Zinc Alendronate as Ossified Catalyst for Glycerol Valorization to Glycerol Carbonate Using Urea as CO_2-Surrogate

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1. Catalyst characterization

The morphology of bare Na-ALN and all the ossified zinc alendronate catalysts were determined using an "Apreo LoVac" Field Emission Scanning Electron Microscopy (FESEM) instrument. The elemental study was employed with Aztec Standard Energy Dispersive X-ray Spectroscopy (EDS) system coupled to FESEM. All the powder samples were gold coated before performing FESEM-EDS analysis. For High Resolution Transmission Electron Microscope (HR-TEM), all the catalyst samples (powder form) were sonicated in water and drop casted on a 200-mesh carbon-coated Cu grid and dried in vacuum chamber. The Tencai G2 20 S-TWIN (FEI) is a 200 kV TEM used to obtain high resolution imaging. The Powder X-Ray Diffractions (PXRD) for bare Na-ALN and all the ossified zinc alendronate catalysts in this work were acquired using a Rigaku Mini Flex II diffractometer at 25 °C. Cu Kα radiation, when employed as an X-ray source, has a wavelength of 1.54Å. PXRD measurements were made with a $2\theta = 5°$ to $40°$ with a $2°\text{min}^{-1}$ scan rate. Nitrogen (N_2) physisorption was conducted using the Belsorb Mini X adsorption apparatus at a temperature of 77 K. Prior to analysis, they were preheated at 95 °C for 6 h in a nitrogen flow before being subjected to the BET instrument to determine the specific surface area. The total pore volume was calculated based on the nitrogen volume stored in pores at 0.99 relative pressure, and the pore diameter distributions were determined using the Barrett-Joyner-Halenda (BJH) method from the desorption isotherms. Fourier Transform Infrared (FT-IR) spectra was generated using AlPHA BRUKER between the wavenumber 400-4000 cm^{-1}. X-ray absorption spectroscopy (XAS) measurements were carried out at the BL-17C beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. For the extended X-ray absorption fine structure (EXAFS) analysis, the raw spectra were processed by first subtracting the pre-edge and post-edge backgrounds, followed by normalization to the edge step to account for variations in absorption intensity. The normalized absorption spectra were then converted from energy space to photoelectron wavevector space (k-space), and a k^3-weighting was applied to enhance the signal contributions from atoms located in different coordination shells around the absorbing atom. The subsequent EXAFS fitting and structural interpretation were performed using the Artemis software, utilizing structural models informed by earlier physical characterization data. The theoretical scattering paths required for fitting were generated using the FEFF8.0 code, which simulates X-ray absorption based on the local atomic environment around the absorbing element. By employing Al Kα micro-focused monochromator with an energy of 1486.7 eV and double-focusing hemispherical analyzer with the dual beam source, X-ray Photoelectron Spectroscopy (XPS) was performed. Catalysts were dried under vacuum over night before performing XPS analysis. The thermal stability of all the ossified catalysts including bare Na-ALN was checked using thermogravimetric analysis (TGA). TGA was performed under nitrogen atmosphere upto 650 °C using TGA-60, SHIMADZU equipment at a heating rate of 10 °C min^{-1}. The Atomic Absorption Spectroscopy (AAS), model AA-700 spectrometer, SHIMADZU, was used to quantify the amount of zinc metal present the synthesized ossified catalyst and even after each cycle of spent catalyst study. The surface active acidic and basic sites were determined by NH_3 and CO_2-Temperature Programmed Desorption (NH_3 and CO_2-TPD), respectively using BEL Microtrac BEL crop. Bel cat II instrument. The synthesized catalysts including bare Na-ALN were initially degassed in He gas flow (50 mL min^{-1}) at 100 °C for 2h and cooled to an ambient temperature before adsorption. Saturated adsorption of NH_3 and CO_2 were obtained by purging NH_3 and CO_2 gas at a flow rate of 30 $mLmin^{-1}$ at an ambient temperature with 10°min^{-1} ramp rate for 30 mins. After that flush the samples with He gas for 1h keeping 30 mL min^{-1} flow rate at an ambient temperature. Finally, the samples were heated upto 600 °C at 10°min^{-1} to get the TPD profiles. All NMR experiments were conducted on a JEOL spectrometer (Model: JNM-ECZL600G, JEOL Ltd., Japan) equipped with a 3.2 mm MAS double (HFX) resonance probe operating at resonance frequencies of 599.6 MHz for ^1H, 150.9 MHz for ^{13}C, and 242.9 MHz for ^{31}P. NMR experiments are conducted at room temperature unless stated otherwise. Samples with Na-ALN:Zn stoichiometric ratios of 0:1, 1:1, 1:2, and 2:1 were packed into 3.2 mm rotors and spun at a magic angle spinning (MAS) frequency of 15 kHz. 13C spectra were acquired using a cross-polarization magic angle spinning (CP-MAS) experiment with 1H decoupling, while 31P spectra were recorded via direct excitation with 1H decoupling to enhance resolution and sensitivity. Radiofrequency power settings and spectral referencing were calibrated using adamantine as an external standard.

