Electronic Supplementary Material (ESI) for Green Chemistry

Supplemetary Information

Aqueous-microwave synthesized carboxyl functional molecular ribbon coordination framework catalyst for the synthesis of cyclic carbonates from epoxides and CO_2

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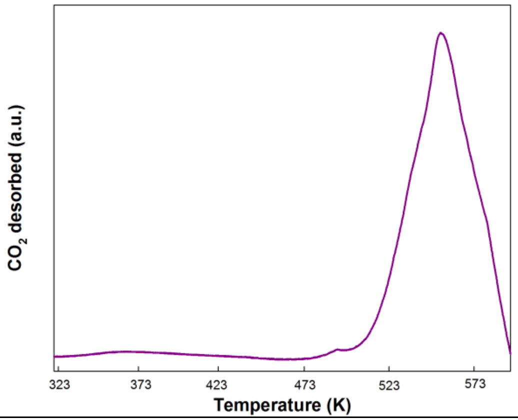
1. Knoevenagel condensation (base site) and acetalization (acid site) reactions

Knoevenagel condensation was performed with CHB(M) and CHB(S) as catalyst for the condensation between benzaldehyde and malononitirile to yield benzylidenemalononitrile. For this, 1 mol% CHB catalyst was added to 10 mmol each of benzaldehyde and malononitirile in presence of 10 mL 1,4-Dioxane at room temperature for 2 hours. The catalyst was filtered off and the filtrate was analyzed for GC to estimate the conversion and hence the initial rate (r_0). Acetalization was performed by the reaction of 10 mmol benzaldehyde and 10 mmol ethanol without any solvent for 2 hours at 60 °C using CHB(M) and CHB(S) respectively as catalysts to yield 1,1-diethoxymethylbenzene. The product was estimated using GC to find r_o value for acetalization.

2. Temperature Programmed Desorption (TPD)

Table S1. CO_2-TPD (Temperature Programmed Desorption)



Catalyst	CO_2-TPD (mmol/g)		
	Weak base[a]	Strong base[b]	total
CHB(S)	0.9	28.6	29.5

[a] 323 ~ 423 K. [b] 423 ~ 573 K.

3. Instrumentation

The catalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and field-emission scanning electron microscopy (FE-SEM). The XRD patterns were obtained on a Philips PANalytical X'pert PRO Model power diffractometer operating at 40 kV and 30 mA using Ni-filtered Cu-Kα radiation ($\lambda = 1.5404$ Å). The diffractograms were recorded in the 2θ range 5°–55°. The FT-IR spectra were obtained on a Vertex 80V Microscopic FT-IR/Raman spectrophotometer at a resolution of 4 cm^{-1}. The TGA measurements were performed on the CHB (microwave synthesized and solvothermally synthesized) samples weighing 3.1 and 6.95 mg, respectively, using an SDT-Q600 analyzer (TA Instruments Inc.). Surface features of the materials were observed using an S-4200 field-emission scanning electron microscope (Hitachi). The surface area was determined by N_2 adsorption at 77 K using a Micromeritics ASAP 2010 instrument. The cycloaddition products were identified and confirmed using gas chromatography/mass spectrometry (GC-MS, Agilent 5975C GC/MSD analyzer), ^1H NMR, and ^{13}C NMR (Varian 500 MHz) techniques. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyses were performed on a Perkin-Elmer Optima 8300 instrument. Estimation of cycloaddition products were performed in gas chromatograph (GC, Agilent 6890N GC analyzer, FID) using HP-5 column with 5% phenyl methyl siloxane packing with the dimensions 30m x 320 μm x 0.25 μm. Temperature gradient: 60 °C held for 5 min, rise 10 °C min^{-1} till 150 °C, held for 5 min, and then again rise 20 °C min^{-1} till 250 °C and held for 5 min. Similarly, the estimation of Knoevenagel condensation and acetalization products were performed in HP 6890 GC with FID detector. Column: HP-INNOWax packed with poly ethylene glycol having the dimension 30m x 320 μm x 0.25 μm. Temperature gradient (acetalization): 120 °C held for 10 min, rise 10 °C min^{-1} till 140 °C. Temperature gradient (Knoevenagel): 120 °C isothermal, held for 15 min. Temperature of the detector was 300 °C in both the GC and all the aforementioned programs. Temperature-programmed-desorption (TPD) profile was acquired using a chemisorption analyzer (BEL-CAT) as follows: prior to measurements, 0.1 g of the sample was activated in He (30 mL/min) at 280 °C for 1 h. The sample was subsequently exposed to the pulses of CO_2 (10%) or NH_3 (10%) in He at 40 °C for 1 h. The sample was then flushed with He (30 mL/min) for 1 h. TPD measurements were carried out by raising the temperature from 40 to 300 °C at a heating rate of 5 °C/min.

