

Synthesis of well-crystallized Cu-rich layered double hydroxides and improved catalytic performances for water-gas shift reaction

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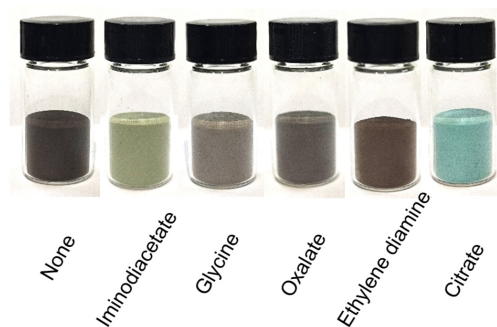


Figure S1. Images of the Cu-Mg-Al LDH samples prepared by using different competitive ligands.

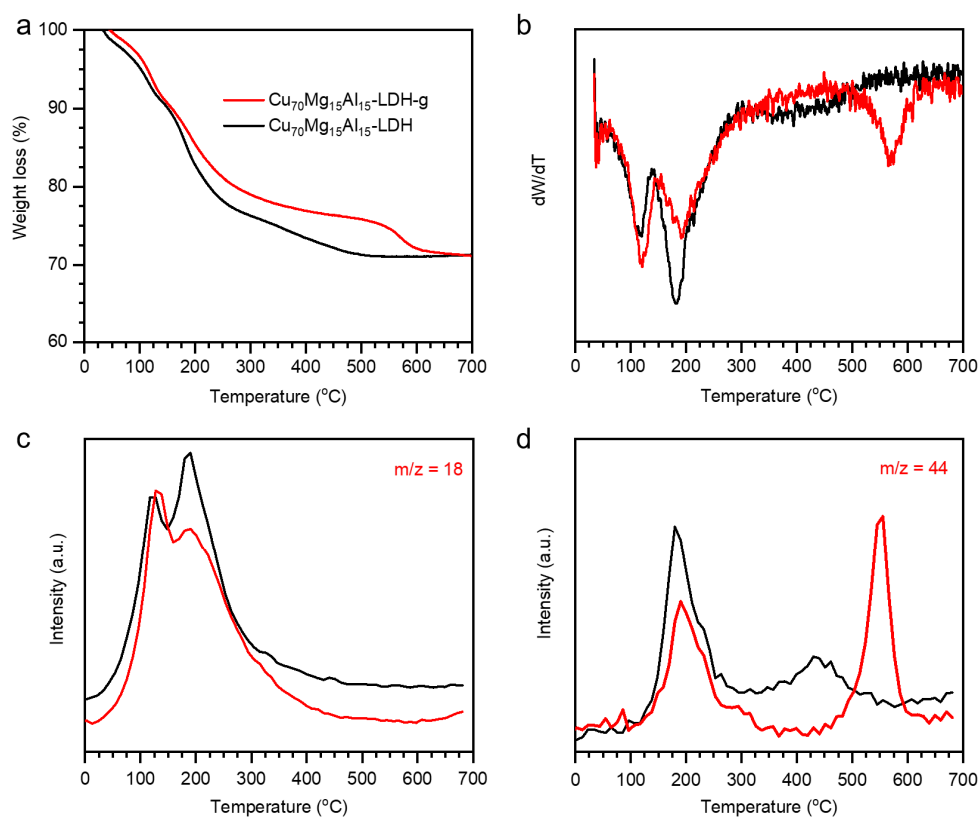


Figure S2. Thermogravimetry-mass (TG-MS) profiles of the $\text{Cu}_{70}\text{Mg}_{15}\text{Al}_{15}\text{-LDH-g}$ and $\text{Cu}_{70}\text{Mg}_{15}\text{Al}_{15}\text{-LDH}$ samples. (a) TG curves, (b) derivative thermogravimetry (DTG) curves, (c) MS curves of $m/z=18$, (c) MS curves of $m/z=44$. These measurements were carried out using a thermogravimetry-mass spectrum coupling instrument (NETZSCH STA 449F3, QMS 403C Aëolos). About 3 mg of sample was loaded into the TG analyzer, and the temperature was programmed to 700 $^{\circ}\text{C}$ at the rate of 10 $^{\circ}\text{C}/\text{min}$ in 40 sccm N_2 flow. TG, DTG, and MS profiles could be simultaneously obtained.

