

Supporting Information

CO₂ hydrogenation to methanol over catalysts derived from single cationic layer CuZnGa LDH precursors

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Synthesis of the catalyst

Synthesis of CZG catalysts by the conventional co-precipitation: Ga^{3+} modified Cu/ZnO catalysts were synthesized using a pH-controlled co-precipitation method, and detailed description can be found elsewhere¹. Hydrated metal nitrate salts were used as the metal precursors: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), and $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich). For a typical preparation procedure, metal nitrates including 3.77g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 5.53g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.75g $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved completely in 100 mL deionized water. A Na_2CO_3 aqueous solution was made by dissolving 3.50 g of Na_2CO_3 in 100 mL of deionized water. The two solutions (metal nitrate solutions and Na_2CO_3 solution) were added simultaneously into a PTFE bottle containing 250 mL of preheated deionized water: A delivery pump with two 50 mL syringes was used to inject the precursor metal nitrate solution at a constant rate of $0.42 \text{ mL} \cdot \text{min}^{-1}$ in an automatic and reproducible manner. An HPLC pump was used to deliver the Na_2CO_3 solution at a rate of $0.35\text{-}0.70 \text{ mL} \cdot \text{min}^{-1}$. The mixture was stirred vigorously to ensure efficient mixing, while pH of the precipitating solution was carefully maintained at 6.5. Once the pre-measured amount of solutions was added into the PTFE bottle, the liquid was aged for 16h, then the precipitate was extracted by centrifugation at 5000 rpm. The centrifuged precipitate was washed with deionized water five times to remove residual Na^+ ions. The resulting wet solid was dried overnight in air at 80°C . The catalysts were labelled as CZ (referring to Cu/ZnO catalysts in the absence of Ga) and CZG x Ga (referring to Ga modified Cu/ZnO catalysts where x indicates the mol % of Ga), see Table S2 for details. A typical measured surface area of CZG5Ga was $84.59 \pm 0.07 \text{ m}^2 \text{g}^{-1}$. We also rinsed two equal portions of powders in acetone for 1h (CZG5Ga-A1) and 18h (CZG5Ga-A2) before they were dried. The measured surface areas were $82.11 \pm 0.10 \text{ m}^2 \text{g}^{-1}$ and $92.97 \pm 0.07 \text{ m}^2 \text{g}^{-1}$, respectively. The procedure for the synthesis is graphically summarized in Fig. S1.

Synthesis of AMO-LDH catalysts via base solution: The metal precursor solution (50 mL) including desired amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich) was added drop-wise into the 50 mL of 0.5 M Na_2CO_3 base solution under rapid stirring. During the nucleation step, the pH value was kept at *ca.* 10.0 by dropwise addition of a 4.0 M NaOH solution. After ageing for 16 h with stirring at room temperature, the mixture was filtered and washed with DI water until the pH was close to 7. The obtained wet cake solid sample was re-dispersed in 200 mL acetone and stirred at room temperature for 1-2 h. Then, the resultant solid was filtered, washed thoroughly with acetone and dried overnight in a vacuum oven at room temperature. The samples were labelled as LDH x Ga where x indicates the mole % of Ga in the synthesis recipe (see Table S2). These washed samples were characterized by XRD or SXRD. The super-fine portions of the washed samples were kept for catalysis use and TEM/AFM characterisation. As similar to the literature, the powder sample with and without acetone treatment showed a large difference in their surface area per gram basis². Typically, the surface areas of LDH30Ga-ww (ww: water washed, no acetone treatment) and LDH30Ga-Aw (Aw: acetone washed) were determined as $36.51 \pm 0.10 \text{ m}^2 \text{g}^{-1}$ and $158.71 \pm 0.17 \text{ m}^2 \text{g}^{-1}$, respectively. The synthesis recipes can be found in Table S2 and the procedure for the synthesis is graphically summarized in Fig. S2.

Calcination of Catalyst Precursors: All precursor materials were calcined under constant air flow ($50 \text{ mL}\cdot\text{min}^{-1}$) at 330°C for 3 h (heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ followed by 1 hour of dwell at 80°C and 150°C) prior to be used.

