# **Supporting Information**

# A fully heterogeneous catalyst Br-LDH for the cycloaddition reactions of CO<sub>2</sub> with epoxides

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## 1. Experimental

#### Materials

Aluminium chloride hexahydrate, aluminium nitrate nonahydrate and magnesium nitrate hexahydrate were provided by Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide, anhydrous sodium carbonate, ethyl acetate and ethanol were obtained from Beijing Chemical Works. Magnesium chloride, potassium bromide, propylene oxide, propylene carbonate, dodecane, propylene glycol, epoxy chloropropane, epoxy bromopropane and 1,2-epoxybutane were supplied by J&K Scientific Ltd. 1,2-Epoxyhexane was purchased from Acros.  $CO_2$  (99.99%) was provided by Beijing Analytical Instrument Company. All solvents and chemicals were used as received without further purification.

#### **Catalyst preparation**

**Preparation of the CI-LDH:** CI-LDH was prepared through the co-precipitation method. The solution of NaOH was introduced into the mixed solution (30 mL) of MgCl<sub>2</sub> (1 M) and AlCl<sub>3</sub>·9H<sub>2</sub>O (0.33 M) dropwise under stirring until pH =  $10 \pm 0.5$ . Generally, the nucleation process needs about 30 minutes. After aging for 24 h, the mixture was filtered, and washed with deionized water and ethanol before drying at 80 °C in the vacuum oven overnight. Finally, the obtained white powder was ground evenly with a pestle.

**Preparation of the Br-LDH:** The catalyst Br-LDH was prepared through the anion exchange method where the chloride anion in the interlayer of the Cl-LDH was exchanged by the bromide anion. The details are as follows: 600 mg Cl-LDH was added to the potassium bromide aqueous solution (0.2 M, 300 mL). After 24 h, the mixture was filtered, washed and then dried in the vacuum oven overnight. Finally, the obtained white powder was ground evenly with a pestle.

**Preparation of the CO<sub>3</sub>-LDH:** The preparation of the CO<sub>3</sub>-LDH was similar to that of the Cl-LDH. The difference was that the metal chloride salt solution was replaced by the metal nitrate solution and the NaOH solution was replaced by the mixture of NaOH and Na<sub>2</sub>CO<sub>3</sub>.

**Preparation of the MgO-Al<sub>2</sub>O<sub>3</sub>:** The MgO-Al<sub>2</sub>O<sub>3</sub> was prepared through the calcination of the CO<sub>3</sub>-LDH in the furnace at  $390^{\circ}$ C for 3 h under the heating rate of  $10^{\circ}$ C/min.

#### **Catalyst characterization**

The catalyst was characterized by transmission electron microscopy (TEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD), nitrogen adsorption-desorption measurement and ICP-AES. We obtained TEM and EDS images through a Hitachi-7700 (100.0 kV, 10.00 uA) and JEOL-2100F (200 kV), respectively. The samples to be characterized were dispersed in ethanol through sonication and then dropped onto copper-grid-supported carbon films. The XRD patterns were recorded on Rigaku D/max-2500 X-ray diffractometer operated at 40 kV and 200 mA with Cu K $\alpha$  ( $\lambda$  = 0.154 nm) radiation. The nitrogen adsorption-desorption isotherm was measured at 77 K controlled by the liquid nitrogen with a gas sorption analyser (Nova 2200e). The sample to be studied was degassed at 80°C overnight. The pore

size distribution curve was calculated through the Barret-Joyner-Halenda (BJH) method. The surface area was calculated from the adsorption data with the Brunauer-Emmett-Teller (BET) method. The contents of Pd in the catalyst were determined by ICP-AES (PROFILE. SPEC, Leeman).

#### **Catalytic cycloaddition reactions**

Generally, the reaction was conducted in a 16 mL Teflon-lined stainless-steel reactor equipped with magnetic stirrer. The gas pressure was accurately controlled by a pressure transducer (FOXBORO/ICT, Model 93) with an accuracy of  $\pm 0.025$  MPa. In a typical procedure, a certain amount of the catalyst and substrate were added into the reactor. Then, the reactor was sealed and charged with CO<sub>2</sub> to desired pressure. Then, the reactor was placed in the furnace set with specified temperature and the stirrer was started (700 rpm). After certain reaction time, the reactor was taken out from the furnace and cooled down in the ice water. CO<sub>2</sub> was slowly released through an ethyl acetate cold trap to adsorb the chemical compounds entrained by CO<sub>2</sub>. After depressurization, ethyl acetate in the cold trap was mixed with the liquid mixture in the reactor and the internal standard dodecane was also added. Finally, the obtained liquid mixture was quantitatively analysed by gas chromatograph (GC) (Agilent 7890B) equipped with capillary column (HP-5, 0.25 mm in diameter, 30 m in length) and a flame ionization detector (FID). The identification of the products was conducted on the GC-MS (Agilent-7890B-5977A) as well as by comparing the retention times of the corresponding standards in the GC traces.

### 2. Supporting figures



Fig S2. The effect of the catalyst dosage (a), reaction time (b), reaction temperature (c) and  $CO_2$  pressure (d) on the cycloaddition reaction of  $CO_2$  with propylene oxide. The yield and the selectivity were determined by GC with dodecane as the internal standard.



Fig S3. Recyclability of the Br-LDH. Reaction condition: catalyst (200 mg), propylene oxide (5 mmol), CO<sub>2</sub> (2 MPa), 80°C, 12 h. The yield and the selectivity were determined by GC with dodecane as the internal standard.



Fig S4. TEM image of the reused Br-LDH



Fig S5. The TEM image (a) and the XRD pattern (b) of the CI-LDH