Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Synthesis of Amino Alcohols, Cyclic Urea, Urethanes, Cyclic Carbonates and Tandem One-pot Conversion of Epoxide to Urethanes using Zn-Zr Bimetallic Oxide Catalyst

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Materials

High purity $Zn(NO_3)_2.6H_2O$, NaOH, urea and glycerol (99%) were purchased from LobaChemie. Na_2CO_3, ethanolamine (99%), diethanolamine (>99%), and ethylene glycol were purchased from Merck, India Pvt. Ltd. All other chemicals used in this work were purchased from Sigma Aldrich India Pvt Ltd.

Catalyst characterization

The materials were characterized by X-ray diffraction (XRD) analysis using a RIGAKU Mini-flex diffractometer in 2θ range of 20-80 degrees with Cu kα (λ = 0.154 nm) radiation. The specific surface area and porous nature of the materials were analyzed using N_2-sorption measurements. The samples were degassed at 573 K for 5 h in the degassing port. The surface area was measured at the relative pressure range of 0.05 to 0.3 using the Brunauer-Emmett-Teller (BET) equation. The distribution of pores was calculated using the Barrett-Joyner-Halenda (BJH) method on a Quantachrome Instrument. The morphologies and microstructures of the synthesized materials were analyzed using Field Emission Scanning Electron Microscopy (FE-SEM), and transmission electron microscope (TEM) 200KV (TALOS F200S G2) at CeNS, Bengaluru. The presence of various elements and their oxidation states were analyzed by X-Ray photoelectron spectroscopy (XPS) on a Thermofisher scientific (Nexsa base) instrument. The nature of acid sites present in the materials was analyzed using the Bruker Tensor-II F-27 instrument FT-IR instrument (pyridine as a probe molecule). The total acidity and basicity of the materials were analyzed by using the Temperature-Programmed Desorption (NH_3 and CO_2 TPD) technique on a Quantachrome, CHEMBETTM TPR/TPD instrument. The sample was preheated at 423 K at a heating rate of 10 deg/min under a continuous He gas flow for 30 min. Then, after cooling to 323 K, NH_3 gas was allowed to adsorb on the sample for 1 h. After adsorption, the excess or physically adsorbed NH_3 was removed by flushing He gas (50 mL/min) for 30 min. Finally, the temperature was ramped from 323-773 K at a rate of 10 deg/min.

Catalytic reaction procedure

1. Synthesis of amino alcohol

Amino alcohols were synthesized by using epoxide and amines. Epoxide (5 mmol), amine (5 mmol), and 25 mg catalyst were taken in a 25 ml two-necked round bottom flask. The flask was fitted with an ice-cooled water condenser and placed in an oil bath at 353 K. After 2 h of the reaction, a small amount of reaction mixture was taken in a vial and diluted with MeOH. The resultant mixture was centrifuged and analyzed by using gas chromatography (GC) (Yonglin; 6100; BP-5; 30 m×0.25 mm×0.25μm), and the product was confirmed by GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 μm).

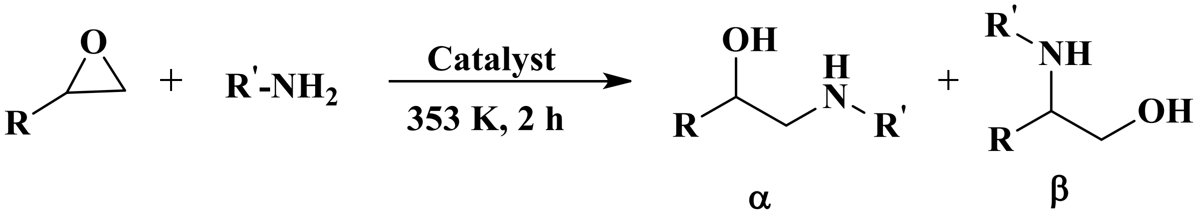
2. Carbonylation reaction for the synthesis of glycerol carbonate and cyclic urethanes

