Electronic Supplementary Information (ESI)

Sustainable Fixation of CO_2 into Epoxides to form Cyclic Carbonates using Hollow Marigold $CuCo_2O_4$ Spinel Microspheres as a Robust Catalyst

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1. Experimental Section

1.1. Materials

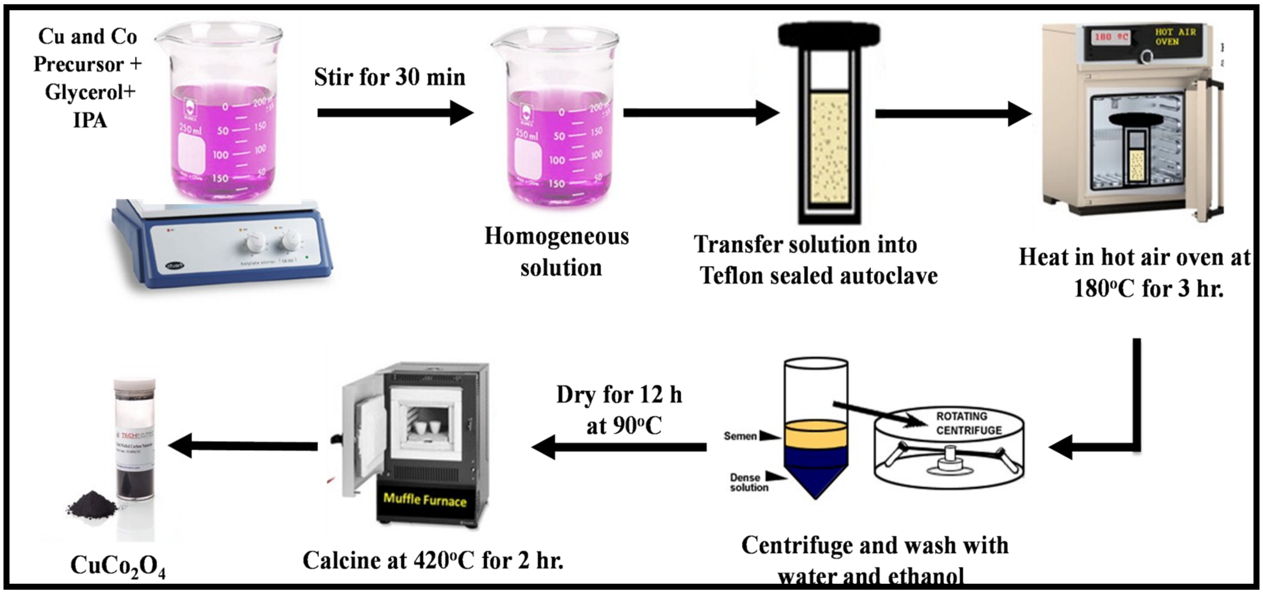
Cobalt nitrate hexahydrate [$Co(NO_3)_2.6H_2O$] (MW: 291.04 g mol^{-1}, 97% purity), copper nitrate trihydrate [$Cu(NO_3)_2.3H_2O$] (MW: 241.60 g mol^{-1}, 98% purity) of analytical grade were purchased from Sigma Aldrich Pvt. Ltd., India. Isopropanol (MW: 60.10 g mol^{-1}, 98% purity) and glycerol (MW: 92.09 g mol^{-1}, 99% purity) were obtained from Avra Pvt. Ltd., India and used without further purification. Distilled water and ethanol (HPLC grade) were used throughout the experiment for washing and synthesis of the catalyst.