4. Hot catalyst filtration test and ICP-OES:

A heterogeneity test was conducted for CHB(M) by hot catalyst filtration test and using ICP-OES. For this, 18.6 mmol of AGE was set for cycloaddition with 1.2 MPa CO_2 at 100 °C using 0.3mmol of CHB(M) (1.6 mol% catalyst) for 5 hours at which conversion reached 49.6%. The contents were immediately filtered while hot and analyzed for GC and ICP-OES, while the filtrate was allowed to react again with 1.2 MPa CO_2 at 100 °C. Sampling was performed at 1 hour intervals and analyzed for GC to check if the reaction proceeded further. Other normal batches of reactions were carried out for the same time intervals for comparison.

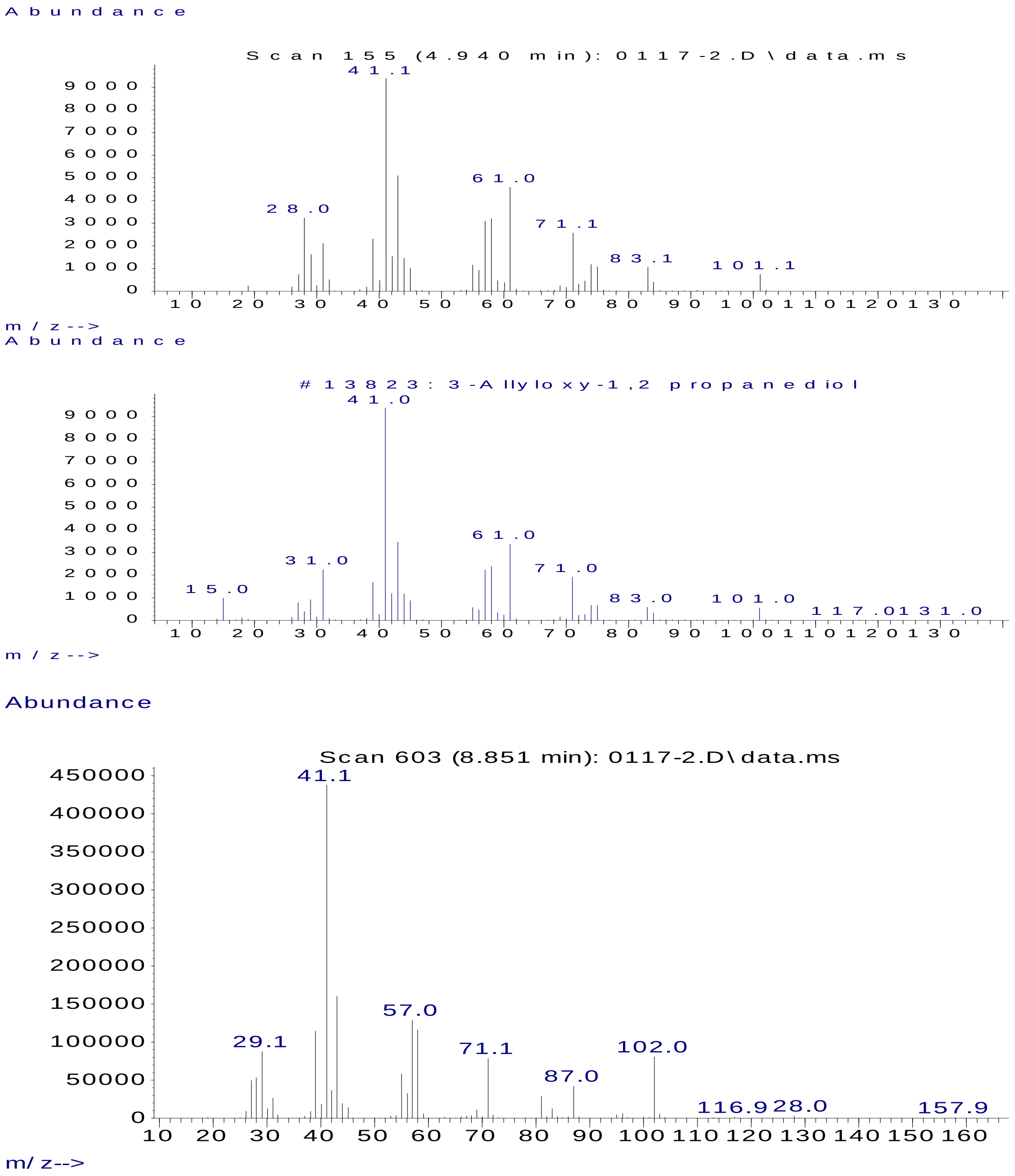


Fig S1. GC-MS analysis report of the cycloaddition of AGE and CO_2, for the ring opened diol side product (RT 4.94), and AGC (8.85) respectively.

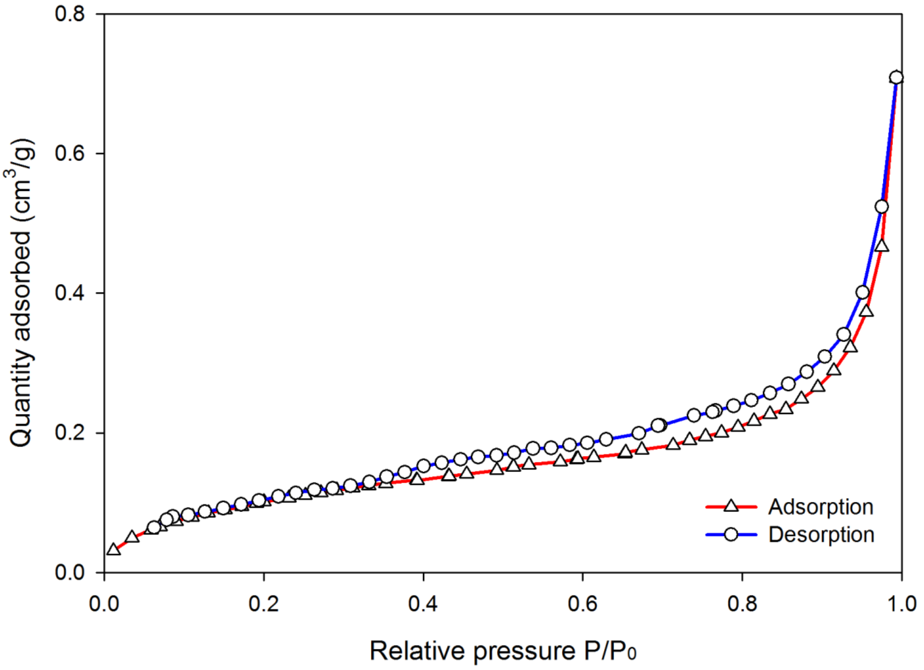


Fig. S2. Nitrogen adsorption-desorption isotherm of CHB(S)