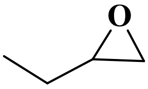
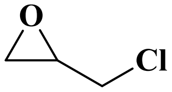
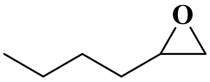
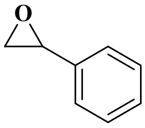
Glycerol carbonate/cyclic urea/urethanes were prepared using urea as a carbonylation agent. Glycerol/amino alcohols/amines and urea were taken in 1:1 molar ratio for this reaction. For example, 2 g glycerol, 1.31 g urea and, 0.15 g catalyst were taken in a 50 ml, two-necked round bottom flask. The flask was fitted with an ice-cooled water condenser and placed in an oil bath at 433 K for 4 h with the continuous flowing of nitrogen gas (5 mL/min) to remove the evolved ammonia during the reaction. After the reaction, 10 ml MeOH was added to the mixture, and the catalyst was separated by centrifugation. The resultant reaction mixture was analyzed by gas chromatography (GC), and the product was confirmed by GC-MS.

3. One-pot tandem reaction for the synthesis of urethanes directly from epoxide

First, amino alcohols were prepared by reacting epoxide (5 mmol) and amine (5 mmol) in a 25 ml two-necked round bottom flask using 25 mg catalyst. The flask was fitted with an ice-cooled water condenser and placed in an oil bath at 353 K. After 2 h of the reaction, urea (5 mmol) was added to the reaction mixture for carbonylation of amino alcohol. The mixture was magnetically stirred at 433 K for 2 h with the continuous flowing of nitrogen gas (5 ml/min) to remove evolved ammonia during the reaction. After the reaction, 10 ml MeOH was added to the reaction mixture, and the catalyst was separated by centrifugation. The resultant reaction mixture was analyzed by gas chromatography, and products were confirmed by GC-MS.

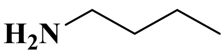
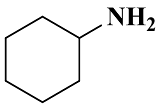
Table S1a. Synthesis of amino alcohols by varying epoxides

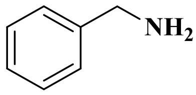
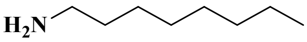


Sr. No	Substrate	[a]Epoxide Conversion (%)	[a]Product selectivity (%)		[a]Other (%)
			α	β	
1		96	92	08	00
2		98	85	12	03
3		65	78	17	05
4		99	40	06	54

Reaction conditions- Epoxide (5 mmol), butylamine (5 mmol), catalyst Zn_2ZrO_x (25 mg), temperature (353 K), time (2 h).[a]Determined using GC.

Table S1b. Synthesis of amino alcohols by varying amines.

Sr. No	Substrate	[a]Epoxide Conversion (%)	[a]Product selectivity (%)		[a]Other (%)
			α	β	
1		96	92	08	00
2		90	96	02	02

3		84	85	06	09
4		63	88	11	01

Reaction conditions- Butylene oxide (5 mmol), amines (5 mmol), catalyst Zn_2ZrO_x (25 mg), temperature (353 K), time (2 h). [a]Determined using GC.

Table S2. Comparative catalytic activity data of Zn_2ZrO_x with various reported catalyst for the glycerol carbonate synthesis.

Entry No.	Catalyst	Reaction conditions	Conv. (%)	Product selectivity (%)	Reference
1	10%Zn/MCM-41	Glycerol 4.6 g, urea 3.08 g, catalyst 0.23 g, temperature 140°C, time 5 h, N_2 flow 20 mL/h	84	98	35
2	ZnO-ZMG	Glycerol/urea ratio 1:1.5, catalyst 5 wt%, temperature 140°C, time 6 h, pressure 1 kPa.		85.97 (yield)	36
3	Zn_2Sn-CoPre-600	Glycerol 2 g, urea 1.31 g, catalyst 0.33 g, temperature 155°C, time 4 h, N_2 bubbling.	96	99.6	47
4	$Zn(C_3H_6O_3)$	Glycerol/urea ratio 1, cat/glycerol 0.01temperature 150°C, time 2.5 h, pressure 2.7 kPa.	85.6	74.3	34
5	50% $Zn_7Al_3O_x$	Glycerol/urea 1, catalyst 5 wt%, temperature 140°C, time 5 h, pressure 3 kPa.	69	84.2	37
6	ZMG	Glycerol/urea ratio 1:1.5, 5 wt% catalyst, temperature 140°C, time 7 h, pressure 40 mbar.	61	90	S1
7	Zn/HT	Glycerol 50 mmol, urea 50 mmol, catalyst 0.25 g, temperature 130°C, time 3h, pressure 3 kPa.	82	80	33
8	Zn_1TPA	Glycerol 2 g, urea 1.30 g, catalyst 0.2 g, temperature 140°C, time 4 h.	69.2	99.4	42
9	Co_3O_4/ZnO	Glycerol/urea ratio 1:1, catalyst 6 wt%, temperature 140°C, time 4 h,	69	100	44
10	Zn_2ZrO_x	glycerol 22 mmol, urea 22 mmol, catalyst 0.15 g, temperature 433 K, time 4 h, N_2 5 mL/min.	95	94	This study