2. Quantitative analysis of reaction products

Quantitative analysis of the reaction products was performed using a SHIMADZU GC-2014 gas chromatography fitted with RTX-5 capillary column (30 m x 0.25 mmID x 0.25 μm df) and flame ionization detector (FID) where N_2 used as carrier gas. Injector and detector temperature was 250 and 280 °C, respectively. Initially, column was heated upto 85 °C. After holding for 3 min at 85 °C, column temperature was raised to 240 °C with 20 °C min^{-1} ramp rate and hold for 6 min with 1:50 split ratio. Commercially available glycerol (from Merck) and glycerol carbonate (from TCI Chemicals) were used as standard to plot calibration curve. 25 mL standard solutions of 7 known concentrations of glycerol and glycerol carbonate were prepared in methanol. After analysing each standard sample in GC using stated parameters, peak area vs concentration was plotted to create calibration curve. The plots of both the compounds with 7 different concentrations have showed good linearity with typical R^2 values of 0.99. The same GC method was used for both, calibration and reaction sample analysis. The molar quantities of reaction mixture were determined by plotting calibration curve. Glycerol conversion, glycerol carbonate ($GlyCO_3$) selectivity, $GlyCO_3$ yield and byproduct selectivity were calculated based on the molar amounts of the respective species, using the equations provided below:

$$Glycerol\ conversion\ (\%) = \left(\frac{moles\ of\ glycerol\ consumed}{initial\ moles\ of\ glycerol}\right) \times 100$$

$$GlyCO3\ selectivity\ (\%) = \left(\frac{moles\ of\ GlyCO3\ formed}{moles\ of\ glycerol\ consumed}\right) \times 100$$

$$GlyCO3\ yield\ (\%) = \left(\frac{glycerol\ conversion\ (\%) \times GlyCO3\ selectivity\ (\%)}{100}\right)$$

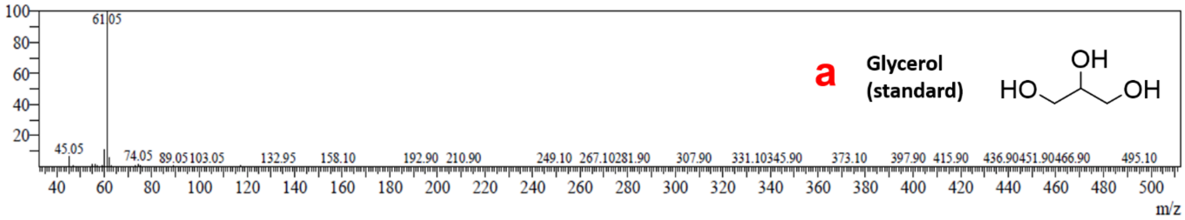
Turn Over Number (TON) and Turn Over Frequency (TOF), reported in comparative advancement study, were calculated using the equations provided below:

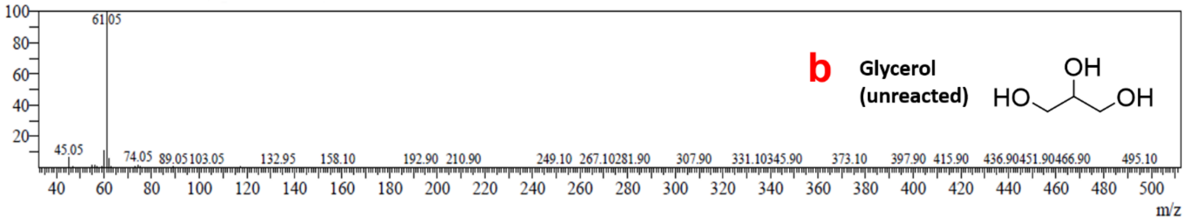
$$TON = \left(\frac{initial\ moles\ of\ glycerol\ \times \%\ conversion}{moles\ of\ catalyst\ active\ sites\ \times\ 100}\right)$$

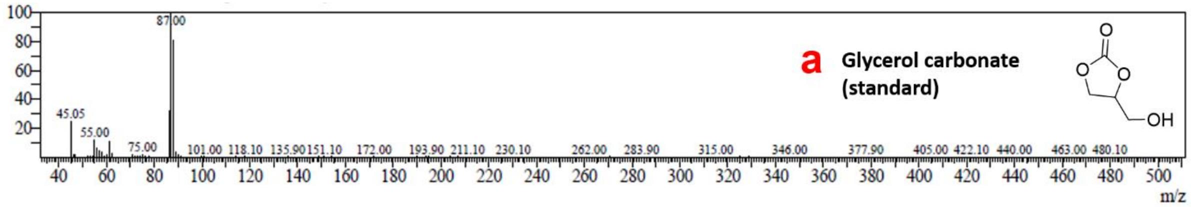
$$TOF\ (per\ hour) = \left(\frac{initial\ moles\ of\ glycerol\ \times \%\ conversion}{moles\ of\ catalyst\ active\ sites\ \times reaction\ time\ (h) \times\ 100}\right)$$

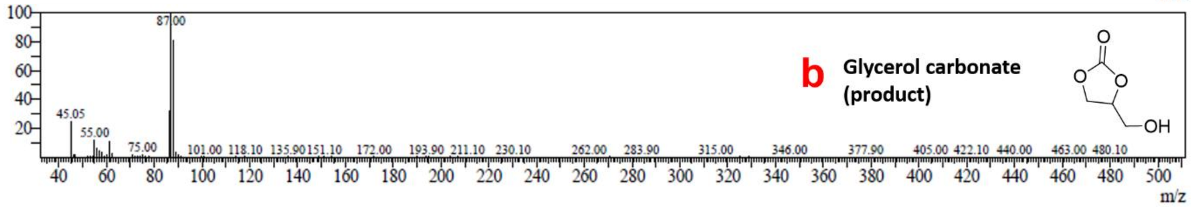
3. Identification of reaction products

Identification of reaction products was achieved using GC-MS/MS on TQ8040 NCI system equipped with Rxi-5Sil MS capillary column (30 m x 0.25 mmID x 0.25 µm df). Same temperature program and conditions as of GC were used in GC-MS/MS. Mass spectra of identified compounds are given below.