For studying the catalytic application of $CuCo_2O_4$ for cycloaddition reactions, the chemicals required were purchased from Sigma Aldrich Pvt. Ltd., India. The reagents used were styrene oxide (MW: 120.15 g mol^{-1}, 98% purity), propylene oxide (MW: 58.08 g mol^{-1}, 98% purity), butylene oxide (MW: 72.11 g mol^{-1}, 98% purity), cyclohexene oxide (MW: 98.14 g mol^{-1}, 98% purity), epichlorohydrin (MW: 92.52 g mol^{-1}, 98% purity), epibromohydrin (MW: 136.98

g mol^{-1}, 98% purity), tetrabutylammonium fluoride (MW: 261.46 g mol^{-1}, 97% purity), tetrabutylammonium bromide (MW: 322.37 g mol^{-1}, 99% purity), tetrabutylammonium iodide (MW: 369.37 g mol^{-1}, 98% purity). The CO_2 gas (99.999% purity) was supplied by Shree Balaji Enterprises, Bangalore, India.

1.2. Catalyst preparation

The marigold $CuCo_2O_4$ microspheres was synthesized using a facile solvothermal method[1], as depicted in **Scheme S1**. Initially, 0.5 mmol of [$Co(NO_3)_2.6H_2O$] and 0.25 mmol of [$Cu(NO_3)_2.3H_2O$] (2:1 ratio) were dissolved in 40 mL of isopropanol. The reaction mixture was stirred for 10 min in order to obtain a homogenous solution following which 8 mL of glycerol was added to the mixture. The resultant pink solution was again stirred for 30 min. Subsequently, the reaction mixture was transferred to a Teflon lined autoclave and tightly sealed in order to evade loss of pressure and maintained at 180 ºC for 3 h in a hot air oven. After completion of reaction, the resultant mixture was allowed to cool down to room temperature naturally and the solid was collected by centrifugation. The obtained solid was alternatively washed with distilled water and ethanol several times in order to remove unreacted precursors and dried in oven for 12 h at 90 ºC and named as Cu-Co double hydroxide glycerate (Cu-Co DH-glycerate precursor). The Cu-Co DH-glycerate precursor acts as soft templates to form $CuCo_2O_4$ spinel microspheres. In order to obtain pure phase of $CuCo_2O_4$, Cu-Co DH glycerate precursor was made to undergo calcination in muffle furnace under static air at 420 ºC for 2 h with a heating rate of 2 ºC min^{-1} and pure $CuCo_2O_4$ catalyst was obtained.



Scheme S1. Schematic representation for preparation of Cu-Co DH-glycerate precursor and $CuCo_2O_4$ spinel

1.3 Catalyst characterization

The thermal stability of the Cu-Co DH-glycerate precursor and hollow marigold $CuCo_2O_4$ spinel microspheres was analysed using thermogravimetric (TGA) analyser with heating rate of 3 °C min^{-1}, from R.T. to 800 °C. The crystallographic nature of the Cu-Co DH-glycerate precursor and hollow marigold $CuCo_2O_4$ spinel microspheres, pure Cu and pure Co was examined and confirmed using powder X-ray diffraction spectroscopy (XRD) noted on a Rigaku X-Ray Diffraction Ultima IV (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan rate of 2º min^{-1} and theta value range of 10-80° at 30 kV voltage and 15 mA current. The morphology and structural identity of Cu-Co DH-glycerate precursor and hollow marigold $CuCo_2O_4$ spinel microspheres was analyzed using Field Emission Scanning Electron Microscope (JEOL JSM-7100F, Singapore) coupled with energy dispersive X-Ray spectroscopy (EDX). The carbon tape on the aluminium metal stub was adequately covered with the powdered sample and subjected to sputtering using gold nanoparticles. Transmission Electron Microscopy was used to check the interior architecture, SAED pattern and lattice fringes of the material using TEM microscope (JEOL JEM-200CX). The accelerating voltage of the electron beam for the microscope was set for 200 kV. The sample was prepared by dropcasting a drop of a dilute solution of $CuCo_2O_4$ in the ethanol on a copper grid. All the copper grids were dried under ambient conditions before analysis.