Table S3. Comparative catalytic activity data of Zn_2ZrO_x with various reported catalyst for the cyclic urea synthesis.

Entry No.	Catalyst	Reaction conditions	Conv. (%)	Product selectivity (%)	Reference
1	ZnO	propylenediamine 0.6 g (10 mmol), Urea 0.6 g (10 mmol), DMF 1 g, catalyst 7.3 mol%, temperature-120°C, time- 10 min Pressure- 71 kPa, MW power- 100-150W	-	99 (yield)	29
2	3,30-(butane-1,4-diyl)bis(1-methyl-1Himidazol-3-ium) chlorine (Ionic liquid)	ethylenediamine 2 mmol, dimethyl carbonate 2 mmol, catalyst 10 wt%, temperature-100°C, time-60 min.	90	91	S2
3	CeO_2	propylenediamine 10 mmol, IPA 200 mmol, CeO_2 0.34 g, temperature- 160°C, time-12 h, CO_2 5 bar.	93	97	S3
4	Zn_2ZrO_x	propylenediamine 22 mmol, urea 22 mmol, catalyst 0.15 g, temperature 433 K, time 4 h, N_2 5 mL/min.	91	98	This study

Table S4. Comparative catalytic activity data of Zn_2ZrO_x with various reported catalyst for the urethane synthesis.

Entry No.	Catalyst	Reaction conditions	Conv. (%)	Product selectivity (%)	reference
1	Cs_2CO_3	aminoalcohol 0.5 mmol, TsCl 1.1 equiv, Cs_2CO_3 3 equiv, acetone 5 ml, room temperature, time-20 h, CO_2 5 bar.	50	100	S4
2	Chlorostannoxane	2-aminoethanol 0.0041 mol, methanol 0.05 mol, chlorostannoxane 0.000017 mol, temperature 150°C, time 6 h. CO_2 1.72 MPa	-	55 (yield)	31
3	CeO_2	2-aminoethanol 10 mmol, ACN 1000 mmol, catalyst 0.17 g, temperature 150°C, time 4 h, CO_2 5 MPa.	97	99	32
4	Zn_2ZrO_x	ethanolamine 22 mmol, urea 22 mmol, catalyst 0.15 g, temperature 433 K, time 4 h, N_2 5 mL/min.	99	92	This study

