FULL PAPER

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High yield room temperature conversion of carbon dioxide into cyclic carbonates catalyzed by mixed metal oxide (CuO-ZnO) nano-flakes/micro-flakes (Cozi-nmf)

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Department of Science and Technology, Ministry of Science and Technology, India, Grant/Award Number: PURSE and FIST programs; University Grants Commission, Grant/Award Number: BSR Fellowship, CAS and UPE Capturing and converting carbon dioxide (CO_2) into useful organic molecules and polymers is the best way of alleviating excessive release of it from industrial sources to the environment. Cyclic carbonate synthesis by cycloaddition from CO₂ and epoxides through a catalytic process is a 100% atom economic reaction established five decades ago. Despite the availability of many efficient catalytic systems, there are shortcomings in either tedious preparatory procedure of catalyst, separation problem associated with homogeneous catalysis, or the requirement of pure CO₂. In this work, we report the catalytic system based on copper and zinc mixed metal oxides (CuO-ZnO) nano-flakes/micro-flakes (Cozi-nmf) for cycloaddition of CO₂ with various epoxides at room temperature under solvent-free conditions. The novel recyclable heterogeneous catalyst was prepared via a simple procedure successfully at room temperature by grinding process. The synthesis of both catalyst and cyclic carbonates described here is greener and used inexpensive source materials to produce them. The yields of the synthesized cyclic carbonates were more than 95%, except for many reactions. The high efficiency of Cozi-nmf as a catalyst is explained based on the availability of the bare catalyst surface, which promoted the hindrance free movement of electrons and adsorption of substrate effectively.

K E Y W O R D S

carbon dioxide capture, catalysis, cyclic carbonates, mixed metal oxides

1 | INTRODUCTION

Owing to the industrial revolution, the atmospheric carbon dioxide (CO_2) level is increasing rapidly, which is the primary cause of global warming. On the other hand, the attractive CO_2 capture reactions represent an alternative and safer way of mitigating the excessive release of it from various industrial sources.^[1] Using CO_2 , it is possible to prepare many organic compounds by carboxylation reaction and specific transformation reactions into carboxylic acids, organic carbonates, urea, methanol, and polymers.^[2] Because CO_2 is an abundant, economic, and nontoxic renewable carbon resource,^[3] the efficient methods that convert it into valuable chemicals are much attractive.^[4] The production of cyclic carbonates by cyclo-addition from CO_2 and epoxides is a 100% atom economic reaction established five decades ago.^[5] However, because of the low reactivity and thermal stability of CO_2 , the transformation of it into several useful products always involves a principal step of activating CO_2 molecules.^[6]

Cyclic carbonates are fascinating compounds finding a wide range of applications such as electrolyte in lithium-ion batteries,^[7] polar aprotic solvents^[8] intermediates for fine chemicals, and building blocks in the

manufacture of pharmaceuticals.^[9] The cyclic carbonates with different functional groups are used as the precursor materials for polymeric materials like polycarbonates, polyurethanes, and polyesters.^[10,11] There are many reports on the development of catalytic systems to activate CO₂. Until now, the efficient catalysts for the cycloaddition of CO₂ with epoxides are confined to materials such as ionic liquids.^[12] organic metal complexes,^[13] organocatalysts, and quaternary ammonium.^[14] Some of the known catalytic systems for epoxide-CO₂ coupling includes Al (III)@cages,^[15] Ti (HPO₄)₂·H₂O,^[16] ZnCl₂/ Al₂O₃,^[17] succinimide-KI,^[18] PCN-222(Co),^[19] PIM2,^[20] and some complexes^[21] of Zn, Co, Mo, Pd, Cr, Al, Cu, Mg, and Sn. Much of the catalytic systems reported to the cyclic carbonate synthesis are homogeneous catalysts. Further, many of these reactions require high temperatures and high pressures of pure CO₂ to induce the reaction with epoxides.