a Glycerol carbonate (standard)
87.00
45.05
55.00
75.00
101.00 118.10 135.90 151.10 172.00 193.90 211.10 230.10 262.00 283.90 315.00 346.00 377.90 405.00 422.10 440.00 463.00 480.10
m/z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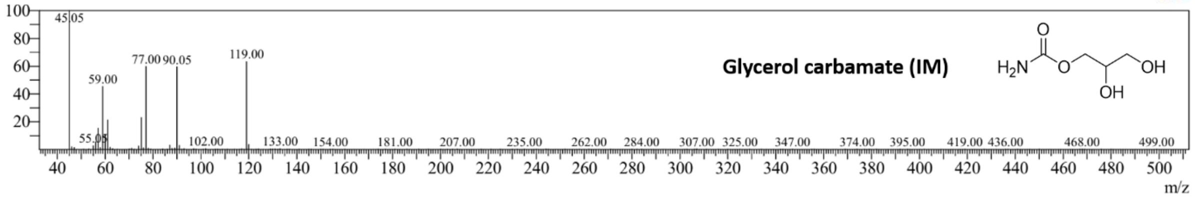
45.05
55.00
75.00
101.00 118.10 135.90 151.10 172.00 193.90 211.10 230.10 262.00 283.90 315.00 346.00 377.90 405.00 422.10 440.00 463.00 480.10
m/z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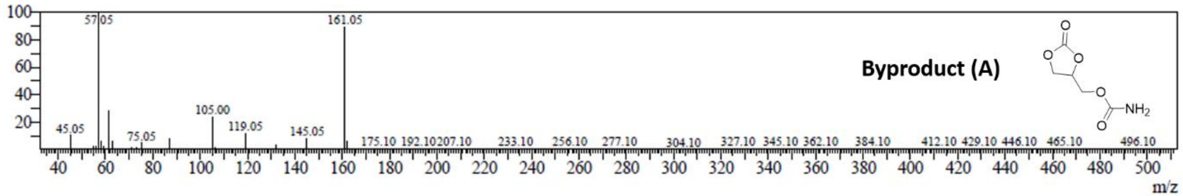
77.00 90.05
119.00
59.00
55.05
102.00 133.00 154.00 181.00 207.00 235.00 262.00 284.00 307.00 325.00 347.00 374.00 395.00 419.00 436.00 468.00 499.00
m/z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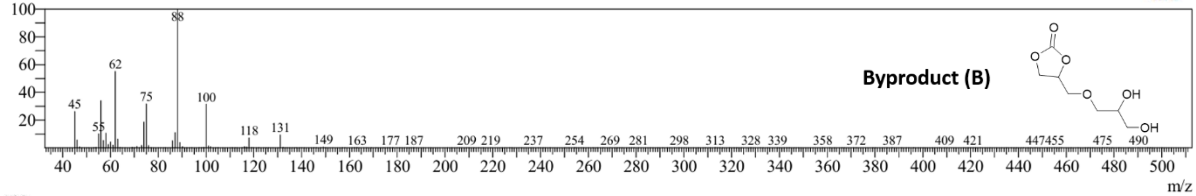
161.05
105.00
119.05
145.05
45.05
75.05
175.10 192.10 207.10 233.10 256.10 277.10 304.10 327.10 345.10 362.10 384.10 412.10 429.10 446.10 465.10 496.10
m/z