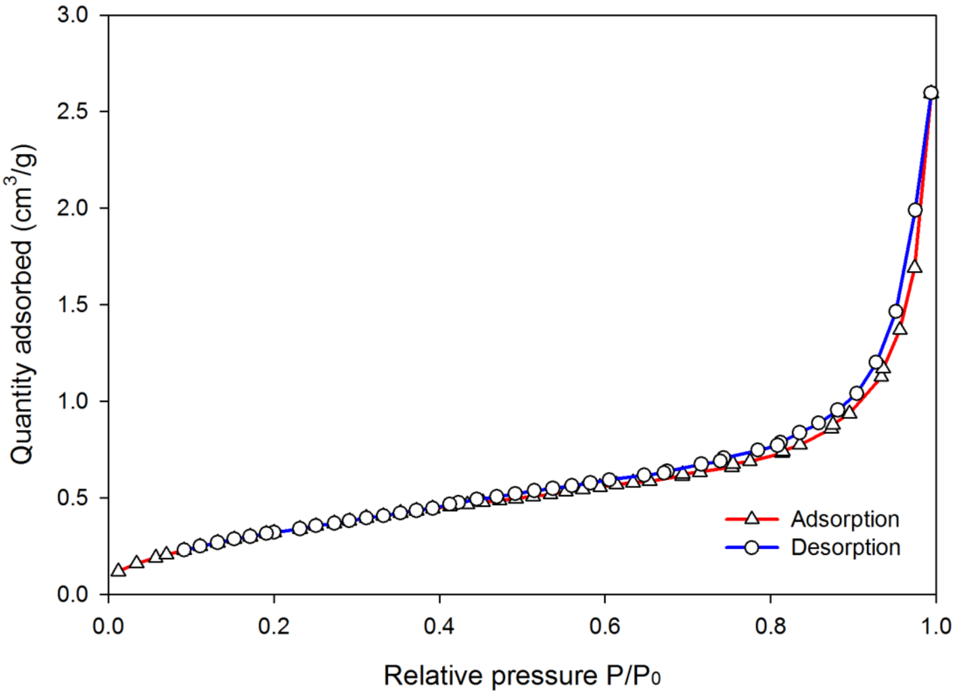


Fig. S3. Nitrogen adsorption-desorption isotherm of CHB(M)

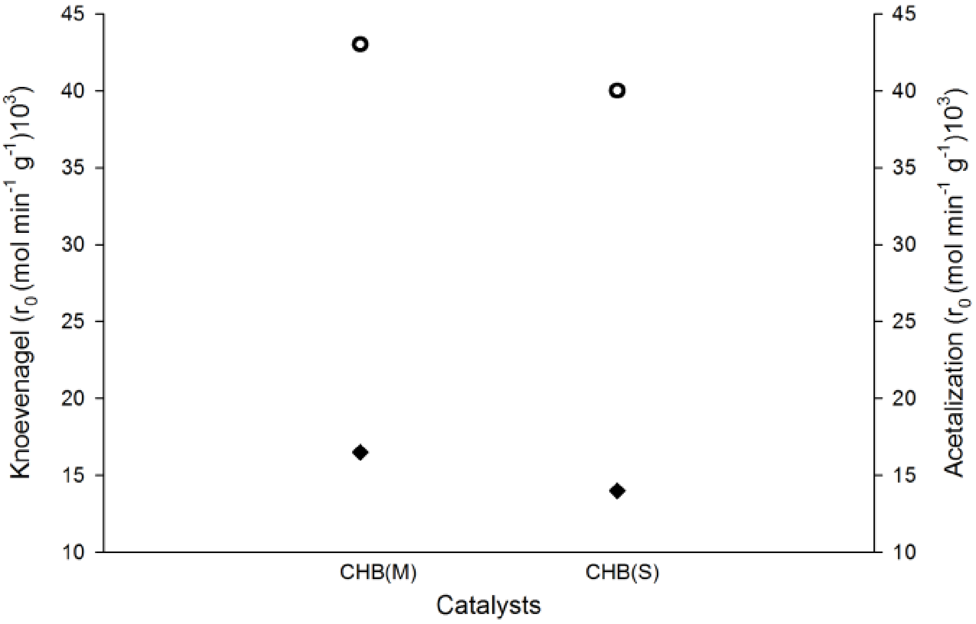


Fig. S4. Initial rates (r0) of acetalization reactions (indicated as ♦) and Knoevenagal condensation (indicated as ○) with CHB(S) and CHB(M) catalysts, corresponding to their acid-base sites.