Generally, the pure CO_2 is obtained by purifying flue gases containing large amounts of CO_2 released from power plants and industrial furnaces. These purification processes are typically time-consuming and involve additional cost and energy. Despite the good catalytic behavior manifested by the catalysts mentioned above, their intrinsic homogeneous nature precludes re-utilization and limits their practical application on an industrial scale, especially those involving tedious preparation procedures.^[5] Therefore, it is essential to develop highly efficient and stable heterogeneous catalysts for converting industrial CO_2 at atmospheric pressure and the mild temperature.^[22]

The semiconducting oxides such as ZnO, TiO₂, CeO₂, ZrO₂, and SnO₂ having different nanostructures are appealing materials due to their unique properties. They find applications in various areas including, catalysis,^[23] photocatalysis,^[24] solar cells,^[25] and gas sensors.^[26] Due to their exciting surface properties, the metal oxides related to CuO and ZnO nanostructures like CuO-NiO, CuO-MgO, CuO-Fe₃O₄, CuO-TiO₂, NiO-ZnO, ZnO-TiO₂, and CuO-ZnO-ZrO₂ have been studies elaborately.^[27–32] Based on many reports on mixed metal oxides, we are interested in developing a versatile catalytic system based on copper and zinc mixed metal oxides (CuO-ZnO) nano-particles/ micro-particles. These materials have been used in many chemical, physics, and materials science fields due to their diversified applications, including catalysis, gas sensors, solar cells, and optoelectronics devices.^[33]

The chemical reactions occur on the catalyst's surface. To use metal oxides in the form of nano-particles/microparticles as a catalyst in any reaction, their active centers at the surface should be free from any hindrance and exposed to the interaction with the substrate. Moreover, a critical scan in the literature revealed that most reactions through different physical and chemical pathways required high temperatures to produce copper oxide-zinc oxide (CuO-ZnO) nanocomposite.^[34] Therefore, we have designed a simple procedure and synthesized the CuO-ZnO nano-flakes/micro-flakes (**Cozi-nmf**) successfully with the exposed surface and explored their catalytic activity for CO₂ capture reactions. We have synthesized CuO and ZnO in a 1:1 ratio to attain a high specific surface area. We have established the novel recyclable heterogeneous catalysis of **Cozi-nmf** having exposed surfaces for cycloaddition of CO₂ with various epoxides at room temperature under solvent-free conditions. The synthesis described here is greener and used inexpensive source materials to produce catalyst and cyclic carbonates.

2 | EXPERIMENTAL SECTION

2.1 | Materials

ZnCl₂, CuCl₂, and epoxides were purchased from Sigma-Aldrich. Anhydrous sodium hydroxide was purchased from Merck, India. Solvents were dried and distilled using standard procedure and then used for work up and column chromatography. Thin layer chromatography was done using commercially available (MERCK) plates with silica gel 60–120 mess.

2.2 | Instrumentation

Powder X-ray diffraction (PXRD) patterns of Cozi-nmf was recorded on a Bruker D8 X-ray diffractometer $(\lambda [Cu-K\alpha] = 1.54 \text{ Å})$, employing a scan rate of 1° min⁻¹ for the range of 20°C to 80°C. Field emission-scanning electron microscopy (FESEM) images of Cozi-nmf and its energy-dispersive X-ray spectrum (EDAX) were recorded using Ultra 55 Carl Zeiss instrument) operated at variable voltages. The Cozi-nmf sample was suspended in isopropanol and then dispersed on ITO plates to record FESEM micrographs. TEM images of Cozi-nmf were acquired by using an FEI Technai G2 20 STEM instrument at an acceleration voltage of 200 kV. The Cozi-nmf sample for TEM analyses was dispersed in isopropanol, and one to two drops of dispersion were dripped onto a carbon-coated copper grid (200 mesh). XPS spectra were recorded in a Thermo Scientific K Alpha spectrometer equipped with a micro-focused monochromatic X-ray source (Al K α , spot size \sim 400 μ m) operating at 70 W. An optimum concentration of Cozi-nmf was drop-casted onto a quartz substrate for the XPS analysis.