The XPS analysis was performed to get information about the surface element composition in an ultra-high 80 vacuum chamber fitted out with a hemispherical electron energy analyzer (Perkin Elmer, PHI1257) using non-monochromatized Al Kα source with an excitation energy of 1486.7 eV at room temperature with a pressure of 4×10^{-10} Torr. The samples were characterized by a Micro Raman spectrometer (Renishaw in Via Raman microscope) with a laser excitation wavelength of 532 nm for the structural integrity. The determination of functional groups for both the samples was done by using Fourier Transform Infrared Spectroscopy (FT-IR) in a Perkin Elmer FT-IR instrument by KBr pellets method in the range of 4000 to 500 cm^{-1}.

The surface area analysis of Cu-Co DH-glycerate precursor and hollow marigold $CuCo_2O_4$ spinel microspheres was performed using Brunauer Emmet and Teller (BET) method on Belsorp-Max (M/s. Microtrac BEL, Japan) under N_2 atmosphere at a temperature of -196 ºC. The corresponding pore size distribution of the catalysts was analyzed using Barrett Joyner Halenda (BJH) method. The catalysts were degassed at 120 ºC for 4 h under vacuum prior to analysis in order to push out absorbed moisture. The thermal degradation of Cu-Co DH-glycerate precursor and hollow marigold $CuCo_2O_4$ spinel microspheres was determined by a thermal analyser within the temperature window of 40 ºC to 800 ºC under continuous N_2 flow with a heating rate of 10 ºC min^{-1}.

The NH_3 temperature programmed desorption (TPD) analysis was performed in order to identify the presence of acidic and basic sites in Cu-Co DH-glycerate precursor and hollow marigold $CuCo_2O_4$ spinel microspheres. This analysis was performed in TPD set-up with a quartz reactor (length: 300 mm, inner diameter: 6 mm) connected to a six-port valve and a thermal conductivity detector (M/s. Mayura Analyticals Pvt. Ltd., India). About 50 mg of the material was loaded in the quartz reactor and subjected to pre-treatment under He atmosphere at 300 ºC for 1 h for desorption of adsorbed moisture and consecutively cooled to 100 ºC after degassing. Subsequently, Cu-Co DH-glycerate precursor and hollow marigold $CuCo_2O_4$ spinel microspheres was saturated with 5% NH_3 gas at 100 ºC for 0.5 h, following which the respective catalysts were stripped in presence of He atmosphere for 0.5 h. Finally, the temperature was amplified linearly from 100 ºC to 750 ºC at a ramping rate of 10 ºC min^{-1} and maintained in isothermal zone for an additional 0.5 h. The obtained peak for the desorbed gas monitored using TCD and was visualized on a monitor connected to the TPD unit.

Similarly, H_2 temperature programmed reduction (TPR) was performed on the above mentioned unit. In a typical analysis, 50 mg of $CuCo_2O_4$ spinel was loaded on the quartz reactor and degassed at 300 ºC for 1 h under He environment. Subsequently, the temperature was reduced to 100 ºC and the He environment was replaced by 5% H_2 with a flow rate of 30 mL min^{-1}. The temperature was linearly increased from 100 ºC to 750 ºC with a ramp rate of 10 ºC min^{-1} and maintained at 750 ºC for 0.5 h in order to attain isothermal zone. The amount of H_2 utilized for reduction was calculated using the standard GC software by injecting a known volume of H_2 through a loop using the six-port valve.

Representative procedure for coupling reaction of epoxide and CO_2

The typical coupling reaction of CO_2 and epoxide was carried out in a stainless steel high pressure reactor (100 mL volume) equipped with a magnetic stirrer and automatic temperature control system. Styrene oxide (1 gm, 8.3 mmol), catalyst (50 mg, 5 wt.%), base (0.246 g, 8 mol%) were added to the reactor and the reaction mixture was then purged with CO_2 gas three times to evacuate the atmospheric air and to attain uniform reaction atmosphere following which the system was pressurized to the desired pressure. The temperature of the reaction was maintained at 80 °C. Then, the system was allowed to undergo cycloaddition for required reaction time under constant magnetic stirring. After completion of the reaction, the high pressure reactor was naturally cooled to ambient temperature, and the excess CO_2 gas was released slowly. The reaction mixture was diluted using ethyl acetate and the catalyst was filtered using Whatmann filter paper. The progress of the reaction was confirmed using crude product by analysing the conversion and selectivity of cyclic carbonates obtained by GC (Agilent 7820A, HP-5 column) equipped with flame ionisation detector. Further, the identification and confirmation of products was done using FT-IR (Perkin Elmer), ^{1}H NMR (Bruker 500 MHz) and ^{13}C NMR (Bruker 125 MHz) using $CDCl_3$ as solvent, GC-MS (Shimadzu QP2010SE GCMS), LC-MS (Agilent (1260 infinity) Technologies).

