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Supporting Information

Synthesis of Glycerol Carbonate by direct carbonylation of Glycerol with CO₂ over Solid Catalysts derived from Zn/Al/La and Zn/Al/La/M (M= Li, Mg and Zr) Hydrotalcites

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Fig. S1 SEM micrograph of the initial materials; (A) ZA-2; (B) HT-1; (C) HT-2; (D) HT-3.

The scanning electron microscopy, SEM, micrograph of Figure S1(A) shows a typical plateshaped crystals which suggests the formation of a layered structure ^{1,2}. It is also found that the plateletlike crystals are homogeneous and dense-stacking. In addition, for HT-x catalysts, the amount of plateshaped crystals increases with the increase of Al content, reaching a maximum for HT-2 and then decreases with a further increase of the Al content, accordance with the results of previous reports ^[1, 3], which described that the atomic ratio of M^{2+}/M^{3+} between 2 to 4 was favorable for the synthesis of HT1 structure. For HT-3, small particles become the main crystal phase. Moreover, it can be found that the introduction of La is not favorable for the formation of hydrotalcite-like structure.

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Fig. S2 FT-IR spectra of Zn/Al/La hydrotalcites A: ZA-2, B: HT-1, C: HT-2, D: HT-3.

Before calcination the prepared materials were characterized by FT-IR and the spectra are shown in Figure S2. The broad peak around 3440 cm⁻¹ can be ascribed to the stretching of OH⁻ groups attached to metal ions and the bending vibration of interlayer water is also found at 1638 cm^{-1 4,5}. In addition, the bands at 1362 cm⁻¹ assigned to the v₃ mode of interlayer carbonate species ⁶. The lower wave number bands at 400–700 cm⁻¹ is due to LDH lattice vibrations (Zn–O, Al–O, La–O, La–O–Zn). The bands at 775 cm⁻¹ and 553 cm⁻¹ can be assigned to Al–O stretching modes ⁴. It can be found that the peaks of Al–O become weaker with the introduction of La, especially for HT-1 and HT-3, which probably resulted from the followed reasons. Firstly, as reported by previous report ⁴, partial La³⁺ replaced Al³⁺ at the octahedral sites. In addition, the introduction of La is not favorable for the preparation of hydrotalcite-like structure.

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Fig. S3 TG-DTG curves of the prepared samples.

Figure S3 presents the TG profiles of the precursors. In general, three weight loss stages can be observed on TG curve of HTlcs: the elimination of physically adsorbed or interlayer water molecules (100-200 °C), the removal of both the hydroxyl groups from the HTl network and the carbonate anions from the interlayer anion (200-400 °C), and the decomposition of metal carbonates (400-600 °C) formed during the former steps of the thermal decomposition. For HT-Mg, the weight loss at around 500-600 °C can be ascribed to the decomposition of the formed MgCO₃. Therefore, after calcinations at 500 °C, Mg may exist in the form of Mg₂CO₃ in CHT-Mg.



Fig. S4 XRD patterns of the prepared Zinc Glycerolate. Δ : zinc glycerolate (JCPDS 23-1975); *:ZnO (JCPDS 36-1451).

Fig. S4 shows the XRD patterns of the prepared zinc glycerolate. It can be found that besides the patterns of ZnO, the main diffraction peaks of zinc glycerolate are presented. The prepared zinc glycerolate was used to explore the interaction with CO_2 by diffuse reflection infrared Fourier transform spectroscopy (DRIFTS).



Fig. S5 TG analysis of zinc glycerolate.

The profile of TG analysis is shown in Fig. S5. The major weight loss around 385 °C can be ascribed to the decomposition of the prepared zinc glycerolate. The result indicates that zinc glycerolate can be used to perform the DRIFTS spectra with CO₂ under 300 °C.