Catalytic test in CO₂ hydrogenation reaction

Catalytic tests in hydrogenation of CO₂ to produce methanol were carried out in a tubular fixed bed reactor (12.7 mm outside diameter) using a 0.1 g calcined catalyst precursor. Before each test, the calcined catalyst precursor was reduced at 290°C for 2 h under atmospheric pressure with pure H₂ stream ($20 \text{ stp mL}\cdot\text{min}^{-1}$, stp = standard temperature and pressure; $P = 101.3 \text{ kPa}$, $T = 298 \text{ K}$). After the reduction, the temperature was cooled to below 50°C and the reactor was pressurized to 4.5 MPa with CO₂/H₂ (1:3 molar ratio) gas mixture. The activities of the catalysts were determined under a constant flow of CO₂/H₂ gas mixture through the catalyst bed ($30 \text{ stp mL}\cdot\text{min}^{-1}$) at desired temperatures ($190\text{--}310^\circ\text{C}$). The activity measurements were taken after at least 2 h on the stream at each selected reaction temperature. The products were quantitatively analysed by an Agilent 7890B gas chromatograph equipped with calibrated thermal conductivity detector (TCD) and flame ionization detector (FID).

Characterization Techniques

The powder X-ray diffraction (PXRD) data was collected by a Philips PW-1729 diffractometer with Bragg-Brentano focusing geometry using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) from a generator operating at 40 kV and 40 mA. Table S1 shows the phase symbol, chemical formula and PDF number which are used in this work.

Table S1 Phase symbol, chemical formula and PDF number which are used in this work.

Phase symbol	Formula	PDF#
A: aurichalcite	(Cu,Zn) ₅ (CO ₃) ₂ (OH) ₁₆	82-1253
M: Malachite	(Cu,Zn) ₂ (CO ₃)(OH) ₂	75-1163
Z: zincite	ZnO	36-1451
T: tenorite	CuO	05-0661
S: Spinel structure	ZnGa ₂ O ₄	86-0415
	CuGa ₂ O ₄	44-0183
#: Aluminum	Al	85-1327

High-resolution synchrotron X-ray diffraction (SXR) data were collected on Beamline I11, Diamond Light Source, UK. Detailed description of the beamline can be found elsewhere³. The energy of the incident X-ray beam was set at 15 keV. The wavelength and the 2 θ -zero point correction were refined using a diffraction pattern obtained from a high-quality silicon powder (SRM640c). At room temperature, the sample powder was loaded in a 0.1 mm borosilicate glass capillary. High-resolution SXR data were obtained from the samples using the multi-analyser crystal (MAC) detectors. The patterns were collected in the 2 θ range 0-150 ° with 0.001° data binning. Each pattern was collected for an hour for good statistics. In total, there were more than 100 *hkl* reflections measured, of which at least 72 independent *hkl* reflections were observed. The quality of the Pawley refinements of SXR data has been assured with a low goodness-of-fit (Gof) factor, a low weighted profile factor (R_{wp}) and a well fitted within experimental errors.

X-ray photoelectron spectroscopy (XPS) was performed on the reduced samples. The samples were calcined and then reduced before they were carefully sealed in a glove bag filled with nitrogen to prevent air exposure. The measurement was conducted using a Quantum 2000 Scanning ESCA Microprobe instrument (Physical Electronics) equipped with an Al K α X-ray radiation source ($h\nu = 1486.6$ eV). A flood gun with variable electron voltage (from 6 eV to 8 eV) was used for charge compensation. The raw data were corrected for substrate charging with the BE of the C peak (285 eV), as shown in the XPS handbook⁴. The measured spectra were fitted using a least-squares procedure to a product of Gaussian–Lorentzian functions after removing the background noise. The concentration of each element was calculated from the area of the corresponding peak and calibrated with the sensitivity factor of Wagner.

Temperature-programmed reduction (TPR) measurements were obtained using a ThermoQuest TPDRO 1100 instrument. Inside the TPR quartz tube, 0.026 g of the calcined catalyst sample was sandwiched between two layers of glass wool with a thermocouple placed in contact with the sample. The TPR tube was then inserted into the instrument for helium pretreatment. The helium gas pretreatment (He is running through the TPR tube at 10 mL·min⁻¹ at a temperature ramp of 10 °C·min⁻¹ from 40 to 150 °C, then held for 5 min before cooling) cleaned the catalyst surface by removing any absorbed ambient gas molecules. After the pretreatment, the reduction (5% H₂ in Argon flowing through the TPR tube at 20 mL·min⁻¹ at a temperature ramp of 10 °C min⁻¹ from 40 to 400 °C, then held at 400 °C for 30 min before cooling to room temperature) of catalysts was carried out to reduce the Cu²⁺ within the sample. Cu²⁺ and Cu⁺ were reduced to Cu⁰ by the flow of hydrogen gas in the reduction treatment. The consumption of hydrogen gas changed the conductivity of the gas stream; hence, the change in conductivity was measured and calibrated as a function of both temperature and time to produce the TPR profile.