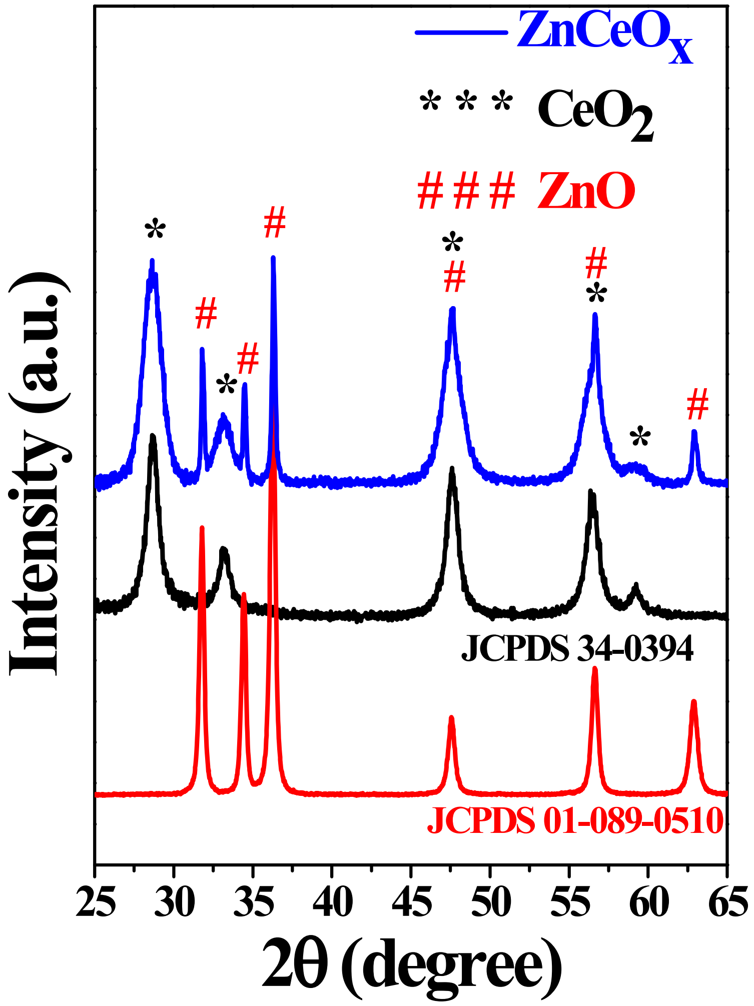


Fig S1. XRD patterns of ZnO, CeO_2, and Zn_1CeO_x.

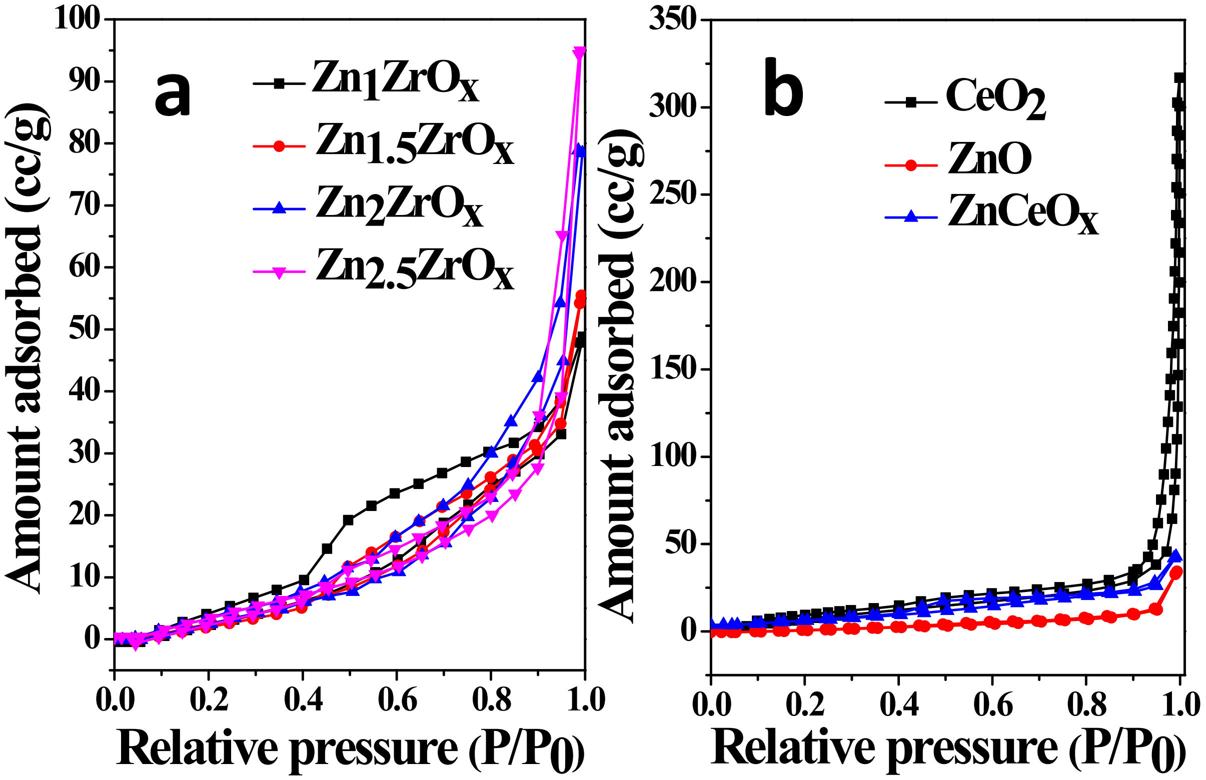


Fig. S2. N_2 adsorption isotherms for (a) Zn_1ZrO_x, $Zn_{1.5}ZrO_x$, Zn_2ZrO_x, and $Zn_{2.5}ZrO_x$, and (b) ZnO, ZrO_2, and Zn_1CeO_x.