¹H NMR and ¹³C NMR spectra of cyclic carbonates in CDCl₃ were recorded on a 500 or 400 MHz spectrometer at room temperature. The chemical shifts (δ) are reported

in ppm scale downfield from the internal standard tetramethyl silane TMS ($\delta = 0.0$). High-resolution mass spectra (HRMS) were recorded using ESI-TOF techniques. TGA was recorded on a PerkinElmer–STA 6000. Surface area analysis was determined from the BET analysis, which was recorded by the Quantachrome instruments. Melting points of cyclic carbonates were measured on a Buchi B-540 apparatus.

2.3 | Synthesis of nanocomposite copper oxide-zinc oxide (CuO-ZnO) nano-flakes/ micro-flakes (Cozi-nmf)

The grinding process for synthesizing **Cozi-nmf** is described as follows: $CuCl_2$ (2 mmol) and $ZnCl_2$ (2 mmol) were mixed uniformly by grinding in an agate mortar for 5 min until the mixture turned black color. After that solid NaOH (8 mmol) was added into the mortar, and the grinding was continued for another 10 min. The resultant black mass was gathered and washed with water followed by absolute methanol several times by centrifugation and then dried at 60°C to get light black powder of **Cozi-nmf**. The whole grinding process was operated at room temperature and exposed to the air. We have extended the reaction to prepare catalyst using 20 mmol of the starting materials in a single reaction.

2.4 | Synthesis of cyclic carbonate from epoxide and CO₂

In a typical reaction (Scheme 1), epoxide (1 mmol), t-butyl ammonium bromide (0.05 mol), and catalyst, **Cozi-nmf** (5 mg) were placed in a 50 ml round bottom flask filled with CO_2 gas from a CO_2 cylinder. After mixing them, CO_2 gas flow was continued purging through the needle dipped in the reaction mixture. The reactions were continued at rt for 3–6 h, and CO_2 was provided by a gas cylinder (1 atm) connected to the flask. After completing the reaction, it was worked up with water and ethyl acetate and dried using anhydrous Na_2SO_4 . The organic solvent was



SCHEME 1 Synthesis of cyclic carbonates from terminal epoxides and CO₂ at 1 bar pressure

evaporated under a vacuum. The reaction mixture was purified by column chromatography on silica gel with ethyl acetate and hexane as eluent to get the purified cyclic carbonates. All compounds were characterized based on their spectroscopic data (S1–S12; ¹H, ¹³C NMR, and HRMS) compared to those reported in the literature.

2.5 | Spectral data of cyclic carbonates

2.5.1 | 4-phenyl-1,3-dioxolan-2-one

Isolated yield: 93%, white solid, mp: 57°C. ¹H NMR (500 MHz, CDCl₃): δ = 4.36 (1H, t, J = 8 Hz), 4.82 (1H, t, J = 8 Hz), 5.70 (1H, t, J = 8 Hz), 7.35–7.39 (2H, m), 7.43–7.46 (3H, m), and ¹³C NMR (126 MHz, CDCl₃ MHz, CDCl₃): 71.11, 77.93, 125.79, 129.16, 129.64, 135.78, 154.79 HRMS calculated for C₉H₈O₃ [M + Na]⁺: 187.1571, found: 187.1572.

2.5.2 | 4-(Phenoxymethyl)-1,3-dioxolan-2-one

Isolated yield: 97%, white solid, mp: 96–97°C. ¹H NMR (400 MHz, CDCl₃): δ = 4.16–4.18 (1H, dd, J = 10 Hz, J = 7 Hz), 4.24–4.27 (1H, dd, J = 10 Hz, 6 Hz), 4.54–4.57 (1H, q), 4.64 (1H, t, J = 8 Hz), 5.02–5.07 (1H, m), 6.92–6.94 (m, 2H), 7.02–7.05 (1H, m), 7.31–7.34 (2H, m), and ¹³C NMR (101 MHz, CDCl₃ MHz, CDCl₃): δ = 66.25, 66.94, 74.05, 114.65, 122.04, 129.70, 154.56, 157.76. HRMS calculated for C₁₀H₁₀O₄ [M + Na]⁺: 217.0471, found: 217.0471.

