Supporting Information

Montmorillonite-Supported Ionic Liquid and Choline chloride as Heterogeneous Catalysts for Efficient CO_2 Cycloaddition to Cyclic Carbonates

Hadiseh Pirbeig Darvishvand, Majid Masteri-Farahani

Faculty of Chemistry, Kharazmi University, 15719-14911 Tehran, Iran

Experimental

Materials

All reagents were used as received without further purification. The chemicals employed include: choline chloride (ChCl), 1-methylimidazole, 1-bromobutane, montmorillonite (MMT), acetonitrile, n-hexane, ethanol, chloroform, epichlorohydrin (ECH), epibromohydrin (EBH), propylene oxide (PO), butane oxide (BO), styrene oxide (SO) and cyclohexane oxide (CHO). All reagents were of analytical grade and were purchased from Merck and Sigma-Aldrich.

Instruments

The structural and physicochemical properties of the synthesized catalysts were systematically characterized using a variety of techniques. Fourier-transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer RXI FT-IR spectrometer with samples prepared as KBr pellets to identify the characteristic functional groups. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D/max-CIII diffractometer with Ni-filtered Cu Kα radiation (λ = 1.5406 Å) to investigate the crystalline structure. Thermogravimetric analysis (TGA) was performed in air using a LINSEIS STA PT-1000 thermogravimetric analyzer over the temperature range of 25–700 °C to evaluate the thermal stability of the catalysts. CHN elemental analysis was performed

using a Perkin-Elmer 2400 SERIES II elemental analyzer to determine the carbon, hydrogen, and nitrogen contents of the samples. Scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and elemental mapping (MIRA II TESCAN) was employed to examine the surface morphology, elemental composition and distribution of the catalyst. Nitrogen adsorption–desorption measurements were carried out on a BELSORP Mini instrument to determine the specific surface area and porosity of the materials. ^{1}H-NMR spectra of the final cyclic carbonate products were recorded on a Bruker Advance 400 MHz spectrometer in $CDCl_3$ solvent.

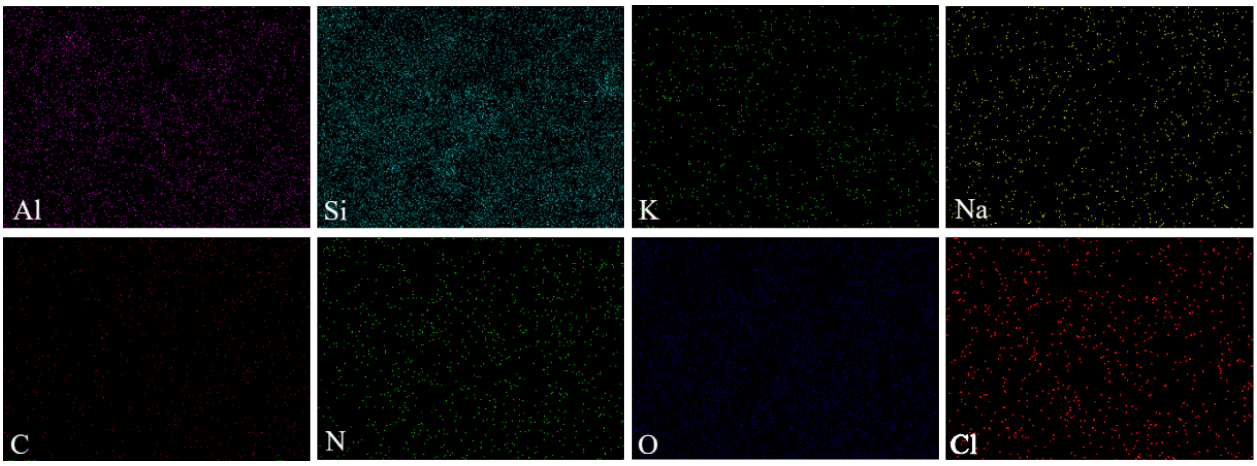

Figure S1. Elemental mapping images of ChCl/MMT catalyst.