The thermal decomposition of the freshly prepared catalyst precursors was studied by a thermogravimetric (TG) method using a SDT Q600 thermal analyzer. Measurements were performed in the temperature range of 20–800 °C under continuous flow of compressed air (100 mL·min⁻¹)

The surface area of the freshly prepared catalyst precursors was determined by N₂ adsorption-desorption at a liquid nitrogen temperature of −196 °C using the Micromeritics ASAP 2020M analyser. Sample degassing was carried out at 200 °C for 3 h prior to the acquisition of the adsorption isotherm. Calculations were conducted according to the Brunauer–Emmett–Teller (BET) method.

Elemental chemical analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS), NexION 300, PerkinElmer. The calcined samples were digested in nitric acid then diluted with MilliQ water prior to carrying out the experiments.

The dispersion (D_{Cu}) and exposed surface area (S_{Cu}) of Cu were determined by dissociative N₂O chemisorption followed by hydrogen pulse reduction. N₂O chemisorption was carried out on a Micromeritics AutoChem II 2920 instrument. Before the measurement, 100 mg of calcined sample was reduced at 350 °C in a 5% H₂/Ar mixture (50 mL·min^{−1}) for 4 h. After cooling to 60 °C, the sample was exposed to N₂O (20 mL·min^{−1}) for 1 h to ensure complete oxidation of surface metallic copper to Cu₂O. Finally, calibrated hydrogen pulse reduction at 300 °C was conducted to determine the amount of surface Cu₂O species. D_{Cu} and S_{Cu} were then calculated by dividing the amount of surface copper by the actual Cu loading determined by ICP-MS.

Transmission electron microscopy (TEM) images were taken using a JEOL 2010 TEM at 200 kV. The sample particles were deposited on an Agar Scientific holey carbon supported copper 400 mesh grid. TEM samples were prepared by sonicating a suitable amount of material in 1 mL ethanol for 15 minutes before dropwise addition of the solution onto the copper grid.

Atomic Force Microscopy (AFM) measurements were collected by Agilent 5400 microscope. AFM samples were prepared by deposition of fresh diluted emulsion of LDH samples onto a clean Si wafer by dip coating. The images were obtained with a Si tip cantilever (MikroMasch NSC35/ALBS) working with frequency and force constant of 150 kHz and 4.52 N·m^{−1}, respectively, using non-contact mode in air at room temperature. Images were recorded with 512 × 512 pixels and 0.5–1 Hz scan rate. Processing and analysis of the images were carried out using the PicoView version 1.20.2 software.

Supplementary Experimental Data

Table S2 Synthesis recipes and determined compositions for CZG and LDH derived samples

Catalysts	Synthesis recipe Cu:Zn:Ga (mol%)	Cu:Zn:Ga from ICP	
		Cu:Zn:Ga (wt%)	Cu:Zn:Ga (mol%)
CZ	40:60: 0	45:55: 0	44:55: 0
CZG5Ga	40:55: 5	43:51: 6	44:51: 5
CZG10Ga	40:50:10	44:46:10	45:45:10
CZG30Ga	40:30:30	44:26:30	45:26:29
CZG40Ga	40:20:40	42:17:41	43:18:39
LDH5Ga	40:55:5	42:54:4	43:53:4
LDH10Ga	40:50:10	43:50: 7	44:49: 7
LDH20Ga	40:40:20	44:41:15	45:41:14
LDH30Ga	40:30:30	45:32:23	47:32:21
LDH40Ga	40:20:40	47:22:31	49:22:29
LDH30Ga-ww	40:30:30	45:31:24	46:31:23

