## **Electronic Supplementary Information (ESI)**

Lewis-Base-Promoted Copper-based Catalyst for Highly Efficient Hydrogenation of Dimethyl 1,4-Cyclohexane Dicarboxylate

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## I. Experimental section

### **Catalysts preparation**

CuMgAl-LDH was prepared by our previously reported separate nucleation and aging step method. Solution A: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O salts with (Cu<sup>2+</sup>+Mg<sup>2+</sup>)/Al<sup>3+</sup> molar ratio of 2 were dissolved in 100 mL of deionized water to give a solution with a total cationic concentration of 1.2 M. Solution B: NaOH and Na<sub>2</sub>CO<sub>3</sub> were dissolved in 100 mL of deionized water to form a mixed base solution. The concentrations of the base were related to those of metal ions in solution A as follows:  $[CO_3^{2^-}] = 2[Al^{3+}], [OH^-] = 1.6([M^{2+}] + [Al^{3+}])$ . Solutions A and B were simultaneously added rapidly to a colloid mill with the rotor speed set at 3000 rpm and mixed for 2 min. The resulting blue suspension was washed several times with deionized water to neutral

(pH=7), aged at 60 °C for 12 h, and finally dried at 70 °C for 24 h. The as-synthesized CuMgAl-LDH was calcined in static air at 600 for 6 h, pelletized, crushed, sieved to 40–60 meshes. Subsequently, the obtained samples were reduced in 10 %  $H_2/N_2$  atmosphere at 300 °C for 2 h at a ramping rate of 2 °C min<sup>-1</sup>. For comparison, traditional Cu-Cr<sub>2</sub>O<sub>3</sub> catalyst (Cu/Cr molar ratio =1.0) was prepared according to the literature (Kawamoto AM, Pardini LC, Rezende LC, Synthesis of copper chromite catalyst. Aerosp Sci Techol. 2004;8:591–598).

#### **Catalyst characterization**

Powder X-ray diffraction (XRD) data were collected at room temperature on Shimadzu XRD-6000 diffractometer with graphite-filtered Cu  $K\alpha$  source ( $\lambda$ = 0.15418 nm), 40 kV, 30 mA.

Elemental analysis was performed on a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscopy (ICP-AES) after the samples were dissolved by using chloroazotic acid.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a JEOL JEM 2100 operated at an accelerating voltage of 200 kV. A droplet of the ultrasonically dispersed powders was placed onto an amorphous carbon-coated copper grid and then dried at ambient temperature.

Elemental mapping was performed using a HITACHI S-5500 scanning transmission electron microscope (STEM) equipped with an Oxford INCA-450 Energy Dispersive Spectrometer (EDS) detector.  $N_2$  adsorption–desorption isotherms of the samples were obtained on a Micromeritics ASAP 2020 sorptometer apparatus at –196 °C. All samples were outgassed prior to analysis at 200 °C for 12 h under 10<sup>-4</sup> Pa vacuum. The total specific surface areas were evaluated with the multipoint Brunauer–Emmett–Teller (BET) method. BET surface areas areas were reproducible to within ± 5%.

X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger spectra (XAES) were recorded on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer at a base pressure of  $2 \times 10^{-9}$  Pa using Al K $\alpha$  X-ray radiation (1486.6 eV photons). Binding energies were calibrated based on the graphite C 1s peak at 284.6 eV.

The reduction behavior of calcined samples was studied by hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) using Micromeritics ChemiSorb 2720 instrument. 0.1 g of sample, which was placed in a quartz U-tube reactor, was degassed at 200 °C for 2 h under argon flow (40 mL/min). Then TPR was conducted in a stream of 10% v/v H<sub>2</sub>/Ar (40 mL/min) with a heating rate of 5 °C /min up to 800 °C. The effluent gas was analyzed by a thermal conductivity detector (TCD).

