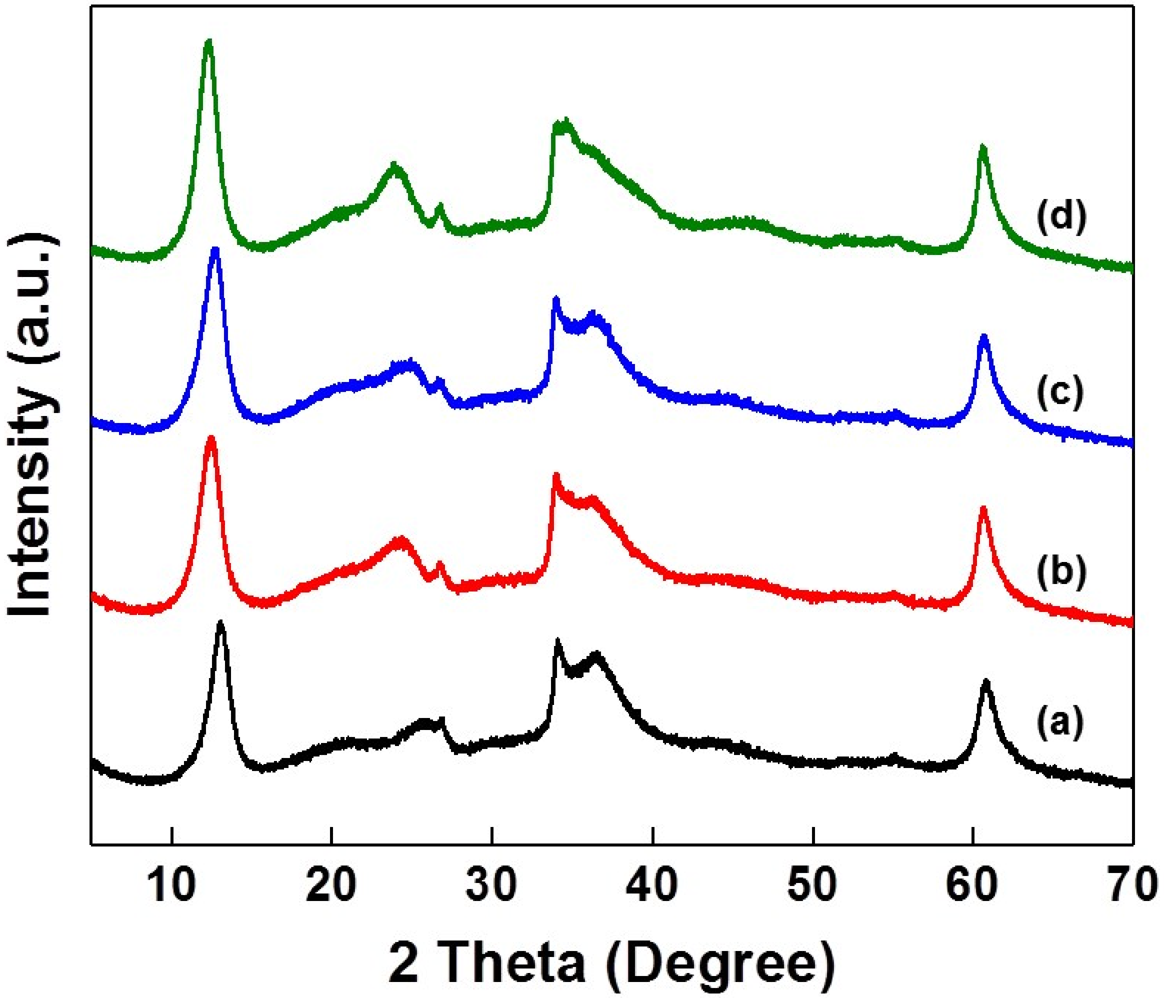


Fig. S3 ^{1}H NMR spectra of AMO-Mg$_3$Al-CO$_3$-LDH-TEVS reaction in chloroform-d_1 at various temperatures. Solid circle • is resonance of CH$_3$- in TVES, hollow circle o is the resonance of -CH$_2$- in ethanol.