2.5.3 | 4-([4-Chlorophenoxy]methyl)-1,3-dioxolan-2-one

Isolated yield: 95%. White solid, m.p. $101-102^{\circ}$ C. ¹H NMR (500 MHz, CDCl₃): $\delta = 4.11-4.15$ (1H, dd, J = 10 Hz, 7 Hz), 4.22-4.26 (1H, dd, J = 10 Hz, 7 Hz), 4.52-4.56 (1H, q), 4.64 (1H, t, J = 8 Hz), 5.02-5.07 (1H, m), 6.84-6.88 (2H, m), 7.25-7.29 (2H, m), and ¹³C NMR (126 MHz, CDCl₃): 66.10, 67.27, 73.96, 115.94, 127.03, 129.40, 129.62154.55, 156.36. HRMS calculated for C₁₀H_{9Cl}O₄ [M]⁺: 228.0212, found: 228.0212.

2.5.4 | 4-([4-Bromophenoxy]methyl)-1,3-dioxolan-2-one

Isolated yield: 94%. white solid, mp:103–104°C, ¹H NMR (500 MHz, CDCl₃): δ = 412–4.14 (1H, dd, J = 10 Hz, 7 Hz), 4.22–4.25(1H, dd, J = 10 Hz, 6 Hz), 4.52–4.55

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(1H, q), 4.64 (1H, t, J = 8 Hz), 5.03–5.07 (1H, m), 6.80–6.83 (2H, m), 7.38–7.43(2H, m), and ¹³C NMR (126 MHz, CDCl₃): 66.11, 67.22, 74.00, 114.32, 116.45, 132.34, 132.55, 154.59, 156.89. HRMS calculated for $C_{10}H_{9Br}O_4$ [M]⁺: 271.9565, found: 271.9562, $C_{10}H_{9Br}O_4$ [M + 2]⁺: 273.9540, found: 273.9540.

2.5.5 | 4-([o-Tolyloxy]methyl)-1,3-dioxolan-2-one

Isolated yield:97%, white solid, mp: 96°C, ¹H NMR (500 MHz, CDCl₃): $\delta = 2.24$ (3H, s), 4.14–4.17 (1H, dd, J = 13 Hz, 7 Hz),, 4.27–4.30 (1H, dd, J = 14 Hz, 7 Hz), 4.59–4.62 (1H, q), 4.66 (1H, t, J = 8 Hz), 5.06–5.10(1H, m), 6.78–6.81 (1H, t, J = 5 Hz), 6.93–6.96 (1H, m), 7.17–7.20 (2H, m), and ¹³C NMR (126 MHz, CDCl₃): 16.00, 66.27, 66.99, 74.22, 110.79, 121.67, 126.90, 131.10, 154.83, 155.75. HRMS calculated for C₁₁H₁₂O₄ [M + NH₄]⁺: 226.0957, found: 226.0957.

2.5.6 | 4-(([1,1'-biphenyl]-2-yloxy) methyl)-1,3-dioxolan-2-one

Isolated yield: 93%, white solid, mp:105–107°C, ¹H NMR (500 MHz, CDCl₃): δ = 3.60–3.70 (2H, m), 3.96–4.02 (2H, m), 4.06–4.08 (1H, m), 7.01(1H, d, J = 8 Hz), 7.09 (1H, t, J = 7 Hz), 7.32–7.36 (3H, m), 7.43 (2H,t, J = 7 Hz), 7.50 (2H, d J = 7 Hz), and ¹³C NMR (126 MHz, CDCl₃): δ = 63.63, 70.17, 70.49, 113.23, 121.81, 127.14, 128.15, 128.77, 129.38, 130.90, 131.49, 138.36, 155.28. HRMS calculated for C₁₆H₁₄O₄ [M + Na]⁺: 293.0797, found: 293.0798.