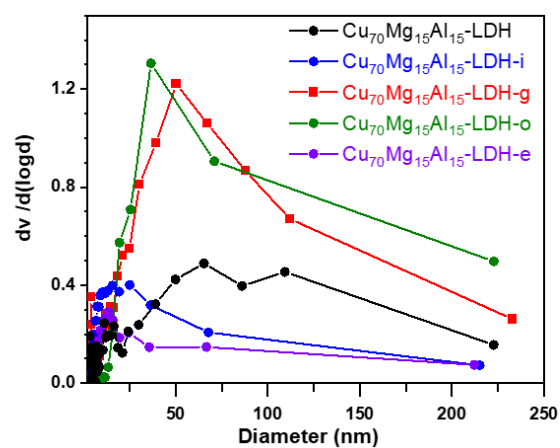


Figure S3. Effect of different competitive ligands on pore size distribution of the calcined Cu-Mg-Al LDH samples.

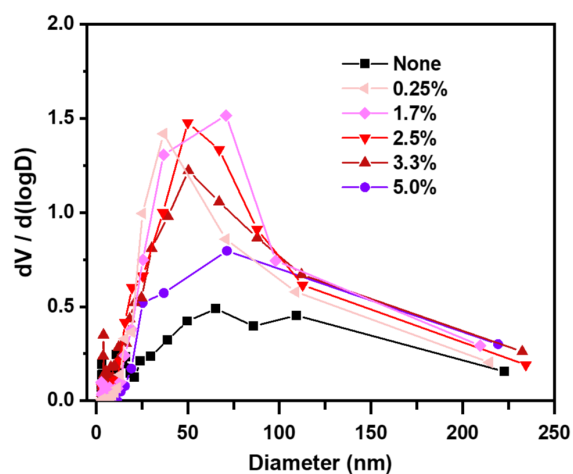


Figure S4. Pore size distribution of the calcined Cu-Mg-Al LDH samples prepared by adding different amount of glycine during the precipitation process.

Table S1. Metal contents of the calcined Cu-Mg-Al LDH samples prepared by adding different amount of glycine ^a

Glycine-adding ratio	Glycine : total metal ^b (mol : mol)	Detected contents by ICP-OES (mmol·g ⁻¹) ^c			Content (wt.%) ^d		
		Cu	Mg	Al	Cu	MgO	Al ₂ O ₃
0	0 : 0.06	9.73	0.79	2.14	81.4	4.2	14.4
0.25%	0.00015 : 0.06	10.46	0.94	2.01	82.6	4.7	12.7
1.7%	0.001 : 0.06	11.03	1.30	2.08	81.6	6.1	12.3
2.5%	0.0015 : 0.06	9.85	1.28	2.06	80.0	6.6	13.4
3.3%	0.002 : 0.06	9.94	1.61	2.04	78.9	8.1	13.0
5.0%	0.003 : 0.06	10.83	1.23	2.06	81.7	5.9	12.5

a. Metal content of the samples was measured by the inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Avio 200). The samples were dissolved with nitrohydrochloric acid before testing.

b. It presents the glycine-adding amount and the total metal amount ($n_{\text{Cu}}+n_{\text{Mg}}+n_{\text{Al}}$) used in the preparation process.

c. These data show the amount of corresponding metal contained per gram of sample.

d. The contents of different compositions were calculated based on the ICP-OES results, and normalized to three components: Cu, MgO and Al₂O₃.