Intensity (a.u.)
(d)
(c)
(b)
(a)
10
20
30
40
50
60
70
2 Theta (Degree)

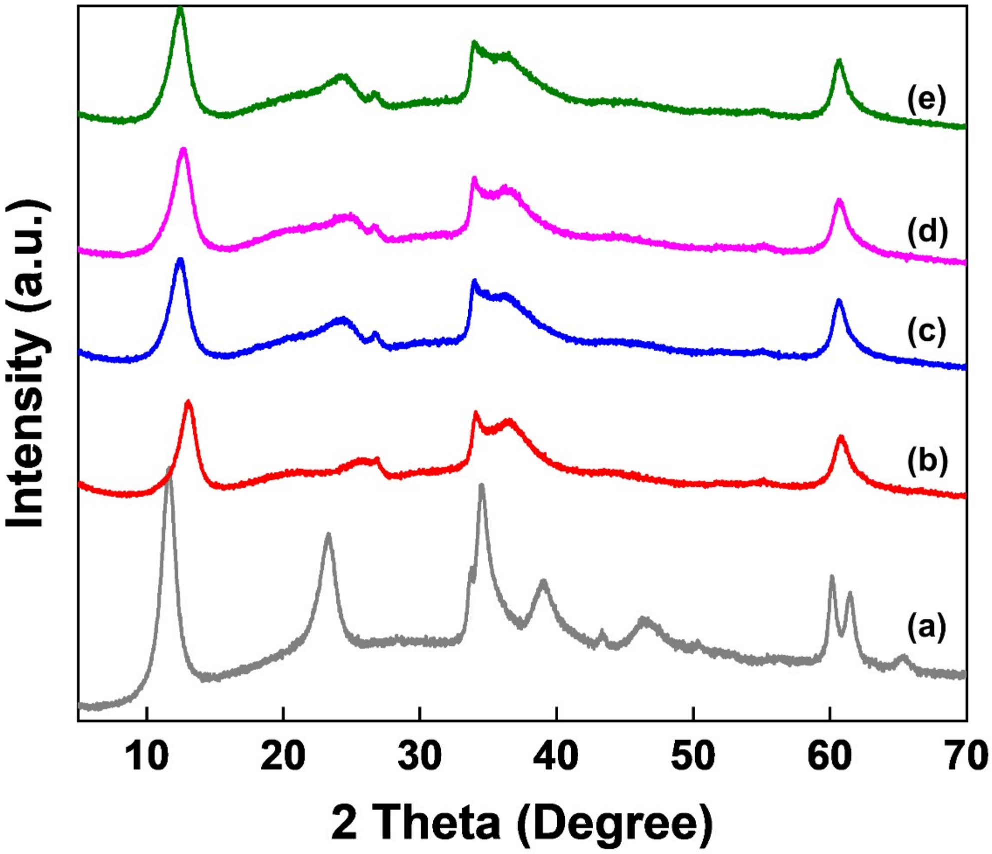


Fig. S4 XRD patterns of (a) AMO-Zn_2MgAl-CO_3 LDH, (b) AMO-Zn_2MgAl-CO_3 LDH (after thermal treatment at 180 °C), (~~b~~c) TEVS modified AMO-Zn_2MgAl-CO_3 LDH, (~~c~~d) TEOS modified AMO-Zn_2MgAl-CO_3 LDH, and (~~d~~e) TMGPS modified AMO-Zn_2MgAl-CO_3 LDH.