2.5.7 | 4-([4-methoxyphenoxy]methyl) -1,3-dioxolan-2-one

Isolated yield: 96%, white solid, mp: 99–100°C, ¹H NMR (400 MHz, CDCl₃): δ = 3.13 (3H, s), 4.24 (2H, d, J = 4 Hz), 4.62–4.64 (2H, m), 5.00–5.06 (1H, m), 6.89–6.97 (3H, m), 7.01–7.06 (1H, m), and ¹³C NMR (101 MHz, CDCl₃): 55.90, 66.42, 69.39, 74.45, 112.57,116.77, 121.04, 123.49, 147.46, 150.43, 154.77. HRMS calculated for C₁₁H₁₂O₅ [M + H] ⁺: 225.0637, found: 225.0636.

2.5.8 | 4-((4-[tert-butyl]phenoxy)methyl)-1,3-dioxolan-2-one

Isolated yield: 98%, white solid, mp:98–100°C, ¹H NMR (500 MHz, CDCl₃): δ = 1.31 (9H, s), 4.14–4.17 (1H, dd, J = 10 Hz, 7 Hz), 4.22–4.25 (1H, dd, J = 11 Hz, 6 Hz), 4.52 (1H, q), 4.62 (1H, t, J = 8 Hz), 5.01–5.06 (1H, m), 6.85–6.88 (2H, m), 7.32–7.34 (2H, m), and ¹³C NMR (126 MHz, CDCl₃): 31.45, 34.15 66.30, 67.06, 74.10, 114.17, 126.47, 144.88, 154.60, 155.55. HRMS calculated for C₁₄H₁₈O₄ [M + NH₄] ⁺: 268.1420, found: 268.1420.

2.5.9 | 4,4'-((1,3-phenylenebis [oxy])bis (methylene))bis(1,3-dioxolan-2-one)

Isolated yield: 90%, colorless gel; ¹H NMR (400 MHz, CDCl₃): δ = 4.11–4.14 (2H, dd, J = Hz), 4.23–4.25 (2H, dd, J = Hz, Hz), 4.51–4.54 (2H, q), 4.63 (2H, t, J = Hz), 5.03–5.07 (2H, m), 6.49 (1H, d, J = Hz), 6.55–6.57 (2H, d, J = Hz), 7.19–7.23 (1H, t, J = Hz), and ¹³C NMR (101 MHz, CDCl₃): 66.14, 67.10, 67.15, 74.05, 101.97, 102.06, 107.95, 130.41, 154.81, 154.82, 159.06. HRMS calculated for C₁₄H₁₄O₈ [M + Na] ⁺: 333.0958, found: 333.0958.

2.5.10 | 4-([Benzyloxy]methyl)-1,3-dioxolan-2-one

Isolated yield: 93%, colorless liquid, ¹H NMR (400 MHz, CDCl₃): δ = 3.62–3.65 (1H, dd, J = 11 Hz, 7 Hz), 3.71–3.74 (1H, dd, J = 11 Hz, 7 Hz), 4.39–4.42 (1H, q), 4.50 (1H, t, J = 8 Hz), 4.57–4.65(2H, m), 4.82–4.85 (1H, m), 7.31–7.33(3H, m), 7.36–7.39 (2H, m), and ¹³C NMR (101 MHz, CDCl₃): 66.32, 68.84, 73.73, 75.00, 127.78, 128.11, 128.60, 137.06, 154.93. HRMS calculated for C₁₁H₁₂O₄ [M + NH₄] ⁺: 226.0954, found: 226.0953.

2.5.11 | 4-ethyl-1,3-dioxolan-2-one

Isolated yield: 74%, colorless liquid, ¹H NMR (500 MHz, CDCl₃): $\delta = 0.98-1.031$ (3H, m), 1.71–1.85 (2H, m), 4.05–4.09 (1H, q), 4.50–4.53 (1H, t, J = 8 Hz), 4.62–4.68 (2H, m), and ¹³C NMR (126 MHz, CDCl₃): 19.72, 68.97, 77.96, 155.06. HRMS calculated for C₅H₈O₃ [M + NH₄] ⁺: 134.1539, found: 134.1530.