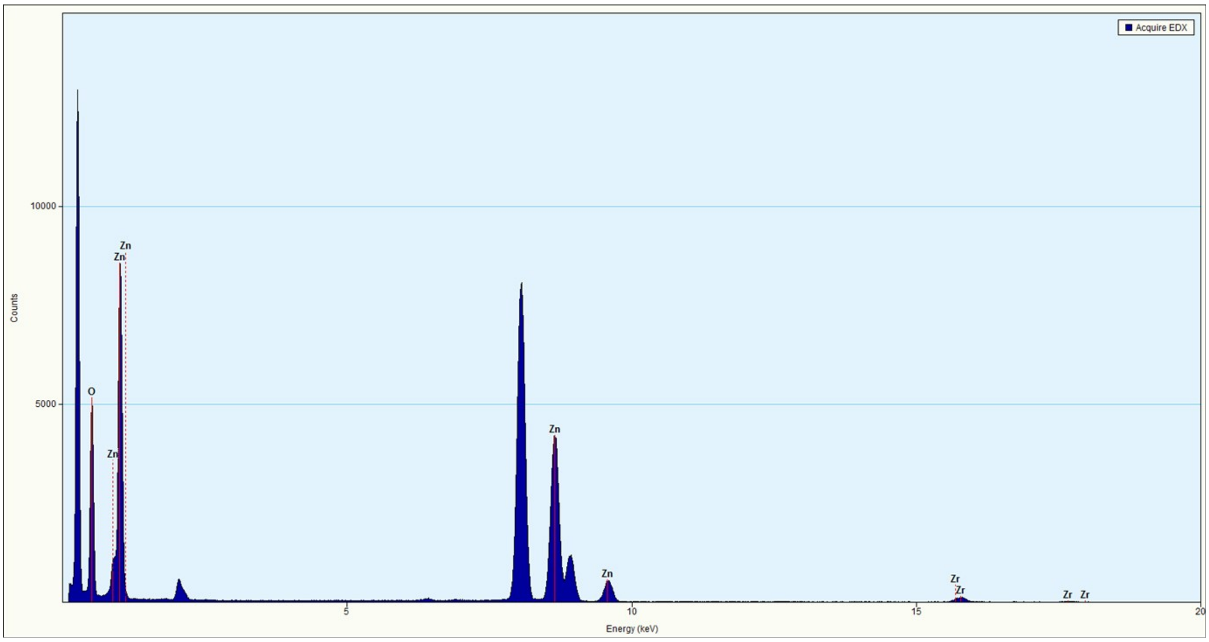


Fig. S3. EDAX spectrum for Zn_2ZrO_x.