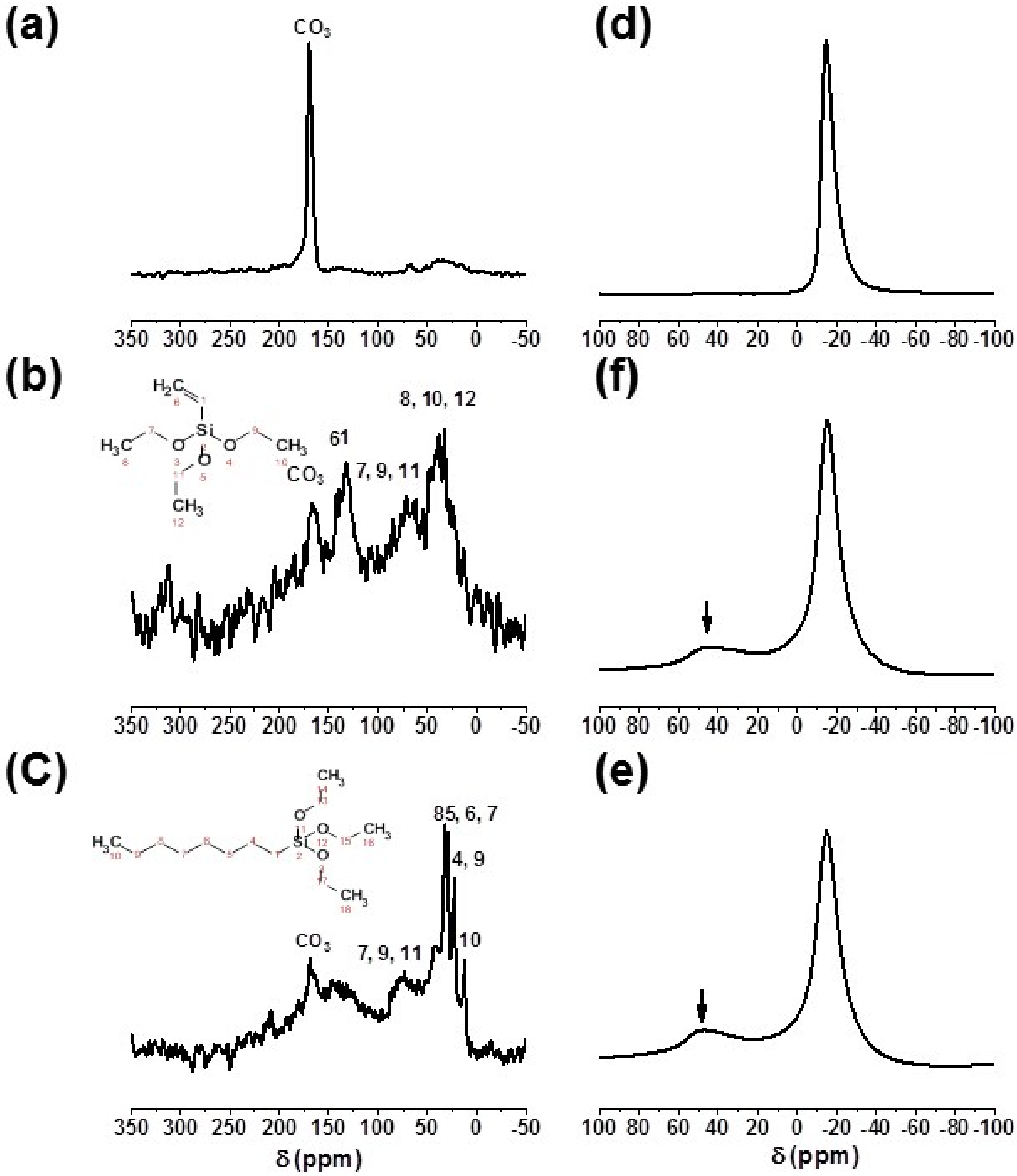


Fig. S5 Solid-state ^{13}C CP-MAS NMR spectra of (a) AMO-Zn_2MgAl-CO_3 LDH, (b) TEVS modified AMO-Zn_2MgAl-CO_3 LDH, (c) TEOS modified AMO-Zn_2MgAl-CO_3 LDH, and solid-state ^{27}Al DP-MAS NMR spectra of (d) AMO-Zn_2MgAl-CO_3 LDH, (e) TEOS modified AMO-Zn_2MgAl-CO_3 LDH and (f) TEVS modified AMO-Zn_2MgAl-CO_3 LDH.