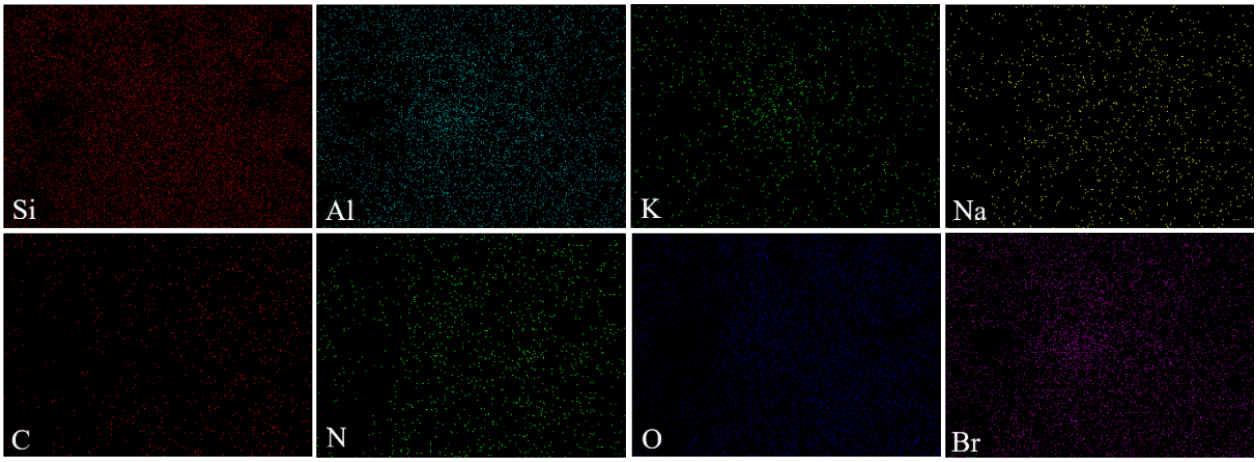

Figure S2. Elemental mapping images of BMIM-Br/MMT catalyst.

Table S1. CHN elemental analysis of ChCl/MMT and BMIM-Br/MMT catalysts.

Catalyst	C (wt%)	H (wt%)	N (wt%)	IL loading (mmol/g)
ChCl/MMT	2.78	1.2	0.77	0.696
BMIM-Br/MMT	4.49	1.18	1.48	0.603

Conversion, selectivity, and yield were determined by ^{1}H-NMR spectroscopy. The calculations were based on the relative integration of characteristic, non-overlapping proton signals from both the starting material (epoxide) and the cyclic carbonate product. Since the chosen signals for both species correspond to the same number of protons (e.g., the methylene protons of the bromomethyl group, Figure S4), the molar ratio was directly proportional to the integrated areas. No internal standard was required. All spectra were processed with consistent baseline correction and manual integration to ensure quantitative accuracy.