The surface areas, dispersions and crystal sizes of  $Cu^0$  particles for samples were determined according to H<sub>2</sub>-N<sub>2</sub>O titration using a Micromeritics ChemiSorb 2720 instrument. Firstly, the calcined sample underwent a H<sub>2</sub>-TPR process in 10% H<sub>2</sub>/Ar mixture from 50 to 300 °C and held the temperature until no more H<sub>2</sub> consumption. After cooling down, the gas was switched to 10% N<sub>2</sub>O/N<sub>2</sub>, and the sample was oxidized at a flow rate of 40 ml/min at 60 °C for 1 h, followed by Ar purging and cooling the sample bed down to room temperature. Finally, H<sub>2</sub>-TPR was carried out again with a gas mixture

of 10 % H<sub>2</sub>/Ar to 300 °C.

The temperature-programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) was conducted on a ChemiSorb 2720 instrument equipped with a TCD. 0.1 g sample was heated at a rate of 10 °C/min to 600 °C under He flow (40ml/min) and maintained at this temperature for 1 h in order to remove the surface impurities. Then the sample was reduced with 10% H<sub>2</sub>/Ar mixture at 300 °C for 1 h. After being cooled to room temperature under He flow, the sample was exposed to pure CO<sub>2</sub> (20 ml/min) for 1 h. Subsequently, the sample was purged with He (40 ml/min) for 1 h and then heated to 800 °C at a rate of 5 °C /min. Desorption of CO<sub>2</sub> was monitored by the TCD.

The in situ FT-IR spectra of CO adsorption were recorded on a Thermo Nicolet 380 FT-IR spectrometer. The sample powder was pressed into a self-supporting wafer (50 mg) and mounted into the IR cell. The sample was first reduced with H<sub>2</sub> (10 ml/min) at 300 °C for 1 h, followed by evacuating for 1 h at 400 °C and then cooling the sample wafer down to room temperature. After acquisition of the background spectrum, the sample was exposed to CO with increasing pressure (500 Pa) at room temperature. Then the cell was evacuated and heated from room temperature to 100 °C. The spectra of CO adsorption on the catalyst were obtained by subtracting the background spectrum.

#### Catalytic test

The hydrogenation of DMCD was carried out using a stainless-steel fixed-bed tubular reactor with an inner diameter of 12 mm. The calcined CuMgAl-LDH sample (3.0 g) was diluted with quartz powders (20–40 meshes) with a dilution ratio 1:1 by mass,

and the diluted catalyst was embedded with quartz powders in both sides of the catalyst bed with a height of approximately 40 mm. The sample was reduced in a 10% H<sub>2</sub>/N<sub>2</sub> atmosphere at 300 °C for 2 h at a heating rate of 5 °C min<sup>-1</sup>. After activation of catalysts, 10.0 wt. % DMCD (purity >99.9 %) in methanol and H<sub>2</sub> were fed into the reactor at a H<sub>2</sub>/ DMCD molar ratio of 203 at different reaction temperature. During hydrogenation, the total pressure was kept at 6.0 MPa, and the room-temperature liquid space velocity of DMCD was 1.0 h<sup>-1</sup>. Finally, the liquid products were analyzed by an Agilent GC7890A gas chromatograph equipped with flame ionization detector and HP-5 capillary column. DMCD conversions were determined by the change of DMCD mole before and after the reaction. The selectivity of CHDM, MCHM and MHMCC were calculated from the equation: selectivity (%) = (moles of product)/(the sum of the moles of all products except methanol) × 100%.

To eliminate internal diffusion, catalysts with different grain diameters were used to check the effect of internal diffusion. It was found that the conversion of DMCD did not vary when the grain diameter of the catalyst was less than 20 mesh. Also, there was no difference in the DMCD conversion under two different catalyst loadings of 2.0 g and 3.0 g when the applied values of LHSV and H<sub>2</sub>/DMCD molar ratio kept constant, which indicated that the external mass transfer limitation could be neglected in the present reaction system.

# **II** Figures



Fig. S1 XRD patterns of Cu-3 catalysts obtained at different calcination temperature: (a) 500 °C; (b) 700 °C.



Fig. S2 XRD patterns of different Cu-based catalysts.



Fig. S3 H<sub>2</sub>-TPR profiles of different calcined CuMgAl-LDH precursors.



Fig. S4 TEM (a) and HRTEM (b,c) images of representative Cu-3 sample.



Fig. S5 Elemental mapping of Cu, Mg and Al atoms over the Cu-3 sample.