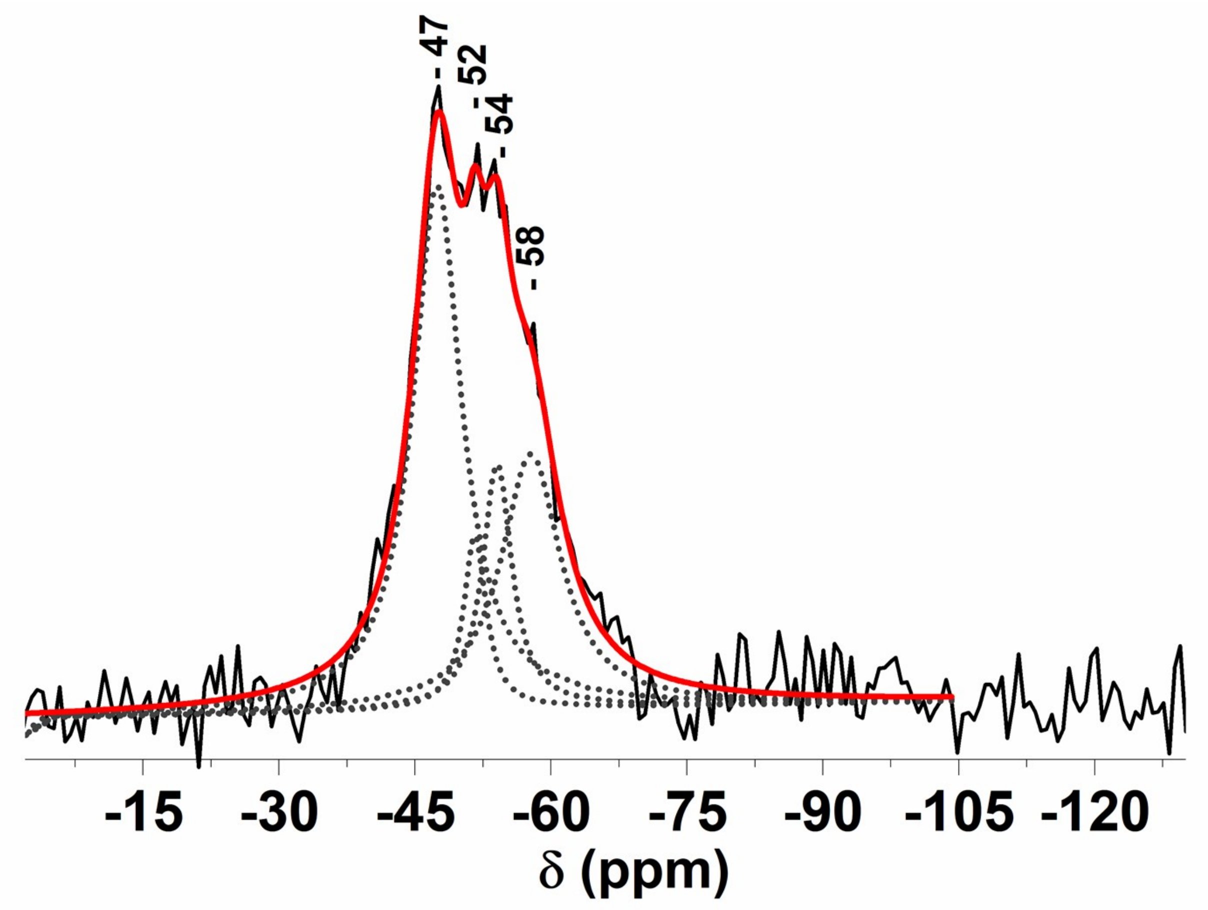


Fig. S6 Solid-state ^{29}Si CP-MAS NMR spectra of TMGPS modified AMO-Zn_2MgAl-CO_3 LDH (the black solid line is the original raw data; the red solid line is the cumulative fit curve and the short dot line are the individual fit curves using Lorentz function).