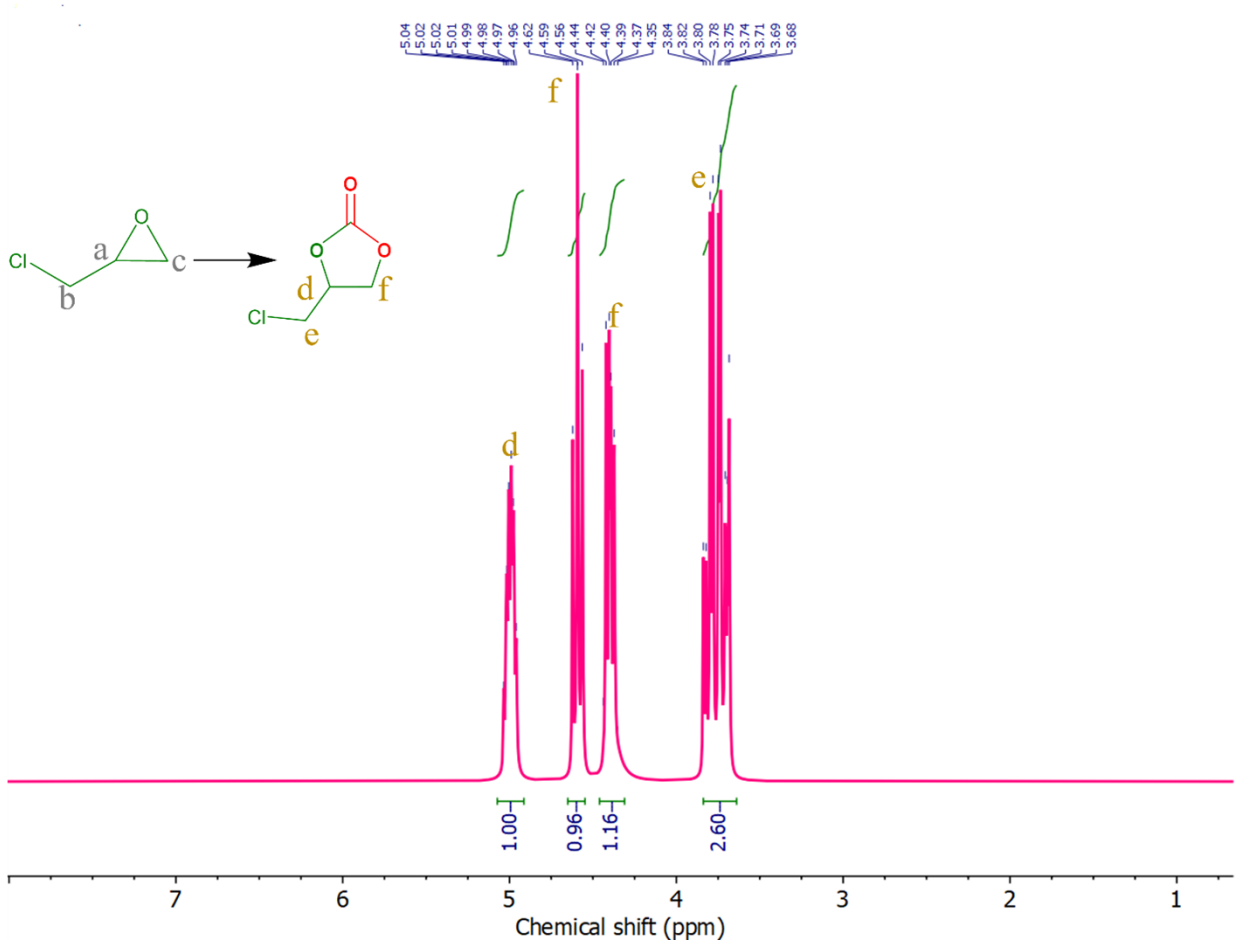

Figure S3. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the CO_2 cycloaddition reaction with ECH catalyzed by ChCl/MMT. Reaction conditions: Catalyst (0.52 mol%, 150 mg), ECH (20 mmol), CO_2 pressure: 1.2 MPa, 160 ℃, 4 h.