Table S2 The stability constant of Cu²⁺ complexes ^a

Coordination reaction	Stability constant (lg β)				Referen ce
	lg β_1	Lg β_2	Lg β_3	Lg β_4	
$\text{Cu}^{2+} + x \text{OH}^- \rightleftharpoons \text{Cu}(\text{OH})_x^{2-x}$	6.5	11.8	14.5	15.6	[39]
$\text{Cu}^{2+} + x \text{glycine} \rightleftharpoons \text{Cu}(\text{glycine})_x^{2+}$	8.57	15.3			[39]
$\text{Cu}^{2+} + x \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_x^{2+}$	4.18	7.70	10.46	12.52	[48]
$\text{Cu}^{2+} + x \text{CH}_3\text{COO}^- \rightleftharpoons \text{Cu}(\text{CH}_3\text{COO})_x^{2-x}$	2.21	3.63			[39]
$\text{Cu}^{2+} + x \text{EDA}^b \rightleftharpoons \text{Cu}(\text{EDA})_x^2$	10.5	19.6			[39]

^a 25 °C, $I = 0$. ^b EDA is ethylenediamine (H₂N-CH₂-CH₂-NH₂).

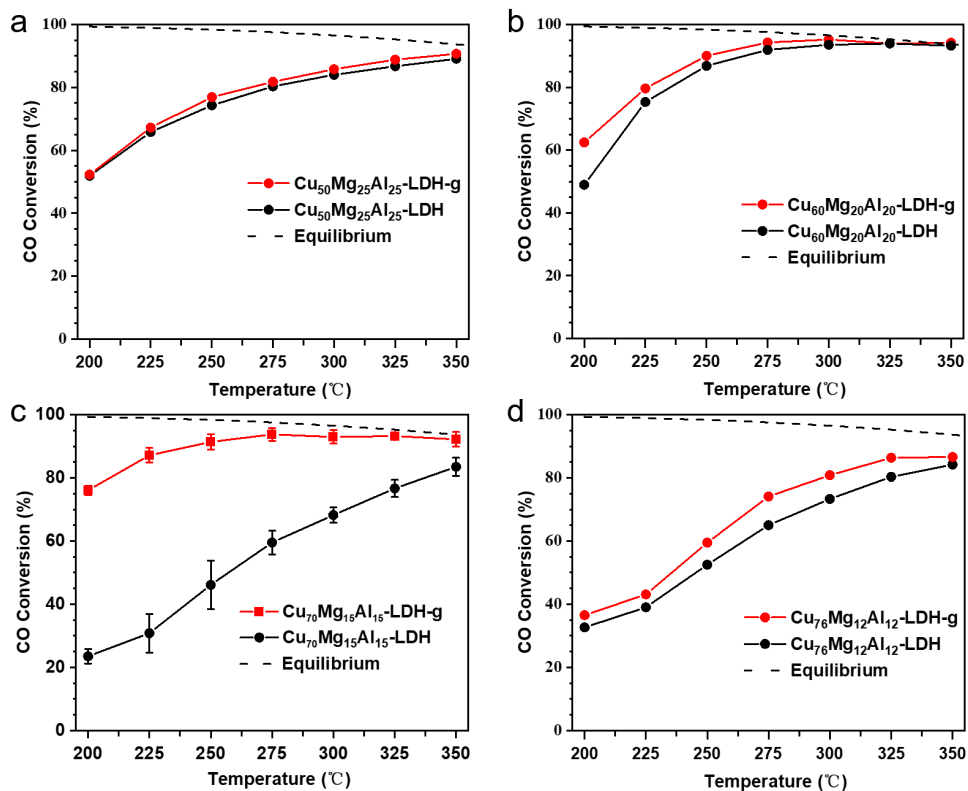


Figure S5. Effect of Cu content on the WGS catalytic performance of the catalysts with/without adding glycine during the coprecipitation process. The glycine-adding amount is 2.5 % of total metal amount ($n_{\text{ligand}}/(n_{\text{Cu}}+n_{\text{Mg}}+n_{\text{Al}}) = 0.025$). Data in Fig S5c are the mean value from three repeat experiments, and error bars are based on the standard deviation from the mean values.