The conversion of styrene oxide (C_{so}) was calculated using the formula $C_{SO} = (SO_{in} - SO_{out}) \times 100 / SO_{in}$ and the selectivity of styrene carbonate (S_{SC}) was calculated using the formula $S_{SC} = Y_{SC} \times 100 / C_{SO}$, where SO_{in} is the amount of SO at the inlet and SO_{out} is the amount of SO in the reaction mass. Y_{SC} is the corresponding yield of SC. The obtained cyclic carbonates as products were also analysed and confirmed by GC-MS and LC-Mass spectroscopy. The residual solid catalyst was washed with 50 mL ethanol and dried in the oven at 90 ºC for 12 h, which was then used for considering the catalyst recyclability. A fresh set of epoxide was run for consecutive cycles under the optimized reaction conditions with recycled catalyst.

Table S1: N_2 adsorption and desorption and surface area analysis

Sr. No.	Catalyst	BET surface area (m^2 g^{-1})	Pore Diameter (nm)	Pore Volume (cm^3 g^{-1})
1.	Cu-Co DH	153.71	3.92	0.2112
2.	$CuCo_2O_4$	47.537	14.27	0.1035

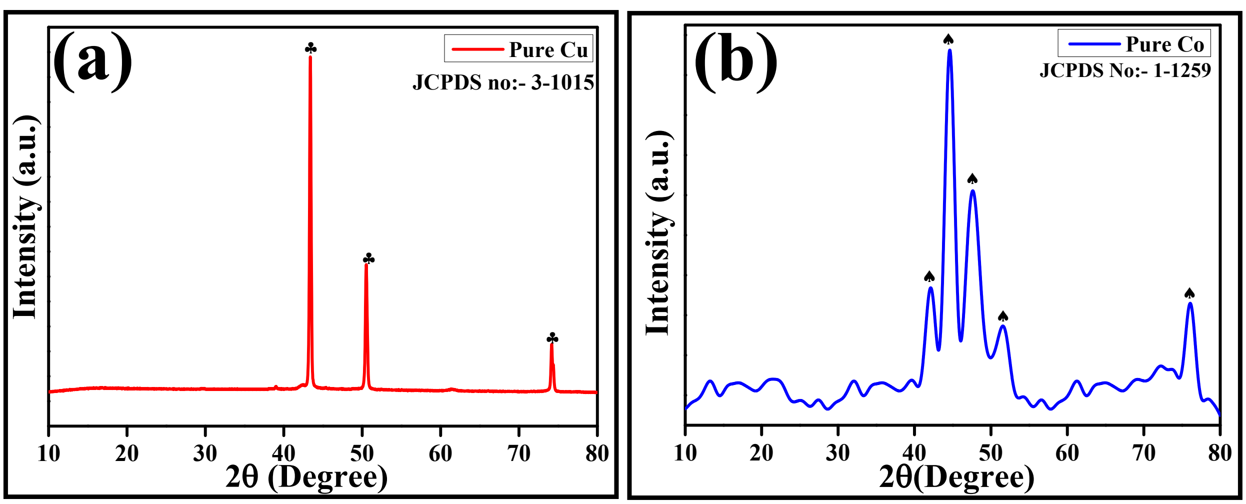


Figure S1. XRD analysis of (a) Pure Cu and (b) Pure Co

References:

1. S. Kamari Kaverlavani, S. E. Moosavifard and A. Bakouei, *Chem. Commun.*, 2017, **53**, 1052–1055.