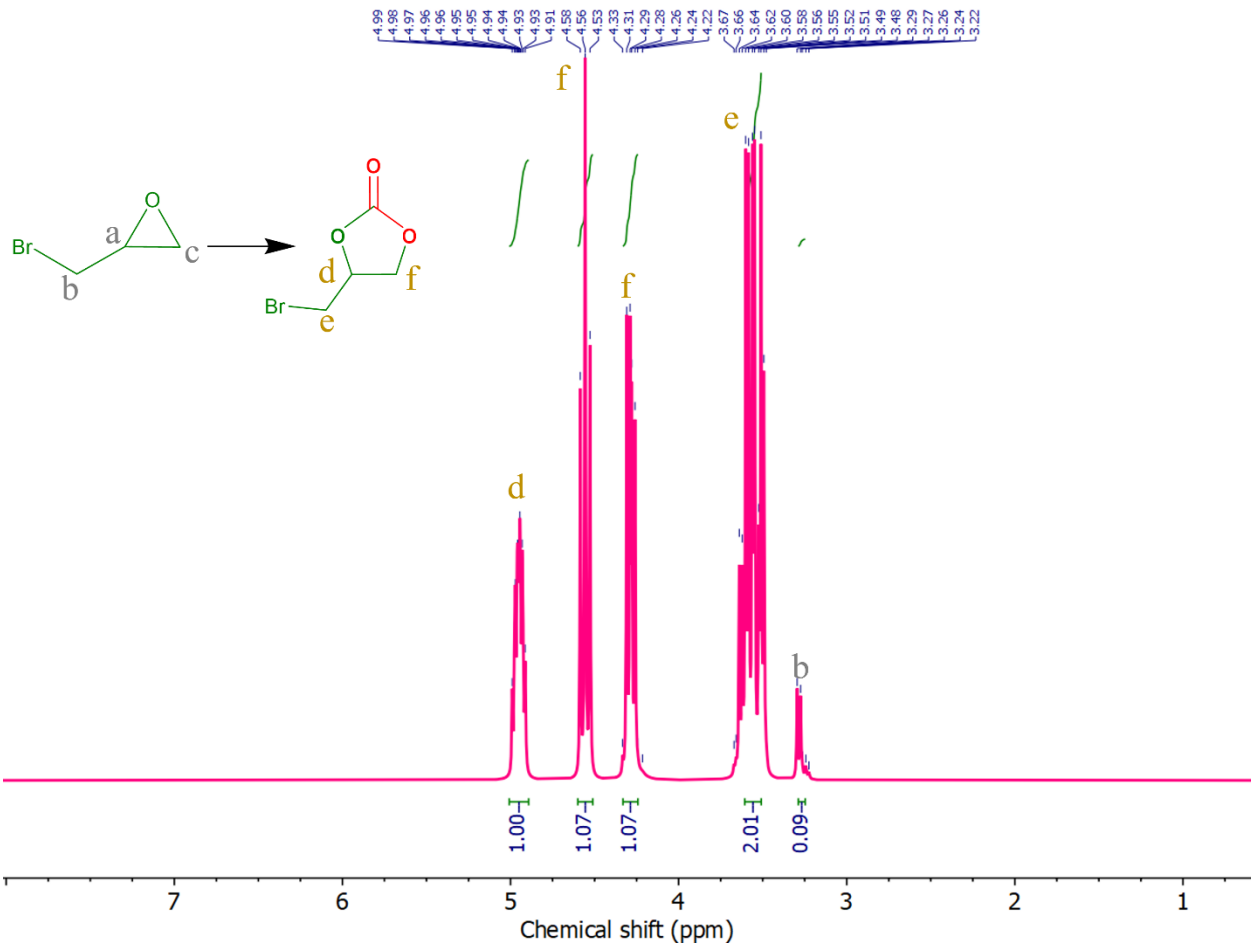

Figure S4. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the CO_2 cycloaddition reaction with EBH catalyzed by ChCl/MMT. Reaction conditions: Catalyst (0.52 mol%, 150 mg), EBH (20 mmol), CO_2 pressure: 1.2 MPa, 160 ℃, 4 h.