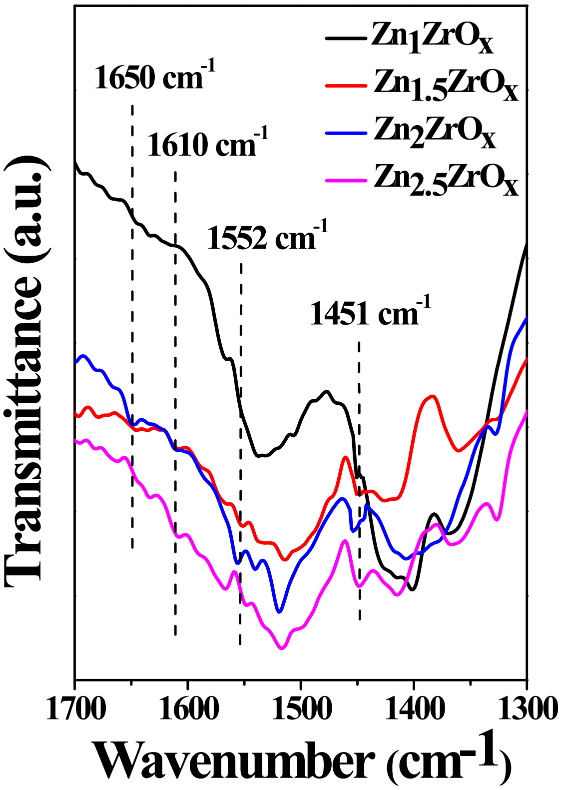


Fig. S4. Pyridine adsorbed FT-IR spectra for Zn_1ZrO_x, $Zn_{1.5}ZrO_x$, Zn_2ZrO_x, $Zn_{2.5}ZrO_x$.

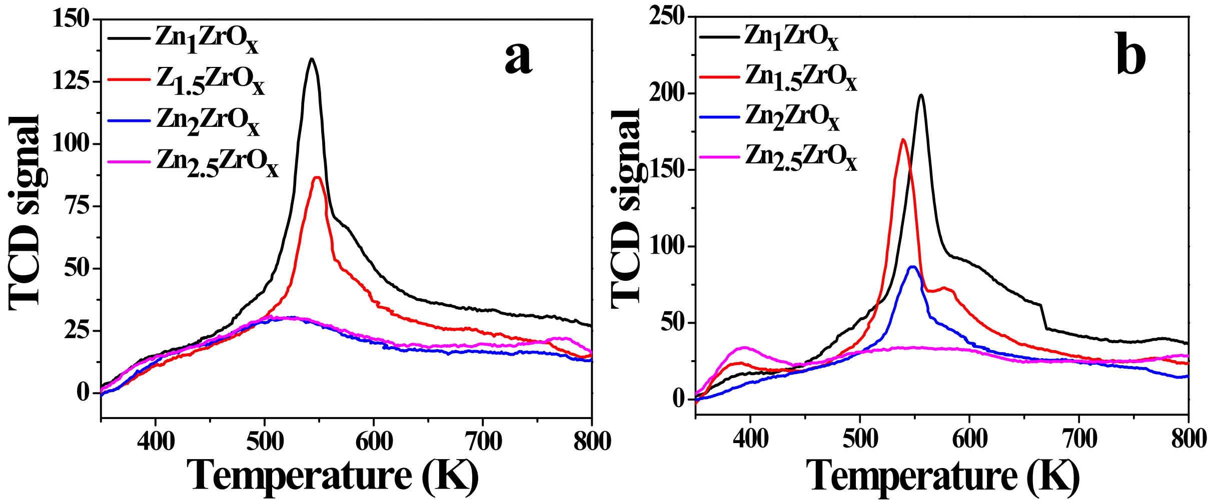


Fig. S5. (a) NH_3-TPD profiles for Zn_1ZrO_x, $Zn_{1.5}ZrO_x$, Zn_2ZrO_x, $Zn_{2.5}ZrO_x$,and (b) CO_2-TPD profiles for Zn_1ZrO_x, $Zn_{1.5}ZrO_x$, Zn_2ZrO_x, $Zn_{2.5}ZrO_x$