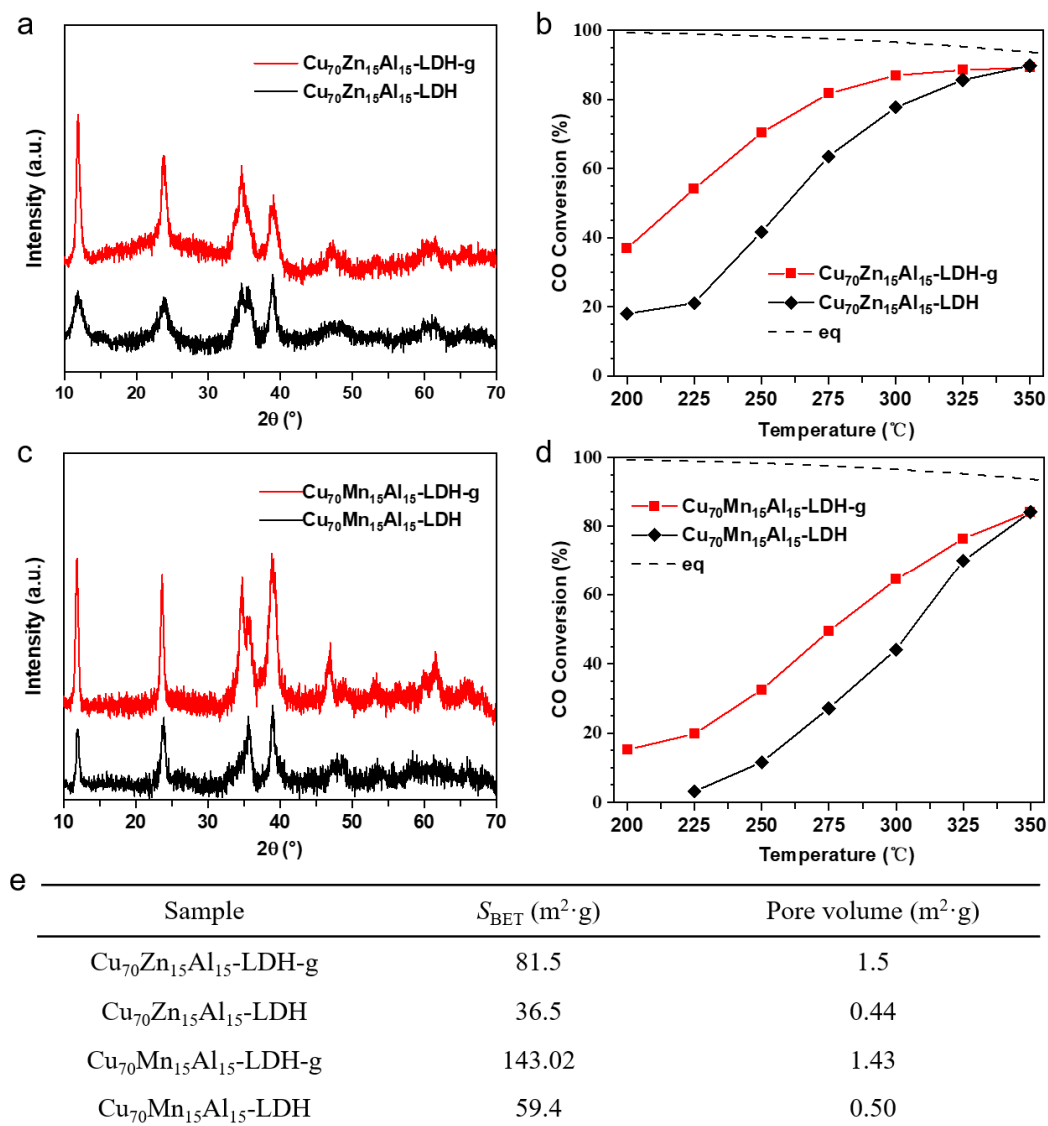


Figure S6. The XRD patterns and CO conversion of WGS for the Cu-Zn-Al LDH and Cu-Mn-Al LDH samples with/without adding glycine ligand in the prepared process. The Cu-Zn-Al LDH and Cu-Mn-Al LDH samples were prepared with the same process and named with the same rule in the experimental section of the main text. WGS conditions: CO/H₂/CO₂/N₂ = 14.6:27.0:9.2:49.2 (molar ratio), 50 mg catalyst, WHSV = 24000 mL·g⁻¹·h⁻¹ (dry-gas base), CO/H₂O = 1/4.

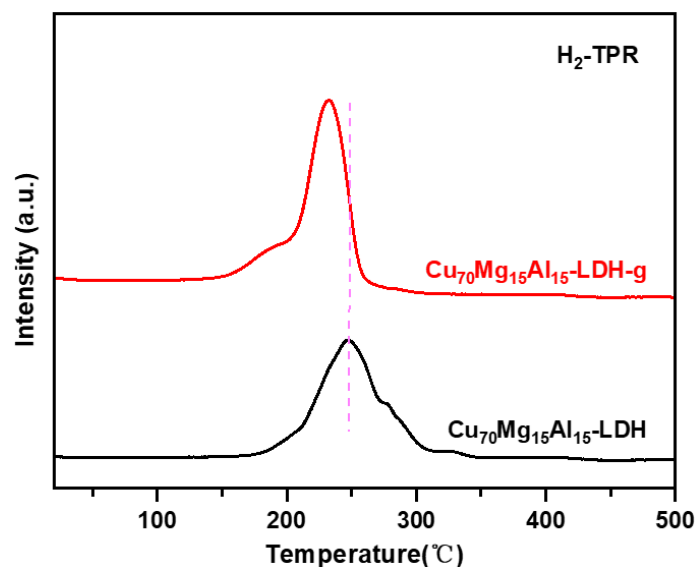


Figure S7. Hydrogen temperature-programmed reduction (H_2 -TPR) of the $\text{Cu}_{70}\text{Mg}_{15}\text{Al}_{15}\text{-LDH-g}$ (adding 2.5% glycine) and $\text{Cu}_{70}\text{Mg}_{15}\text{Al}_{15}\text{-LDH}$ catalysts. Experimental method: 50 mg of the catalyst sample was sealed in a quartz tube reactor and pretreated in Ar atmosphere at 400 °C for 1 h, followed by reduction in a stream of H_2/Ar (1:9, v/v; a total flow rate of $30 \text{ mL} \cdot \text{min}^{-1}$) with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Table S3. Fitting parameters for O 1s-region and $\text{Cu}2\text{p}_{3/2}$ -region of XPS spectra

Catalysts	Peak	Position (eV)	Percentage (%)	$\text{O}_\text{I}/\text{O}_\text{II}$ or $(\text{Cu}+\text{Cu}_2\text{O}) / (\text{CuO}+(\text{Cu}+\text{Cu}_2\text{O}))$
CuMgAl-LDH-g	O_I	531.7	0.63	1.7
	O_II	530.4	0.37	
CuMgAl-LDH	O_I	532.0	0.48	0.92
	O_II	530.4	0.52	
CuMgAl-LDH-g	CuO	934.0	0.23	3.3
	$\text{Cu}+\text{Cu}_2\text{O}$	932.1	0.77	
CuMgAl-LDH	CuO	934.4	0.31	2.2
	$\text{Cu}+\text{Cu}_2\text{O}$	932.4	0.69	