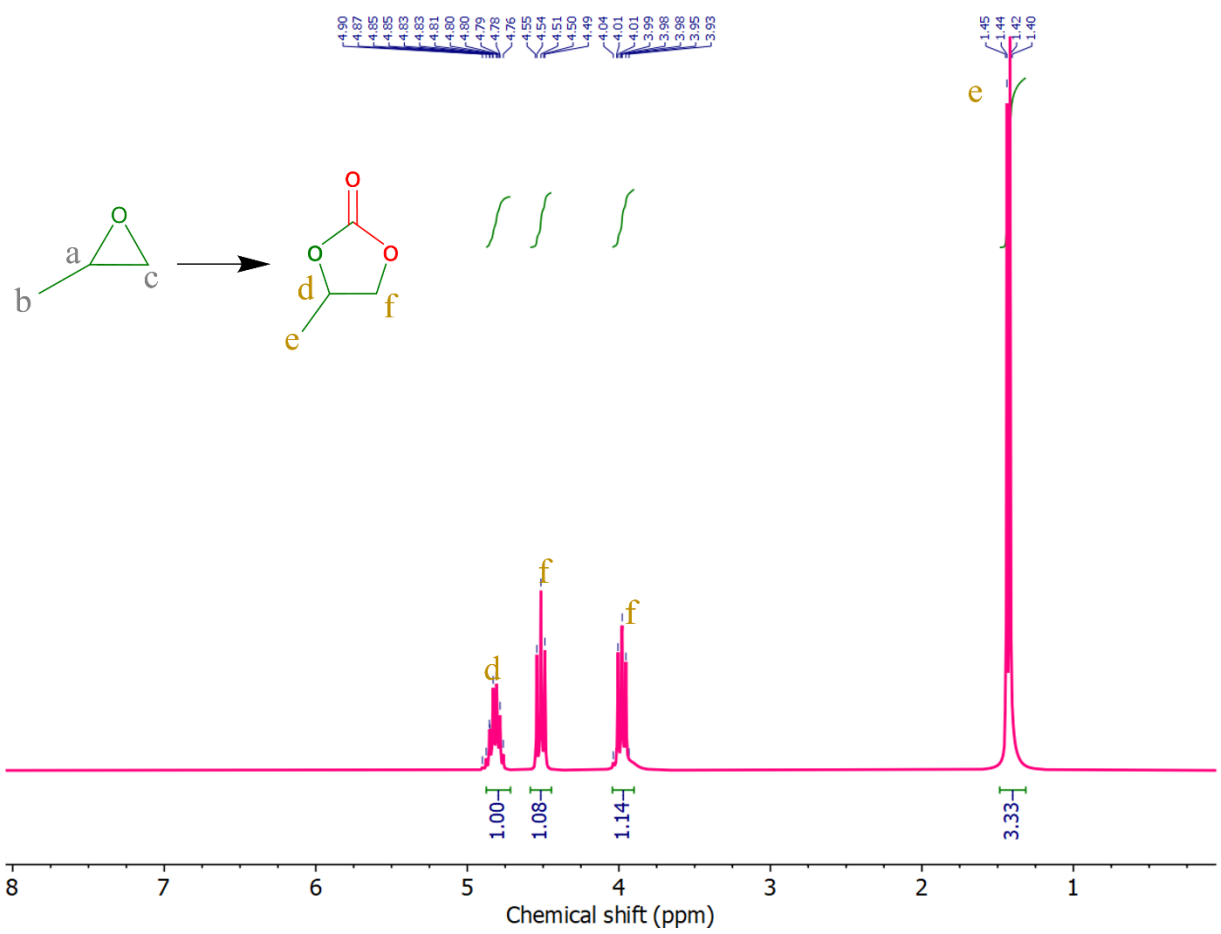

Figure S5. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the CO_2 cycloaddition reaction with PO catalyzed by ChCl/MMT. Reaction conditions: Catalyst (0.52 mol%, 150 mg), PO (20 mmol), CO_2 pressure: 1.2 MPa, 160 ℃, 4 h.