Synthesis: CZG samples

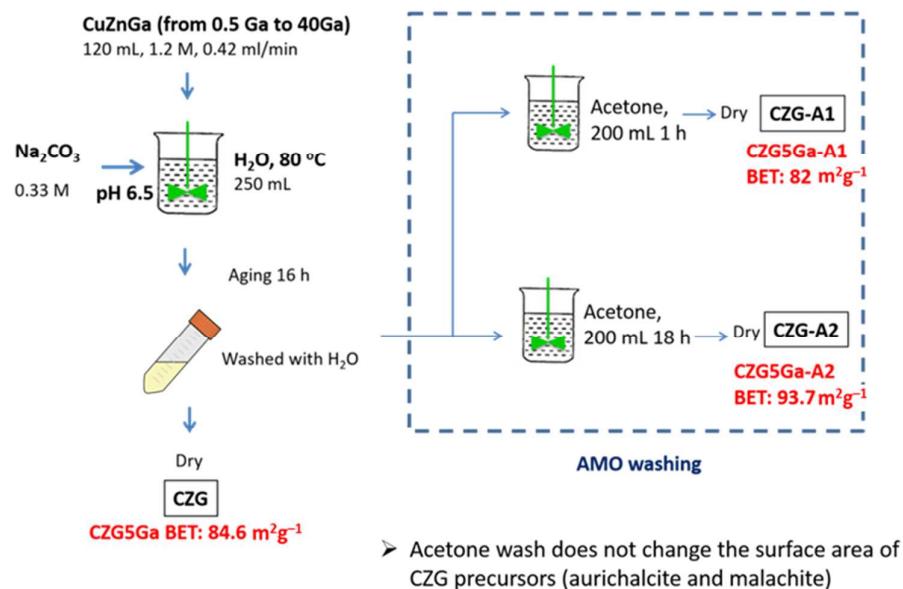


Figure S1. Procedure for the synthesis of CZG samples using co-precipitation

Synthesis: LDH samples

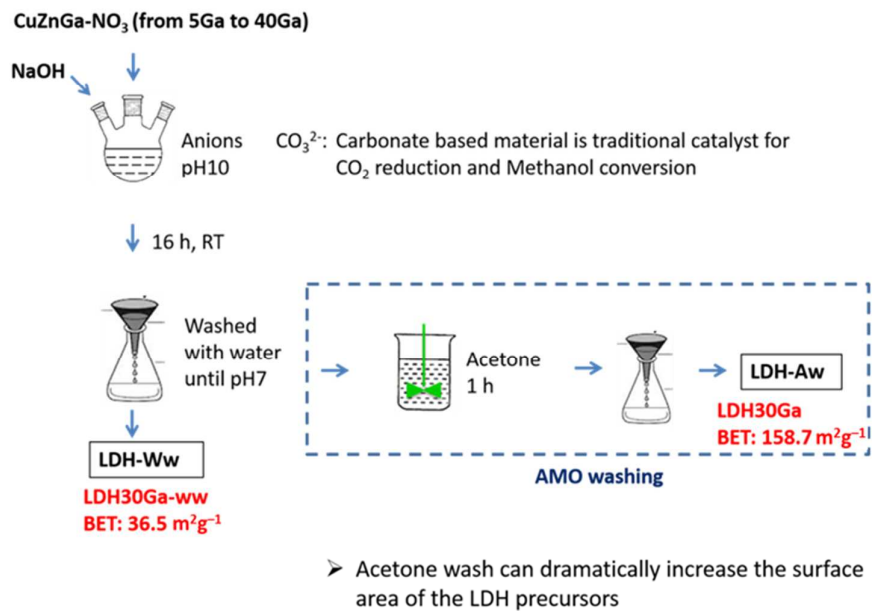
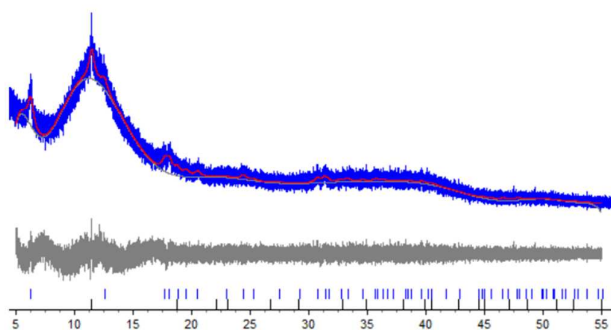
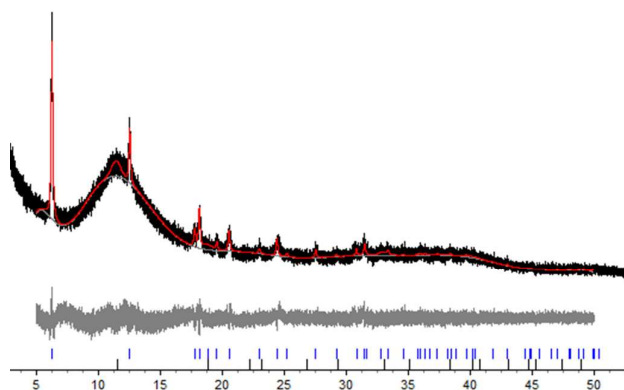