2.5.12 | 4-butyl-1,3-dioxolan-2-one

Isolated yield: 68%, colorless liquid, ¹H NMR (500 MHz, CDCl₃): δ = 0.92 (3H, t), 1.34–1.46 (4H, m), 1.64–1.71 (1H, m), 1.77–1.84 (1H, m), 4.04–4.07 (1H, q), 4.52 (1H, t, J = 8 Hz), 4.66–4.72 (1H, m), and ¹³C NMR (126 MHz, CDCl₃): 13.84, 22.29, 26.47, 33.61, 68.97, 77.38, 69.42, 155.14. HRMS calculated for C₇H₁₂O₃ [M + NH₄] ⁺: 167.0684, found: 167.0686.

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3.1 | Room temperature synthesis of catalyst and its characterization

The procedure involved in the synthesis of materials determines their usability on a large scale. In the present work, **Cozi-nmf** was produced at room temperature by the solvent-free grinding method easily within 10 min. The required product was purified by water. The X-ray diffraction pattern gave preliminary information on the formation of **Cozi-nmf**. The typical powder XRD pattern (Figure 1) obtained from the sample of **Cozi-nmf** exhibited diffraction peaks at 20 values of 31.6, 34.3, 36.0, 47.3, 56.5, 62.7, 66.1, 67.7, and 68.8 (°). The representative (hkl) planes of the corresponding diffraction peaks (100), (002), (101), (102), (110), (103), (200), (112), and (201) were identified to the



FIGURE 1 Powder X- ray diffraction spectrum of Cozi-nmf

ZnO wurtzite phase (JCPDF No: 036–1451). However, diffraction peaks at 20 values of 31.6, 34.3, 36.0, 38.5, 47.3, 48.4, 53.5, 56.5, 57.9, and 61.3 (°) were identified to the lattice planes of [(110), (002), ($^{-1}$ 11), (111), ($^{-1}$ 12), ($^{-2}$ 02), (020), (021), (202), and (113)], which were matching with CuO monoclinic phase (JCPDS No: 80–0076). Further, the existence of three diffraction peaks at 20 values of Cu at 31.3, 34.3, and 36.1 (°) being overlapped completely with ZnO diffraction peaks with the variation of 0.85–1.14 (°), which established the formation of ZnO-CuO composite material.

The analysis of morphological features of Cozi-nmf were by FESEM images (Figure 2a,b) revealed the formation of flake-like particles of CuO-ZnO composite materials (Cozi-nmf) with thickness in nanometer's order while overall size in microns. The elemental mapping images by EDS (Figure 2c) demonstrated the presence of oxygen, zinc, and copper elements throughout architecture, whereas the atomic ratio was matching with CuO-ZnO (Cu: Zn: O = 1:1:2) (Figure 2d-f). The TEM, HRTEM, and SAED analyses of Cozi-nmf are shown in Figure 3. The crystallinity of material was evident clearly from the HRTEM image (Figure 3c) The selected area electron diffraction (SAED) indicated (Figure 3d) corresponds to the plane (110) at d spacing value at 2.7 Å of CuO, and the plane (101) at d spacing value at 2.4 Å ZnO indicated the formation of CuO-ZnO composite material and the bright spots revealed the high crystalline nature.

X-ray photoelectron spectroscopy (XPS) analyses (Figure 4) of **Cozi-nmf** disclosed the oxidation state of elements in the composite. First, the XPS survey spectra of the sample confirmed the presence of Cu, Zn, and O atoms in **Cozi-nmf**. There are no other elements observed except Si and C from the glass plate. The Zn2p spectra showed two symmetric peaks, the peak around 1,024.0 eV corresponds to the Zn2p3/2, and the one



FIGURE 2 FE-SEM image of **Cozinmf**, 200 nm (a), 100 nm (b), EDS spectrum, and (c), Cu, Zn, and O elemental mapping (d–f)



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FIGURE 4 XPS spectrum of **Cozi-nmf** (a) Zn 2p, (b) Cu 2p, (c) O 1s, and (d) survey spectrum

around 1,047.1 eV is assigned to Zn 2p1/2, indicating the oxidation state of Zn (II) ion in the sample. In the Cu2p spectrum, the peaks around 934.5 and 955.5 eV in all the samples confirmed the presence of Cu 2p3/2 and Cu 2p1/2, indicating the oxidation state of Cu (II) (Figure 4b). The O 1s peaks observed around 533.3 eV was assigned to oxygen (Figure 4c).