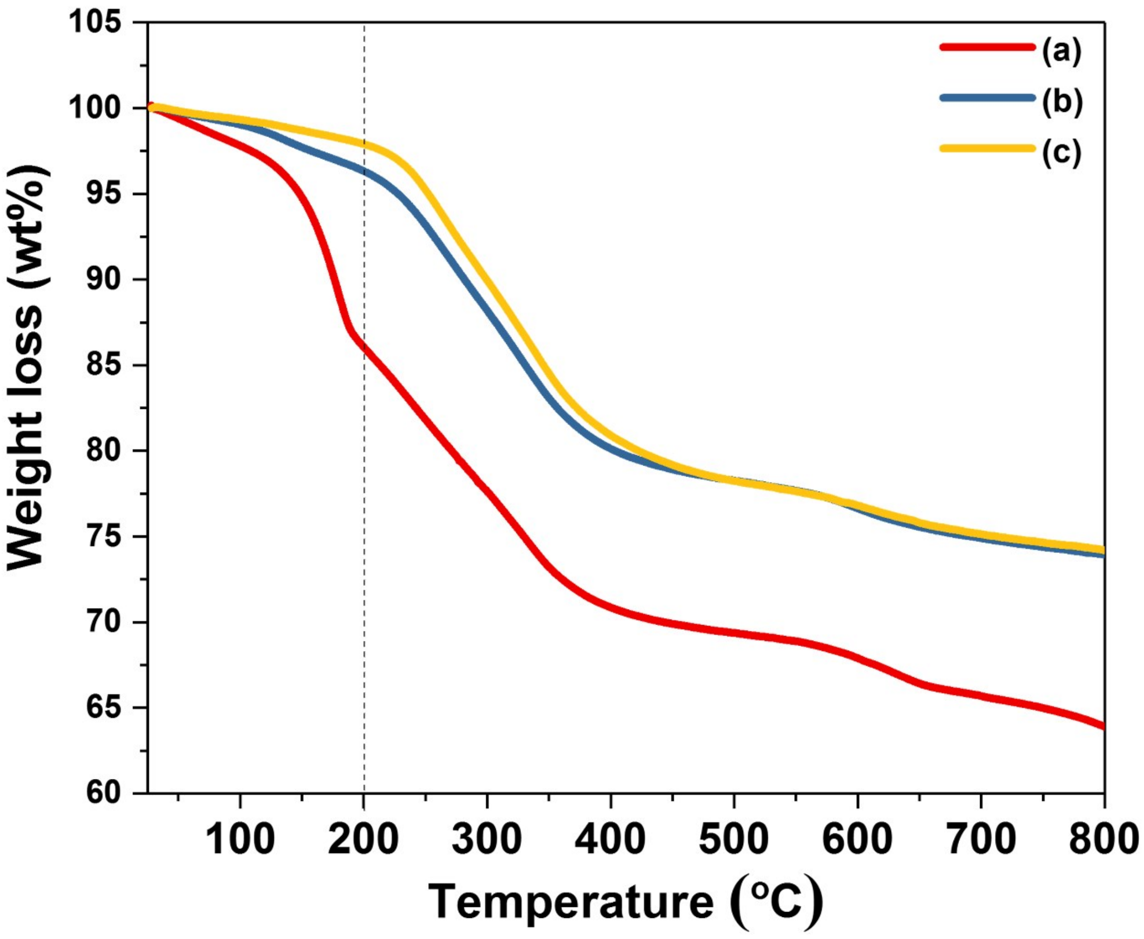


Fig. S7 TGA patterns of (a) AMO-Zn_2MgAl-CO_3 LDH, (b) TEVS modified AMO-Zn_2MgAl-CO_3 LDH and (c) TEOS modified AMO-Zn_2MgAl-CO_3 LDH.