Figure S2. Procedure for the synthesis of AMO-LDH samples via base solution



a	3.1134±0.0011 Å
b	3.1134±0.0011 Å
c	22.6434±0.0011 Å
α	90°
β	90°
γ	120°

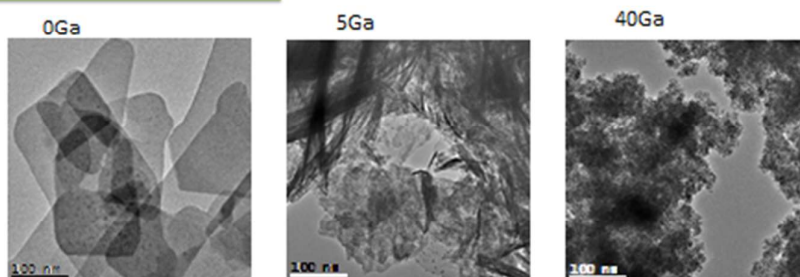
Figure S3a. SAXRD of freshly prepared LDH30Ga by synchrotron XRD (Diamond I11). Pawley refinement with the best fitting parameters of R_{wp} 8.1142; R_{exp} 6.2624; R_p 6.3235; gof 1.2957. $I = 7.1152$. Monodispersed spheres diameter = $4 \times I \div 3 = 9.48$ nm (~ 10 layers)



a	3.1061±0.0010 Å
b	3.1061±0.0010 Å
c	22.6904±0.0010 Å
α	90°
β	90°
γ	120°

Figure S3b. SAXRD of freshly prepared LDH40Ga by synchrotron XRD (Diamond I11). Pawley refinement with the best fitting parameters of R_{wp} 7.9297; R_{exp} 5.7502; R_p 6.1762; gof 1.3790. $I = 27.8994$. Monodispersed spheres diameter = $4 \times I \div 3 = 37.16$ nm (~ 46 layers)

TEM: CZG samples



TEM: LDH samples

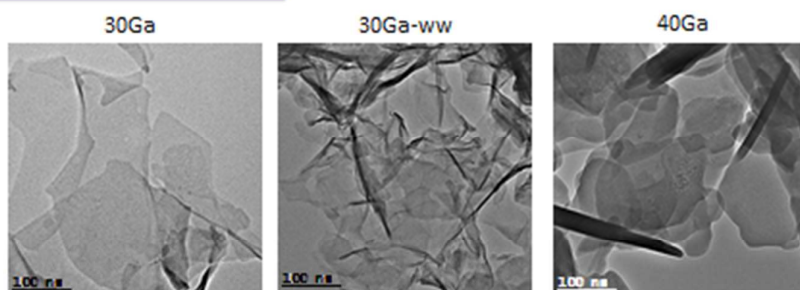


Figure S4a. TEM images of freshly prepared CZG samples and AMO-LDH samples. Upper row: CZG0Ga (bulk form), CZG5Ga (fibrous-like) and CZG40Ga (small particles). Lower row: LDH30Ga (monolayers), LDH30Ga-ww and LDH40Ga (thick layers).

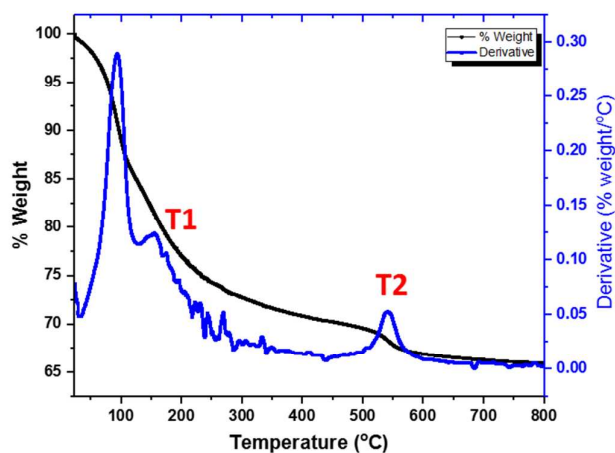


Figure S4b. Thermogravimetric analysis result of the LDH30Ga sample. T1 and T2: Temperature regions at which decomposition of -OH and CO_3^{2-} groups takes place respectively.