3.2 | Stability and surface area

The thermal stability of **Cozi-nmf** was investigated by thermal gravimetric analysis (TGA). The composite **Cozinmf** underwent a sharp weight loss of about 6.3% up to 250°C, corresponding to the surface adsorbed residues (Figure 5). After an initial weight loss, the composite was



FIGURE 5 Thermogravimetric analysis of Cozi-nmf



FIGURE 6 N₂ adsorption and desorption isotherm of Cozi-nmf

TABLE 1Solvent optimizationusing the model reaction the presenceof **Cozi-nmf**

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losing weight of about 4% slowly stable up to 800°C. The availability of surface freely for the interaction with the substrate is essential for effective catalysis. Therefore, the specific surface area of **Cozi-nmf** was measured based on single gas adsorption at a constant temperature, whereas nitrogen gas was used as an adsorbate. The N₂ adsorption–desorption isotherm of **Cozi-nmf** (Figure 6) was determined from the data points in this pressure range P/P0 of 0–1.0, and the surface area was calculated as 45.8 m² g⁻¹. Envisioning here is that this entire surface area will be available for catalysis without any hindrance for the catalytic activity to produce cyclic carbonates.

3.3 | Catalytic activity

The metal oxides in the form of nano-/micro-particles are preferred as catalysts compared to their bulk counterparts because of increased surface area. However, many chemical synthesis procedures of nanoparticles use various long-chain surfactant molecules to stabilize the size of the particles. These organic surfactant molecules not only hide the surface but also hinder the electron movement. Therefore, it is imperative to produce a catalyst whose surface should be free from any hindrance and exposed for substrate interaction. Thus, **Cozi-nmf** is an attractive material for catalysis. We chose the coupling of phenyl glycidyl ether (**PGE**) with CO₂ in the presence of **Cozinmf** as a catalyst to afford phenyl glycidyl carbonate (**PGC**) as the model reaction (Scheme 1). First, we have scanned the reaction conditions, including the reaction



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temperature, reaction time, and CO_2 pressure (1 atm), to optimize the cyclic carbonates yield. Among the various reactions tried with solvents like toluene, CH₃CN, CH₃OH, CHCl₃, DMSO, DMF, and H₂O, the reaction without solvent showed superior activity over other solvents (Table 1) because of the low solubility of CO₂ into conventional solvents.^[35]

To test the advantage of having mixed metal oxide composite as the catalyst, we have performed controlled reactions of PGE with CO_2 under the optimized condition in the presence of ZnO and CuO nanoparticles, also the catalyst **Cozi-nmf** (Table 2). No product was obtained when the reaction was performed in the absence of **Cozinmf**. The observed yield of PGC in the presence of ZnO and CuO was 15% and 35%, whereas a much higher 97% yield was obtained using **Cozi-nmf** as the catalyst. The high surface area of **Cozi-nmf** that available freely without any capping agent was the reason for better catalytic activity in this CO_2 fixation reaction.

The reaction without solvent at room temperature for 3 h using scanty 5 mg (0.06 mmol) of Cozi-nmf at 1 atm pressure of CO_2 (Table 3, entry 8) gave the best result in terms of yield (98%) and time. In contrast, with less than 5 mg of **Cozi-nmf**, the reaction became sluggish with a low product yield. Using the optimized reaction conditions, we have studied the performance of Cozi-nmf in the chemical fixation of CO₂ over different functional group substituted epoxides. The epoxides, such as phenyl glycidyl ether substituted with electron-donating [-CH₃, $-OCH_3$, -C $(CH_3)_3$ and electron-withdrawing groups (-Cl, -Br, -Ph) were used as the substrate in the reaction. As shown in Table 3 (Entries 1–11), most substrates were converted efficiently to corresponding cyclic carbonates with excellent selectivity and high conversion. It was observed that terminal epoxides with both electrondonating and electron-withdrawing groups were transformed into the corresponding cyclic carbonates with almost quantitative yields (93-98%) within 3–6 h under at 1 atm CO₂ pressure. Other than phenyl glycidyl ether, the reaction with three different substrates (Table 3), styrene oxide (Entry 1, 93%) and 1, 2 epoxy butane (Entry 11, 74%), and 1, 2 epoxy hexane yielded the corresponding cyclic carbonate in moderate to good yields (Entry 12, 68%).