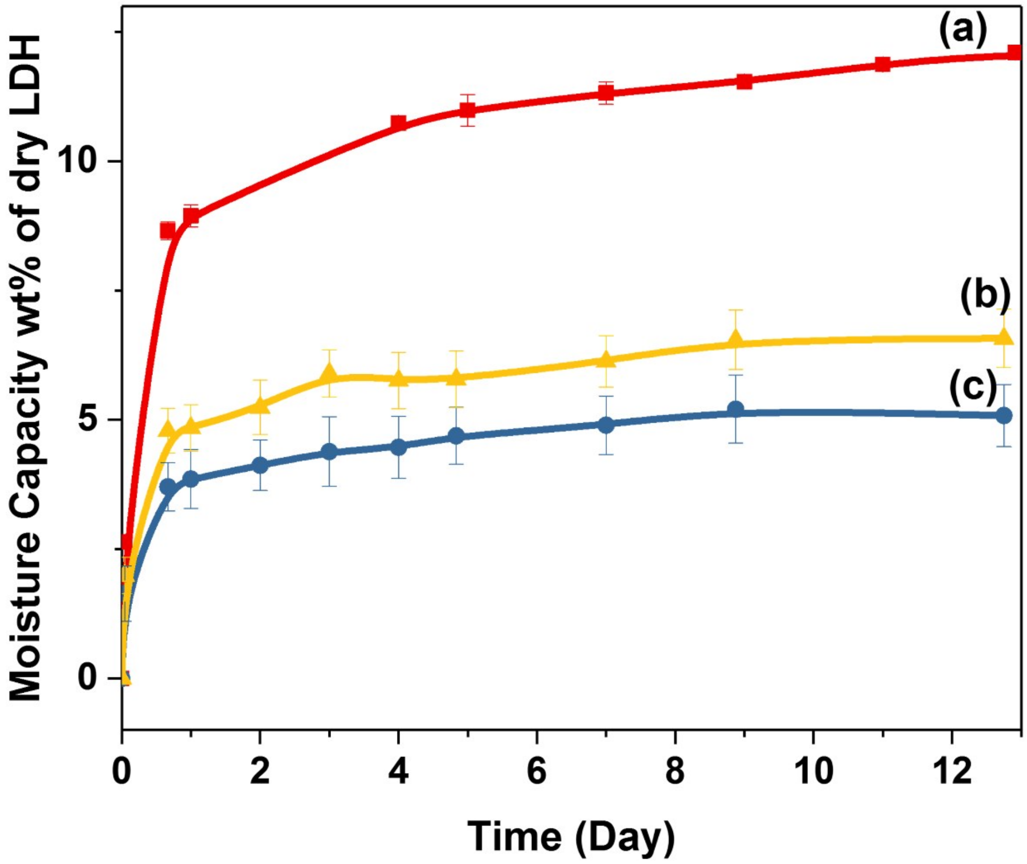


Fig. S8 Water vapour uptake of (a) AMO-Zn_2MgAl-CO_3 LDH, (b) TEVS modified AMO-Zn_2MgAl-CO_3 LDH, and (c) TEOS modified AMO-Zn_2MgAl-CO_3 LDH.