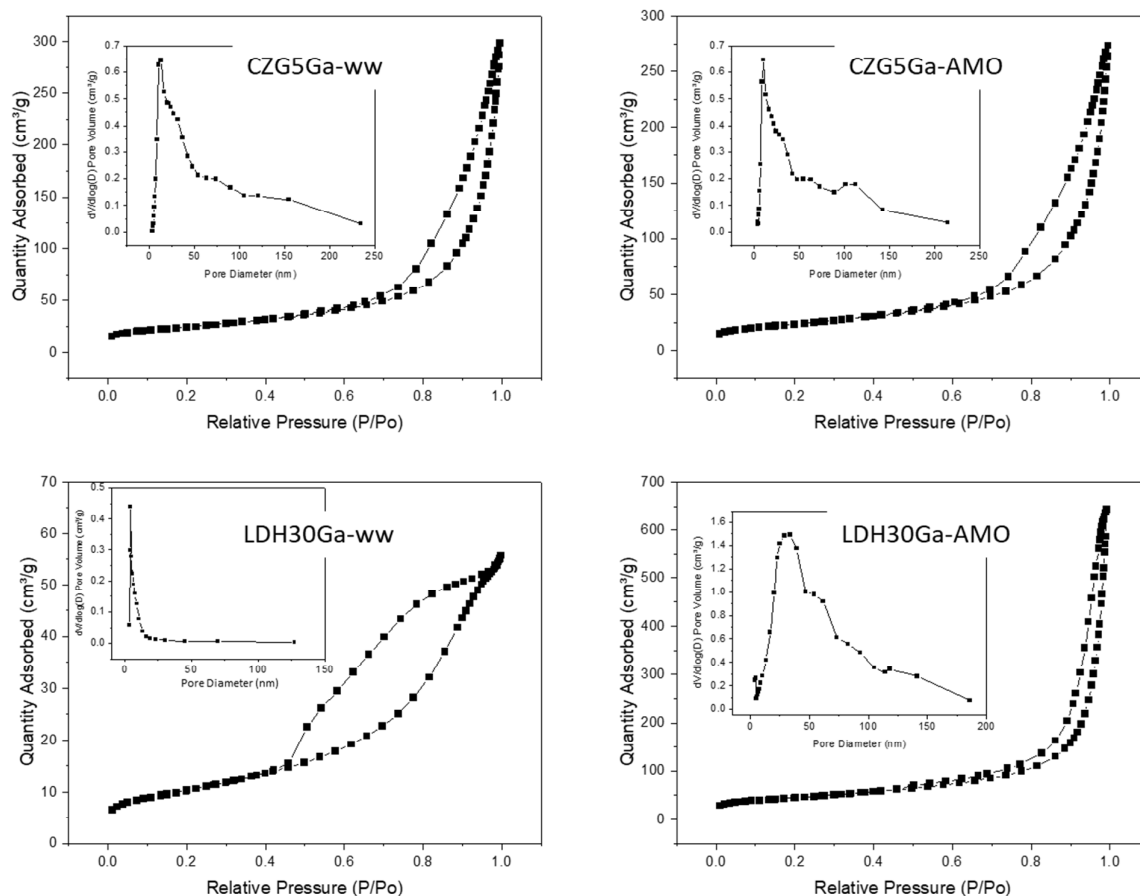


Figure S5. N_2 adsorption/desorption isotherm and pore size distributions (insert) of CZG5Ga and LDH30Ga precursors made via water wash (ww) or acetone treatment (AMO).

Porosity investigation of CZG and LDH: Influence of water/AMO solvent treatments.

From Fig. S5, N_2 adsorption isotherms of all the selected samples show the Type IV isotherm. Capillary condensation in the isotherms indicates that the samples are mesoporous in nature. For the CZG5Ga, both water washed and AMO treated samples display the type IV with a H3-type hysteresis loop, which is attributed to the presence of large mesopores with a pore size distribution continuing into the macropore domain⁵. It can be seen from Fig. S5 that there is no obvious difference between CZG5Ga-ww and CZG5Ga-AMO, indicating the acetone treatment does not influence the pore structure of the CZG5Ga sample. On the contrary, the isotherm of the LDH30Ga sample shows a significant difference upon the acetone solvent exfoliation process. The LDH sample without AMO treatment (LDH30Ga-ww) shows a Type IV isotherm with the H2 hysteresis loop, indicating the disordered pore structure which is due to the compaction/aggregation of the LDH platelets⁶. After the AMO treatment, see the LDH30Ga-AMO sample, a major increase of porosity is observed. Moreover, the hysteresis loop changed into H3-type, which is usually observed on solids containing non-rigid aggregates of plate-like particles (slit-shaped pores)⁷, implying the acetone exfoliation happened effectively on the LDH structure.