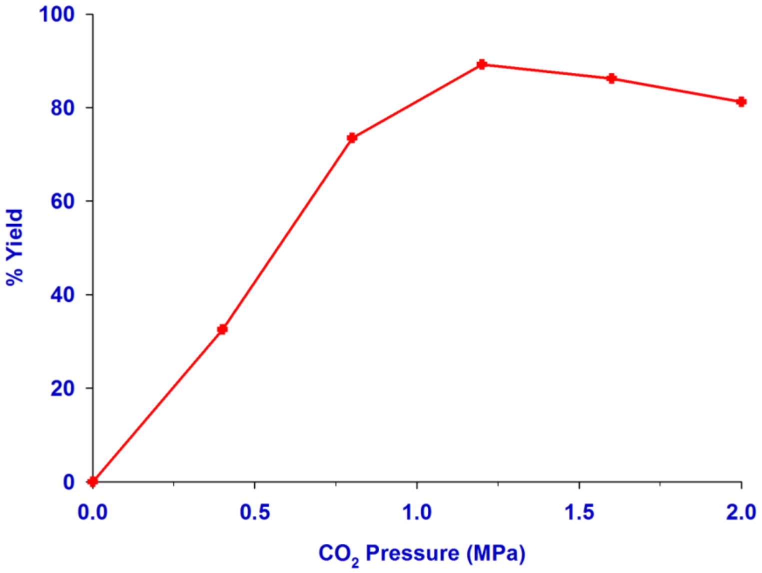


Fig. S5. Effect of CO_2 pressure on the reactivity of AGE and CO_2 using CHB(M)/TBAB system (0.3mmol/0.3mmol) at 80 °C for 6h.

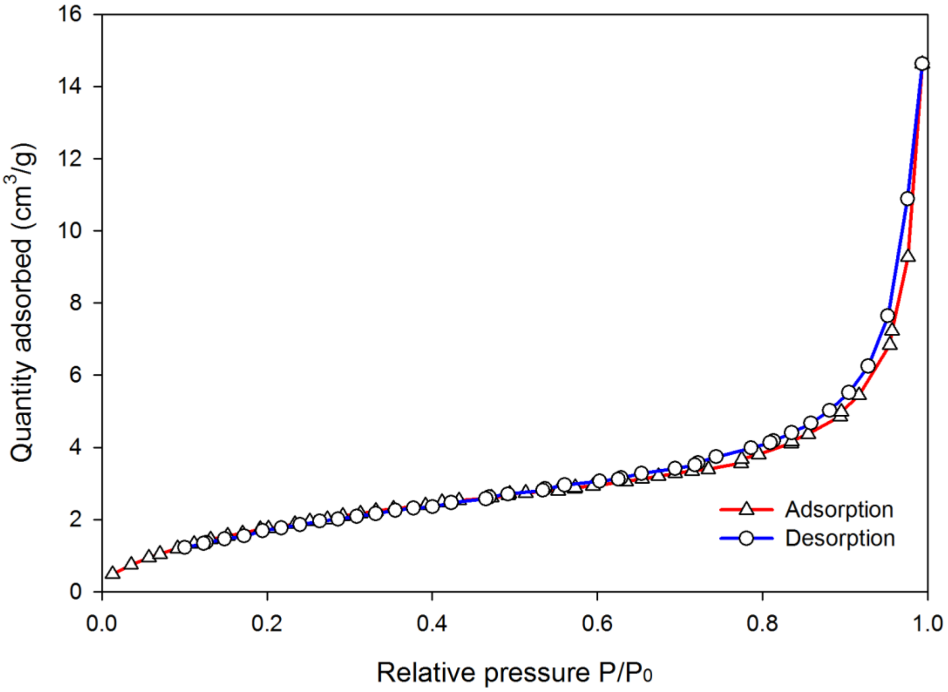


Fig. S6. Nitrogen adsorption-desorption isotherm of recycled CHB(M)