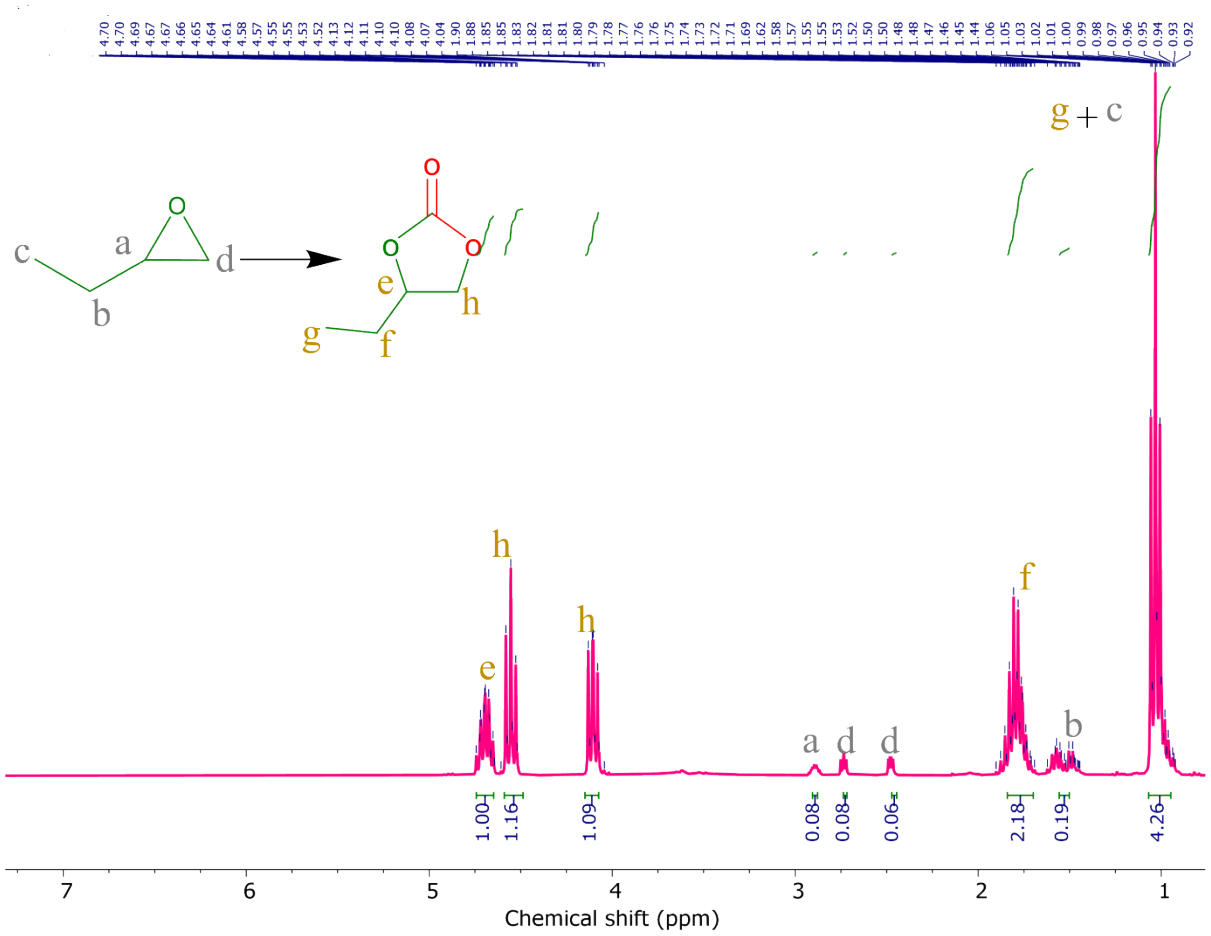

Figure S6. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the CO_2 cycloaddition reaction with BO catalyzed by ChCl/MMT. Reaction conditions: Catalyst (0.52 mol%, 150 mg), BO (20 mmol), CO_2 pressure: 1.2 MPa, 160 ℃, 4 h.