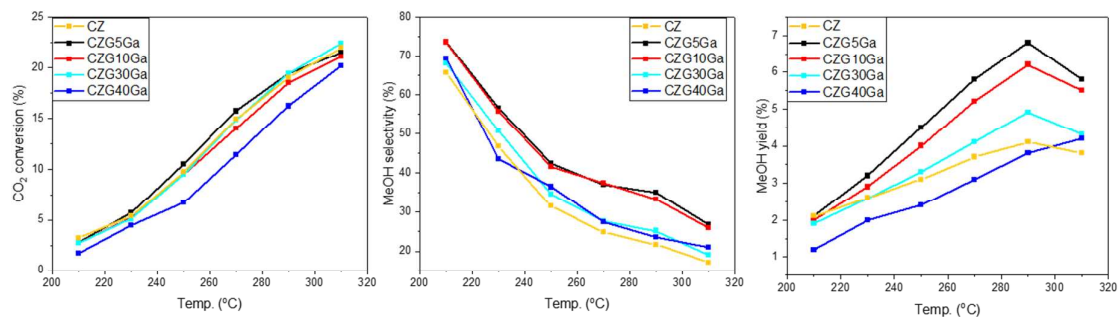


Figure S6 Conversion, selectivity and yield for each CZG sample in CO₂ hydrogenation to methanol.

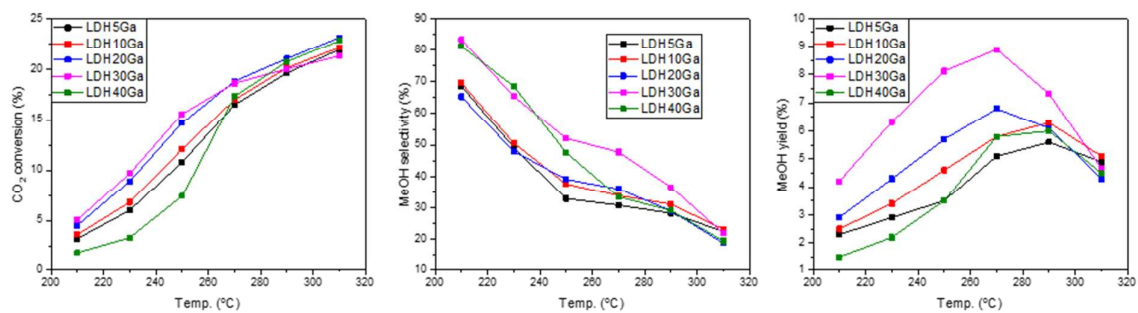


Figure S7. Conversion, selectivity and yield for each AMO-LDH precursor catalyst in CO₂ hydrogenation to methanol

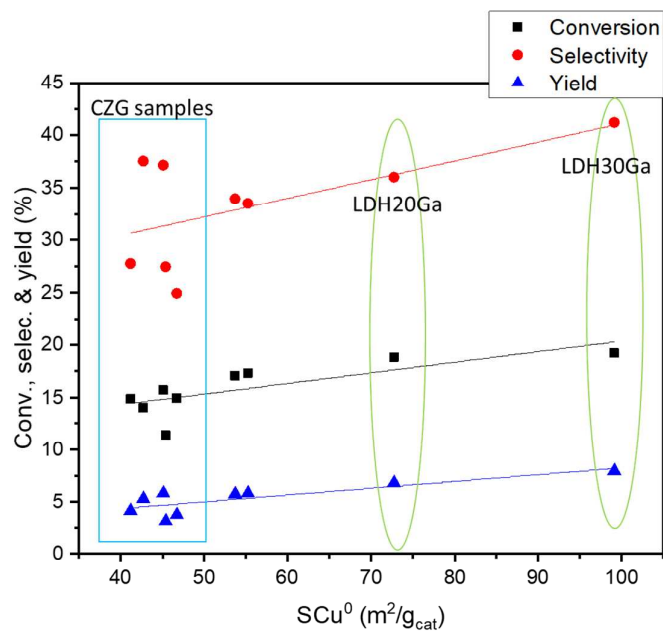


Figure S8a. Correlation of catalytic performance with Cu surface area for CZG and AMO-LDH precursor catalysts