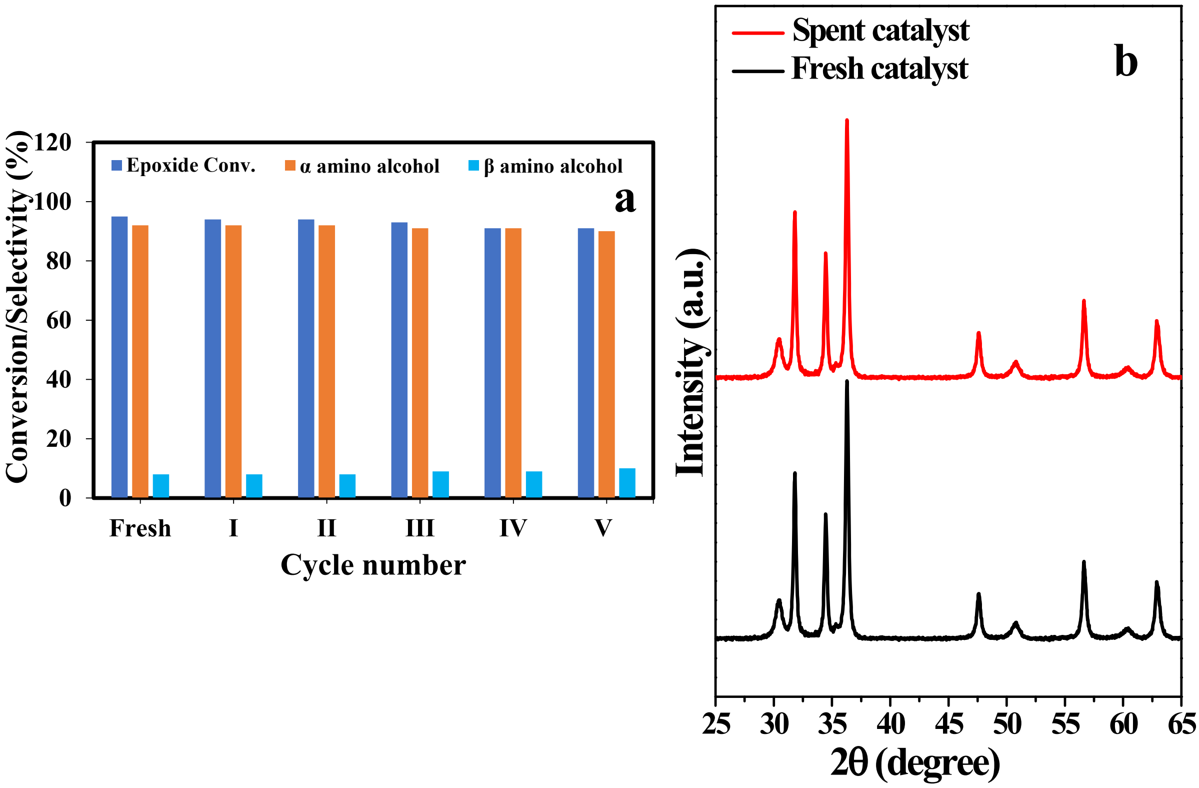


Fig. S6. (a) Recyclability of Zn_2ZrOx in the aminolysis of butylene oxide with butylamine (b) XRD patterns of the fresh and the spent catalyst.

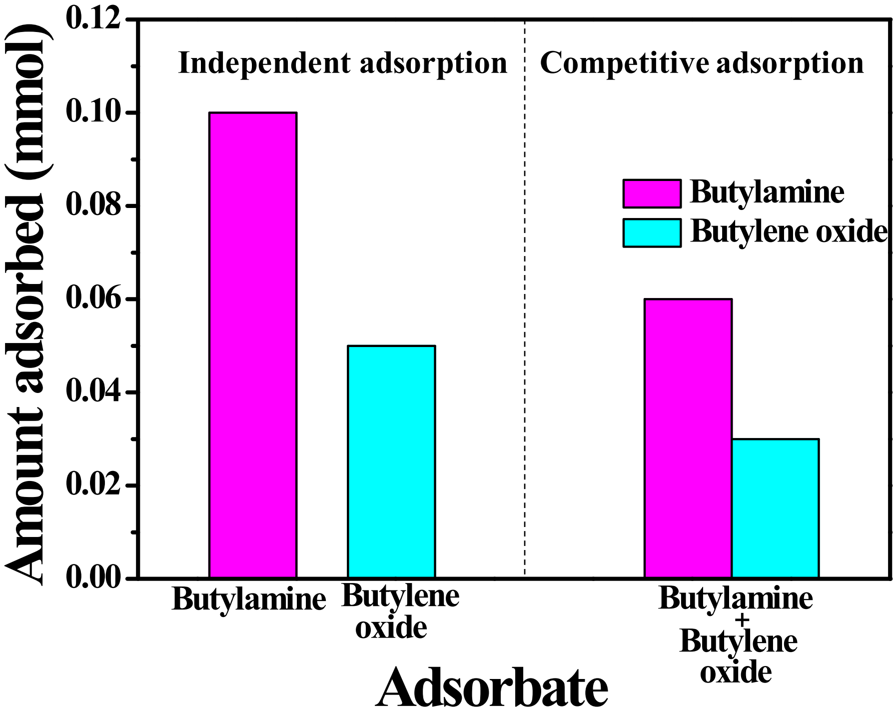


Fig. S7. Amount of butylamine and butylenes oxide adsorbed on Zn_2ZrOx during the independent adsorption and competitive adsorption experiments.