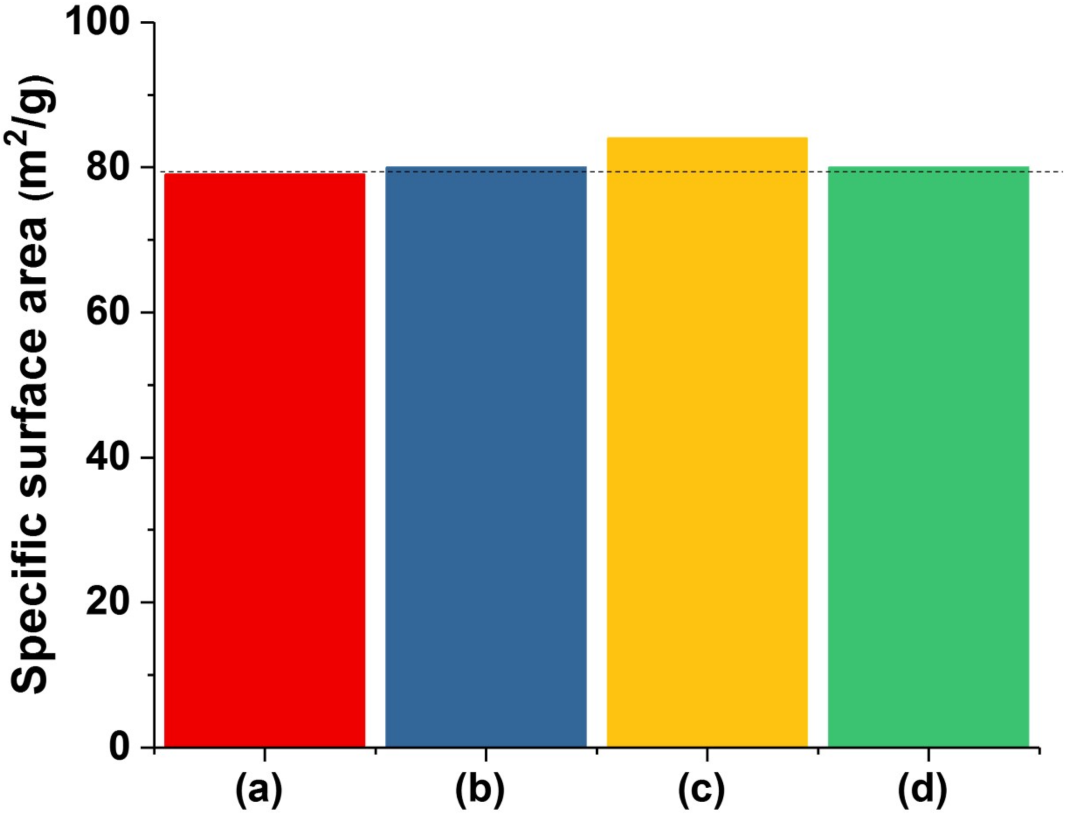


Fig. S9 Specific surface area of (a) AMO-Zn_2MgAl-CO_3 LDH, (b) TEVS modified AMO-Zn_2MgAl-CO_3 LDH, and (c) TEOS modified AMO-Zn_2MgAl-CO_3 LDH, and (d) TMGPS modified AMO-Zn_2MgAl-CO_3 LDH.