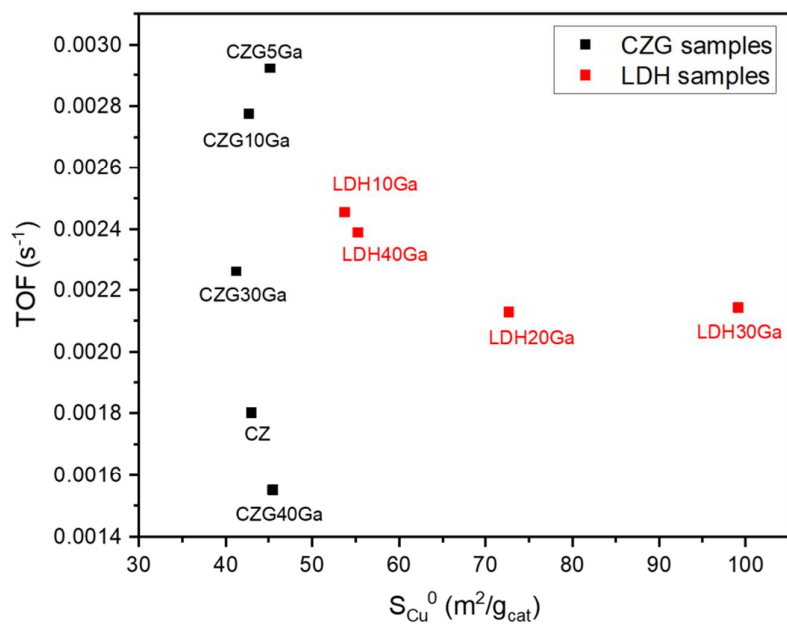


Figure S8b. Correlation of TOF with Cu surface area for CZG and AMO-LDH precursor catalysts

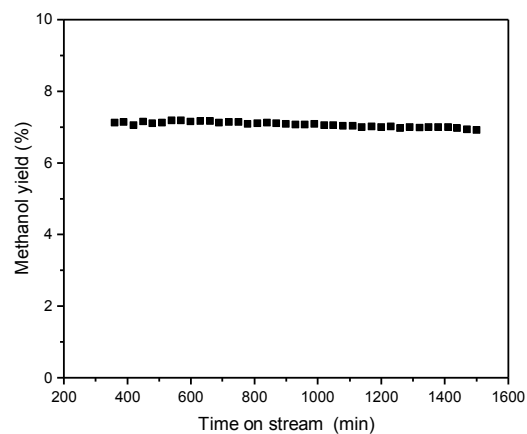


Figure S9. The changes of methanol yield (%) for the methanol synthesis at 290 °C with time on stream over LDH30Ga catalysts.

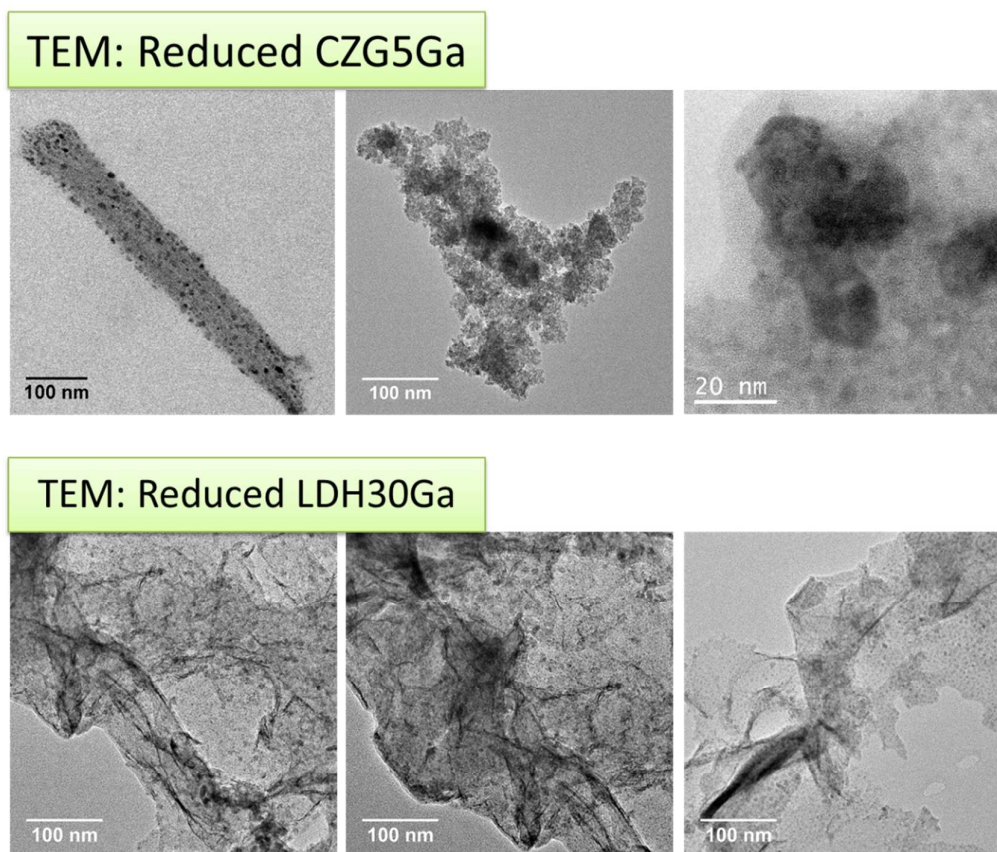


Figure S10. TEM images of reduced CZG5Ga (upper row) and LDH30Ga (lower row).

Supplementary References:

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