We have compared the catalytic activity of **Cozi-nmf** with that of known heterogeneous catalysts used for the synthesis of cyclic carbonates (Table 4). The comparative study showed that other reported reactions involved use of protic compounds, additives, and solvents for epoxide activation. Moreover, those catalytic systems required either high pressure,^[36] high temperature to activate CO₂, whereas our designed **Cozi-nmf** having high Lewis acidic nature of surface might facilitate CO₂ insertion at rt with 1 atm pressure. The simplicity of synthesis makes **Cozi-nmf** stand in a better position.

3.4 | Recyclability of Cozi-nmf as catalyst

A heterogeneous catalyst needs to be examined for its ease of separation, recoverability, and reusability. The reusability of **Cozi-nmf** was examined in the synthesis of cyclic carbonate using the illustrative reaction between CO_2 and PGE. After the reaction time, the reaction mixture was centrifuged to separate the solid **Cozi-nmf** from the reaction mixture. The catalyst was then thoroughly washed with distilled water followed by methanol and dried in an oven at 100°C for 5 h before reuse. As seen in Figure 7, the catalyst can be efficiently recycled and reused five times. The results indicated that after fivetime reuse of catalyst, the product's yield decreased from 97% to 90%.



TABLE 2Synthesis ofphenylglycidyl carbonates withdifferent catalysts

TABLE 3 Synthesis of different cyclic carbonates by using Cozi-nmf as catalyst



Note. Reaction conditions: epoxide (1 mmol), Cozi-nmf (5 mg), rt, 1 atm of CO₂. Yields refer to those of isolated pure product.

Catalyst	CO ₂ (bar)	Time (h)	Temperature (°C)	Yield (%)	Ref.
Al (III)@cages	1	48	RT	54	Ng et al. ^[15]
Ti (HPO₄)₂·H₂O	1	6	RT	87	Chowdhury et al. ^[16]
$ZnCl_2/Al_2O_3$	1	4	100	100	Bondarenkoa et al. ^[17]
Succinimide-KI	0.4	6	70	94	Li et al. ^[18]
PCN-222(Co)	1	18	50	90	Carrasco et al. ^[19]
PIM2	1	8	130	96	Wang et al. ^[20]
Cozi-nmf	1	3	RT	97	This work

TABLE 4 Comparative study on the catalytic activity of Cozi-nmf with numerous catalysts using PGE as substrate



nanometallio

FIGURE 7 Recycling results of the CuO-ZnO catalyst in the synthesis of cyclic carbonates

4 | CONCLUSION

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We have synthesized **Cozi-nmf** with a high surface area of around 45.8 $m^2 g^{-1}$ by grinding method within 10 min. It was used as the catalyst for cycloaddition of CO₂ with various epoxides to produce cyclic carbonates. The syntheses described here were performed in solvent-free conditions and used inexpensive and recyclable surfactant-free heterogeneous catalysts. The yields of the synthesized products were more than 95% except for styrene and aliphatic carbonates. The high efficiency of **Cozi-nmf** as a catalyst is because of the availability of the bare catalyst surface, which promoted the hindrance free movement of electrons and adsorption of substrate effectively. Though many other CO₂ capture reactions are known to proceed in the solvent-free condition, the simplicity in the synthesis of **Cozi-nmf** and cyclic carbonates promises large-scale use of the method.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

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AUTHOR CONTRIBUTIONS

Venkateswara Rao Velpuri: Conceptualization; formal analysis; investigation; methodology. Krishnamurthi Muralidharan: Conceptualization; supervision.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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