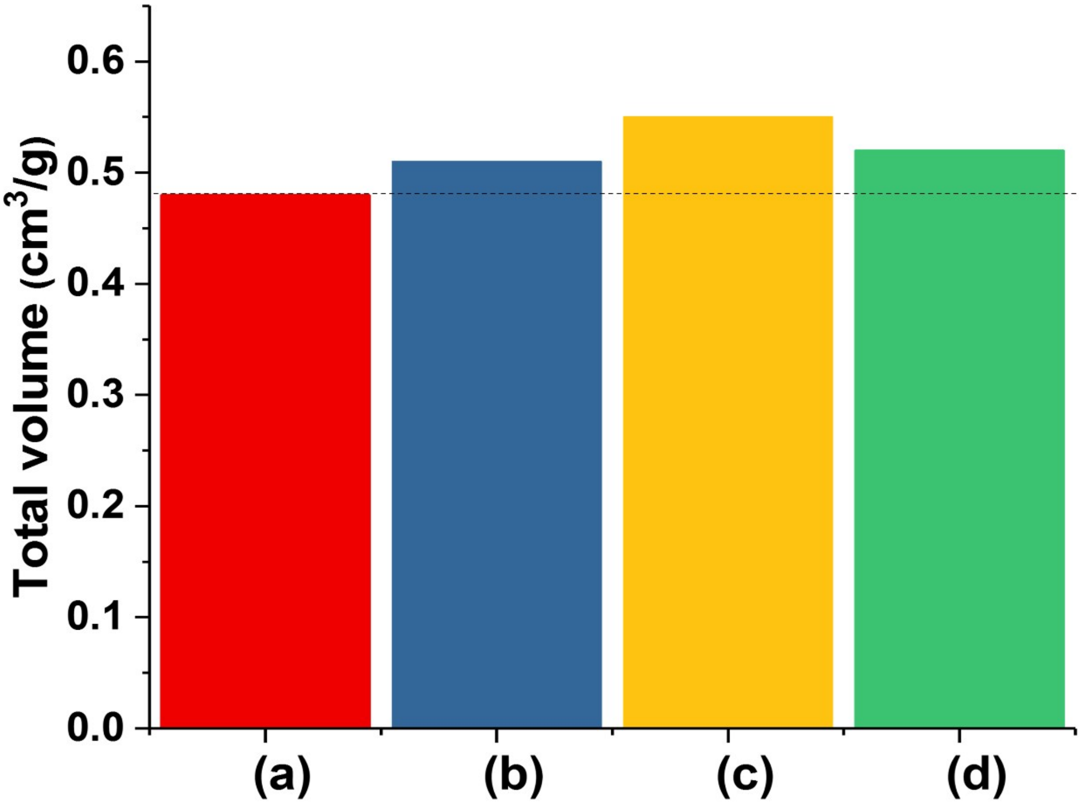


Fig. S10 Total pore volume of (a) AMO-Zn_2MgAl-CO_3 LDH, (b) TEVS modified AMO-Zn_2MgAl-CO_3 LDH, and (c) TEOS modified AMO-Zn_2MgAl-CO_3 LDH, and (d) TMGPS modified AMO-Zn_2MgAl-CO_3 LDH.

Table S1. The lattice parameters of AMO-LDHs before and after silane-modification.

LDH	**Modifier**	**d spacing (Å)**		**Lattice parameter (Å)**	
		d (003)	**d (110)**	***c***	***a***
AMO-Zn_2MgAl-CO_3 LDH	None	6.80	1.52	20.4	3.05
	TMGPS	7.23	1.52	21.7	3.05
	TEVS	7.15	1.52	21.5	3.05
	TEOS	7.03	1.52	21.1	3.05

Table S2. Summary of Solid-state ^{29}Si CP-MAS NMR spectra of TMGPS modified AMO-Zn_2MgAl-CO_3LDH.

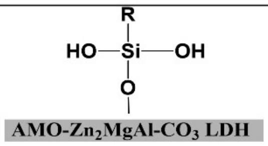
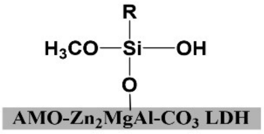
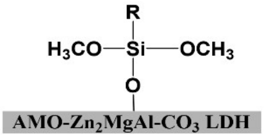
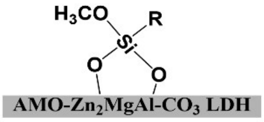
Chemical shift (ppm)	**Relative population (%)**	**Assignment**	**T^n notation**	**Scheme**
- 47	49	Hydrolyzed monodentate 1	T^1	
- 52	8	Hydrolyzed monodentate 2	T^1	
- 54	14	Monodentate	T^1	
- 58	29	Bidentate	T^2	

Table S3. The water content and water vapor adsorption capacity of all samples

LDH	**Modifier**	**Water content (wt%)***	**Water vapor adsorption capacity (wt% of dry LDH)**
AMO-Zn_2MgAl-CO_3 LDH	None	14	12
	TMGPS	4	4.4
	TEVS	3.6	5
	TEOS	2.1	6.6

* water content is the release of water when it is heated up to 200 °C, obtained from TGA.