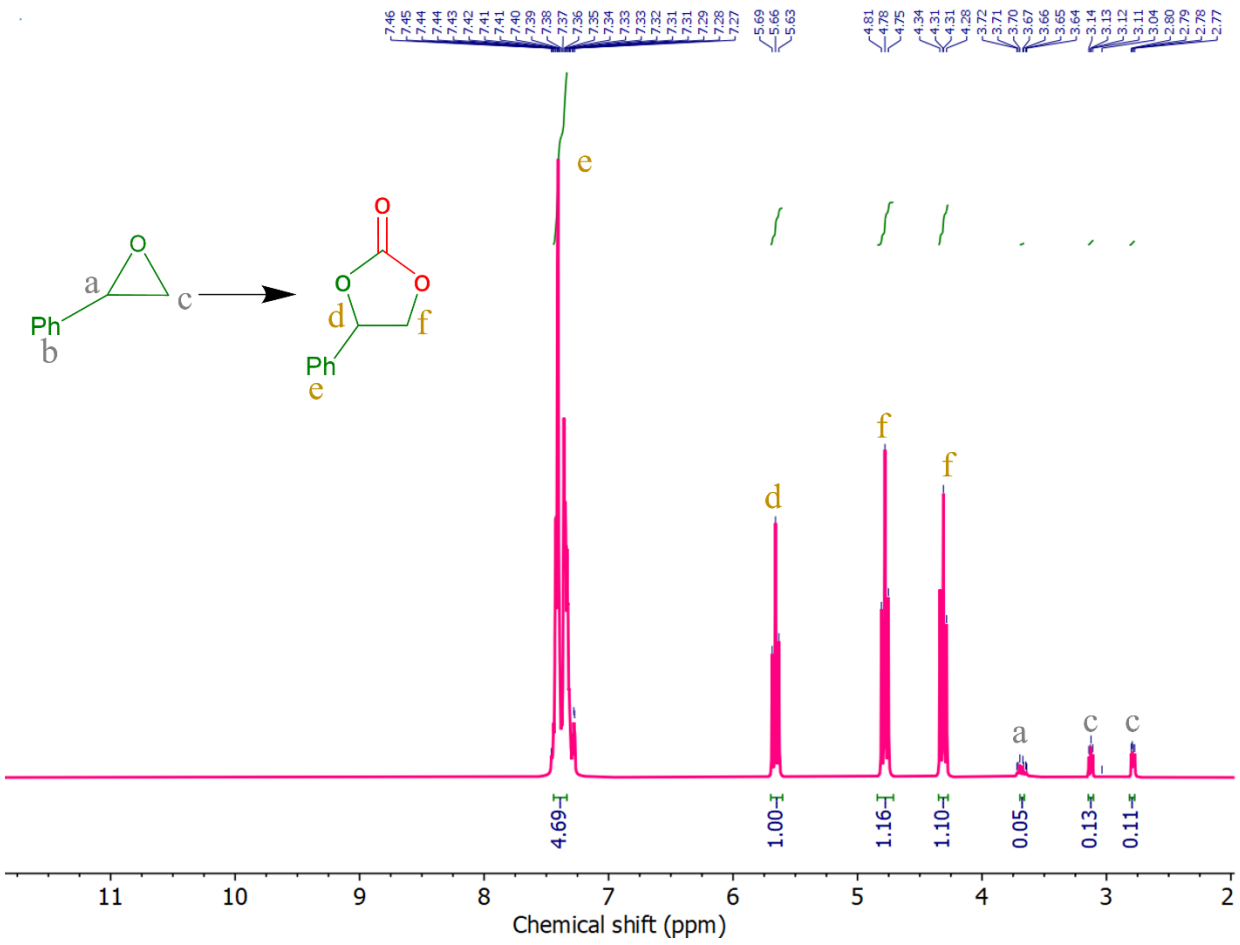

Figure S7. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the CO_2 cycloaddition reaction with SO catalyzed by ChCl/MMT. Reaction conditions: Catalyst (0.52 mol%, 150 mg), SO (20 mmol), CO_2 pressure: 1.2 MPa, 160 ℃, 4 h.