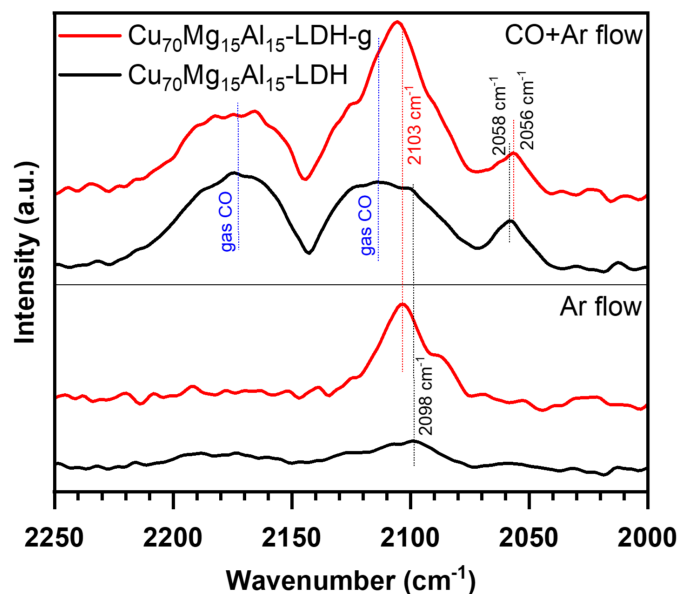


Figure S8. CO- DRIFT spectra for the Cu₇₀Mg₁₅Al₁₅-LDH-g (adding 2.5% glycine) and Cu₇₀Mg₁₅Al₁₅-LDH catalysts. All of the in-situ DRIFTS spectra were collected by using a Bruker TENSOR27 FTIR spectrometer. About 10 mg of the catalyst was reduced in-situ in H₂ flow at 300 °C for 0.5 h in the reaction cell before the test. After the temperature cooled to 30 °C, a mixture gas (CO : Ar = 5 : 95, 30 mL·min⁻¹) is introduced and the spectra in “CO+Ar” flow was recorded after 5 min adsorption. Then pure Ar is introduced, and the data in Ar flow is recorded after 5 min purge.

The vibrational bands at 2103 and 2098 cm⁻¹ should be arising from CO adsorbed at the defective sites of Cu(111) facets [41,47]. The vibrational bands at 2058 and 2056 cm⁻¹ should be arising from CO adsorbed at the terrace sites of Cu(111) facets [41,47]. A 5 cm⁻¹ blue shift, from 2098 cm⁻¹ in the Cu₇₀Mg₁₅Al₁₅-LDH catalyst to 2103 cm⁻¹ in the Cu₇₀Mg₁₅Al₁₅-LDH-g catalyst is observed, suggesting a strong electron transfer between Cu species and oxide supports [22].

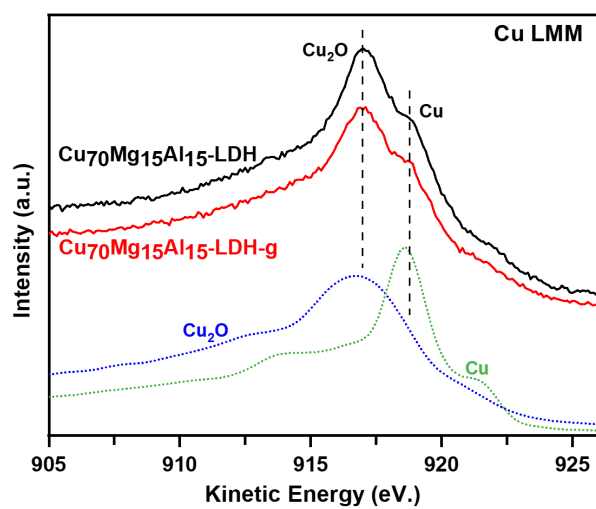


Figure S9. The Auger spectra of Cu LMM for the catalysts after 24 h on stream at 300 °C in WGS reaction.