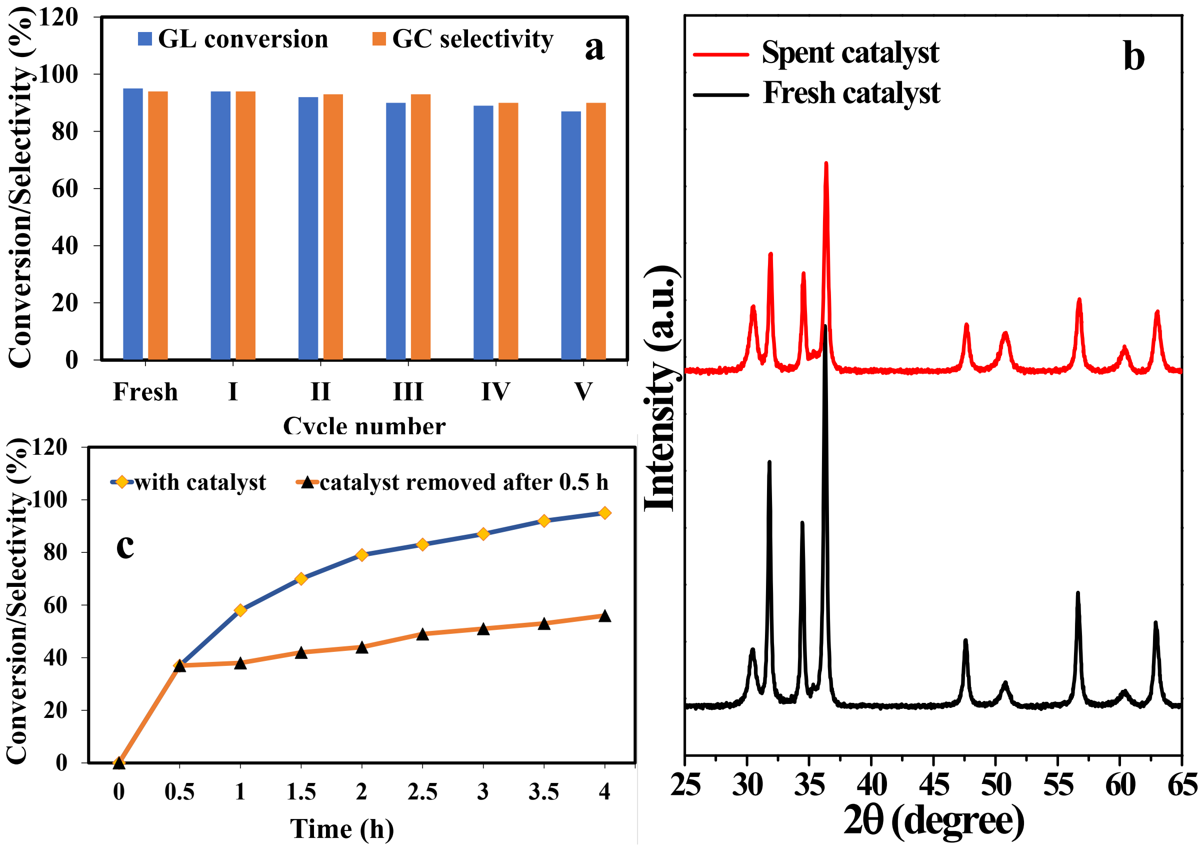


Fig. S8. (a) Catalyst recyclability in the conversion of glycerol to glycerol carbonate with urea as a CO source, (b) XRD patterns of fresh and spent catalyst, (c) hot-filtration test of Zn_2ZrO_x during the glycerol to glycerol carbonate synthesis using urea as a sacrificial CO source.

References

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S3.	M. Tamura, K. Noro, M. Honda, Y. Nakagawa and K. Tomishige, *Green Chem*., 2013, 15, 1567–1577.
S4.	T. Niemi, I. Fernandez, B. Steadam, J. K. Mannisto and T. Repo, *Chem. Commun*., 2018, 54, 3166—3169.