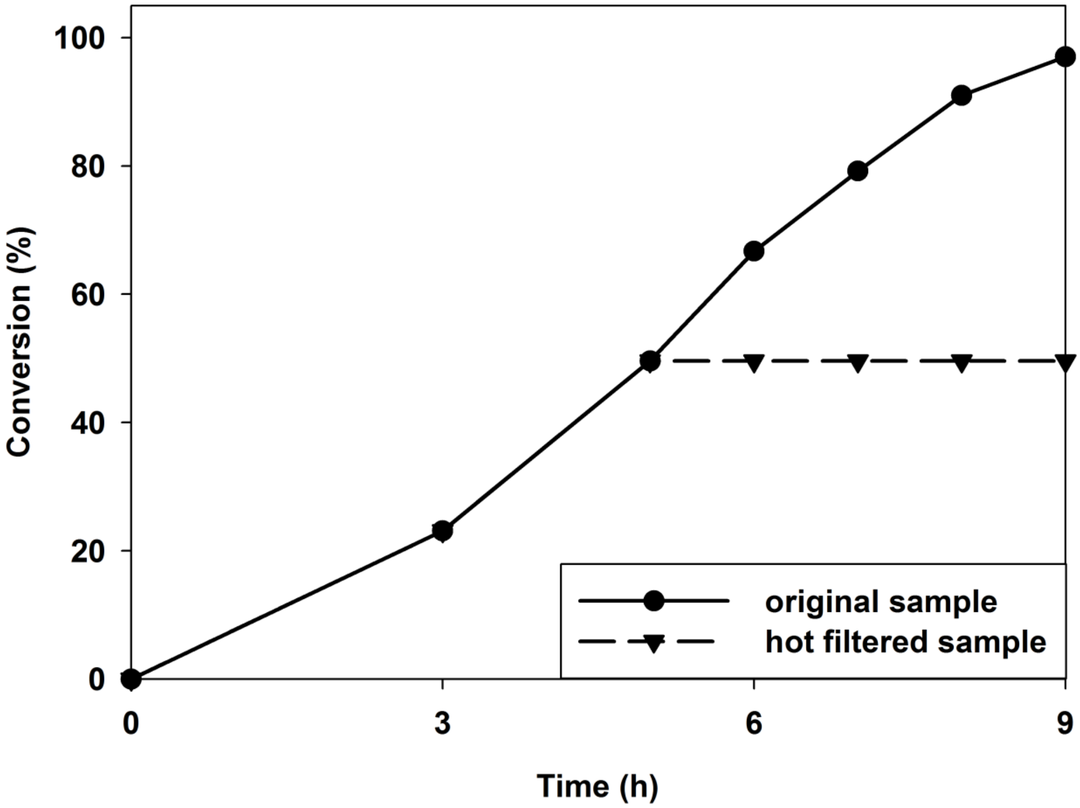
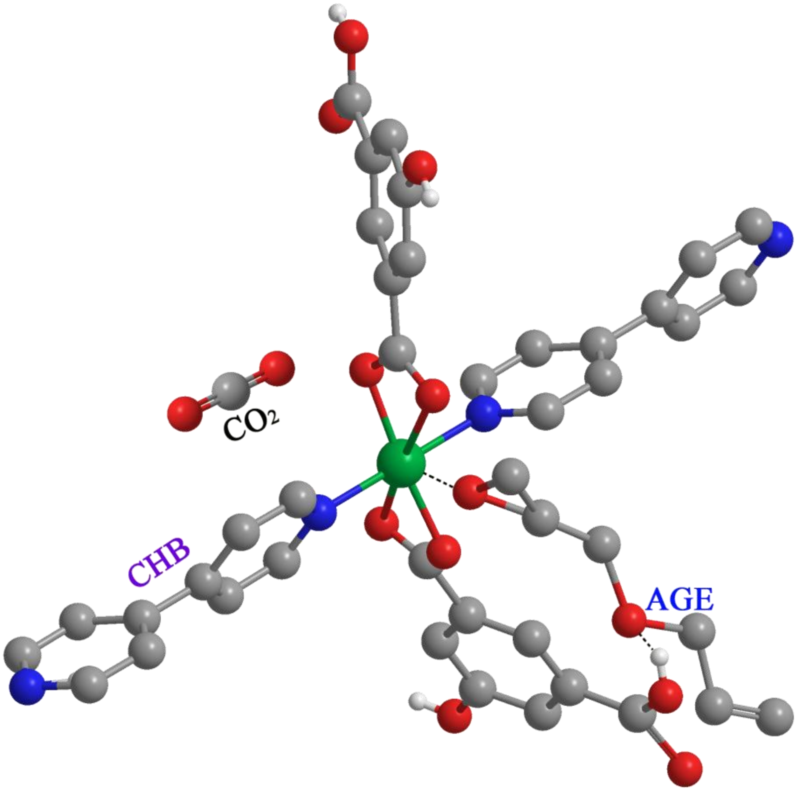
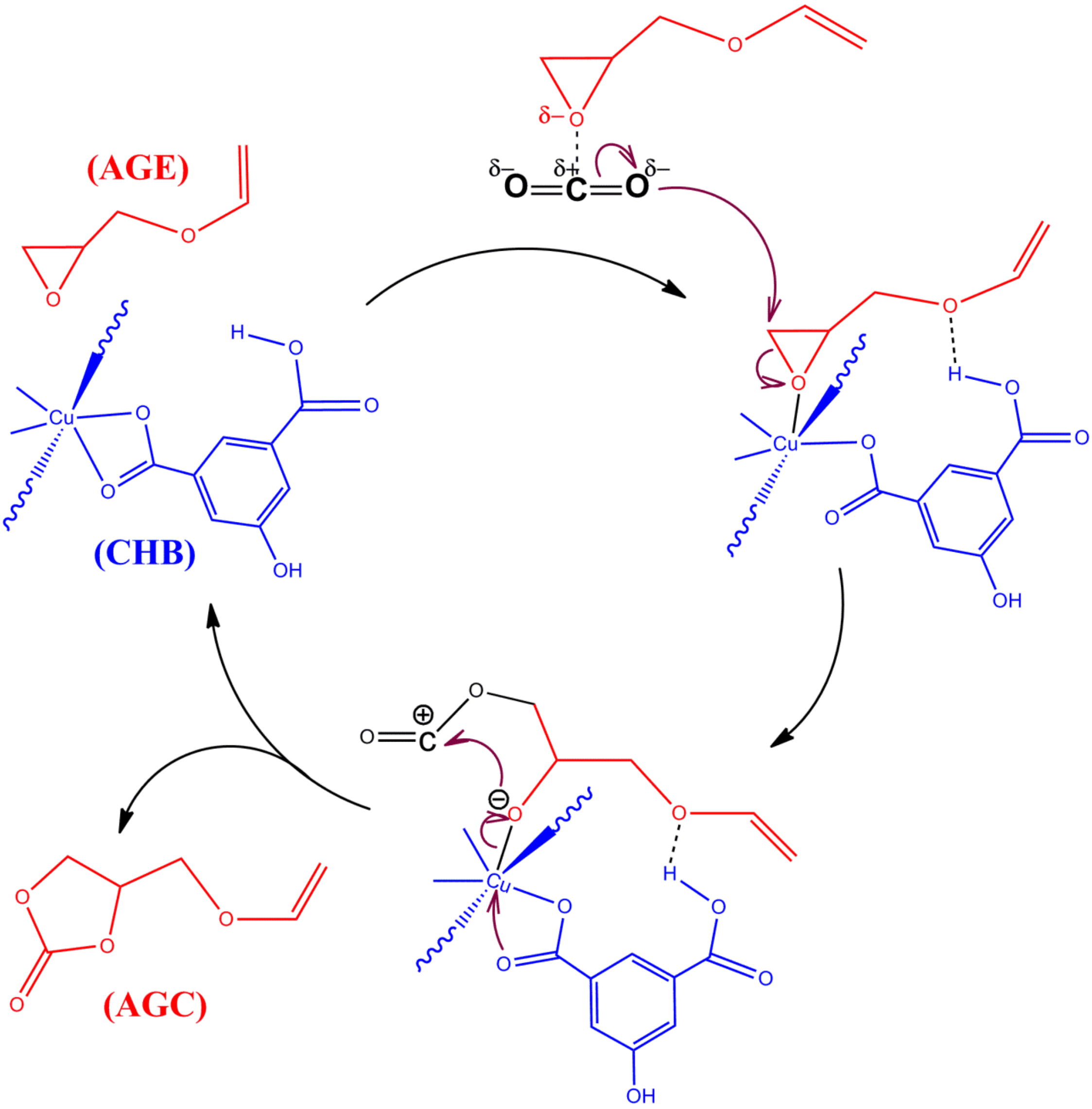


Fig. S7. Hot filtration test. 1.6mol% catalyst CHB(M) 100 °C at 1.2 MPa CO_2. Hot filtration was done at 49.6% conversion, at 6 hours.



Scheme S1. The dual CHB(M)-AGE interaction prior to the cycloaddition reaction



Scheme S2. Plausible mechanism of the cycloaddition of CO_2 and AGE catalyzed by CHB