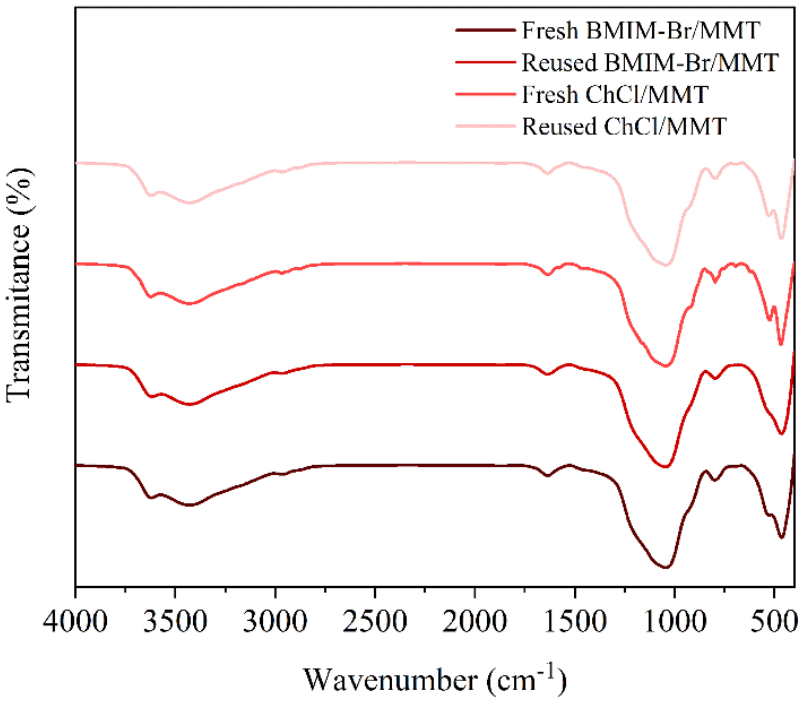

Figure S8. FT-IR spectra of the fresh and reused catalysts after 5th runs.

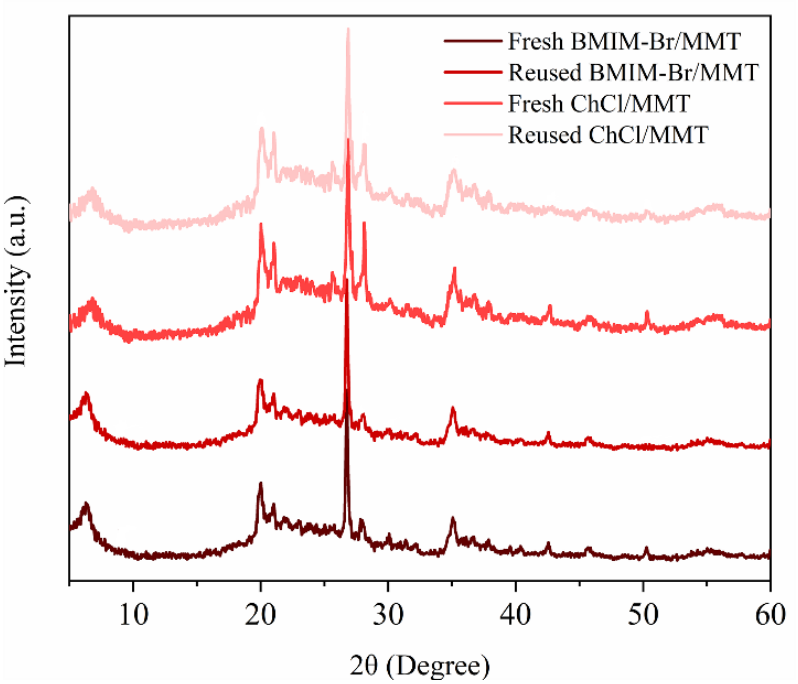

Figure S9. XRD patterns of the fresh and reused catalysts after 5th runs.