Byproduct (B)
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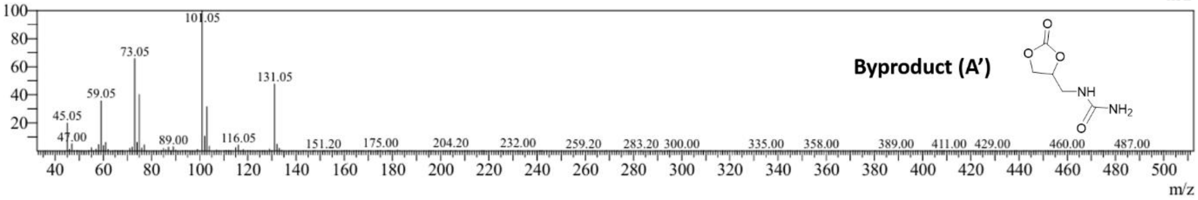
62
75
100
45
55
118 131
149 163 177 187 209 219 237 254 269 281 298 313 328 339 358 372 387 409 421 447455 475 490
m/z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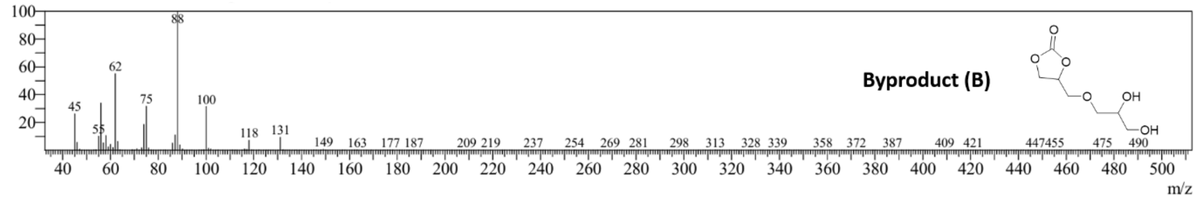
73.05
131.05
59.05
45.05
47.00
89.00
116.05
151.20 175.00 204.20 232.00 259.20 283.20 300.00 335.00 358.00 389.00 411.00 429.00 460.00 487.00
m/z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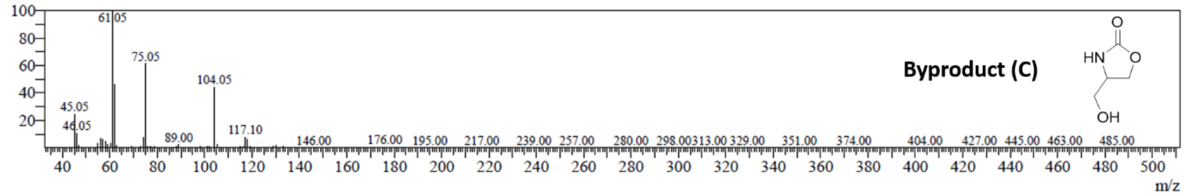
62
75
100
45
55
118 131
149 163 177 187 209 219 237 254 269 281 298 313 328 339 358 372 387 409 421 447455 475 490
m/z


Byproduct (C)
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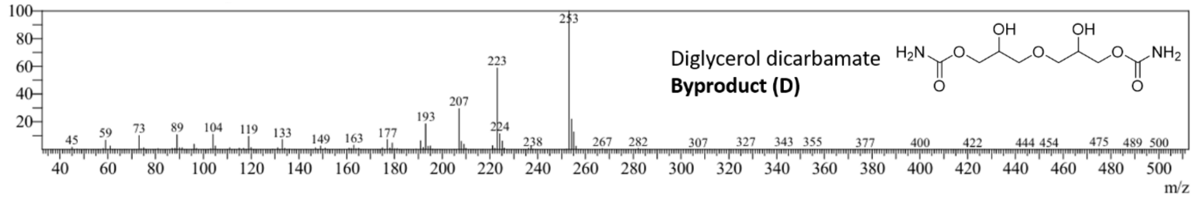
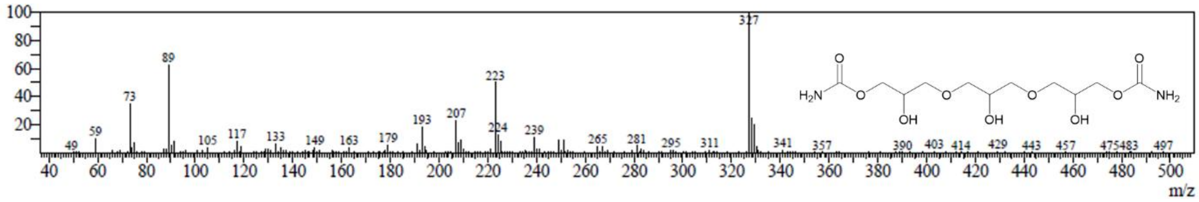
75.05
104.05
45.05
46.05
89.00
117.10
146.00 176.00 195.00 217.00 239.00 257.00 280.00 298.00313.00 329.00 351.00 374.00 404.00 427.00 445.00 463.00 485.00
m/z


Diglycerol dicarbamate
Byproduct (D)
253
223
207
193
224
45 59 73 89 104 119 133 149 163 177 238 267 282 307 327 343 355 377 400 422 444 454 475 489 500
m/z

Extended byproduct observed in 1:1.5 and 1:2 glycerol to urea ratio



4. DTA spectra

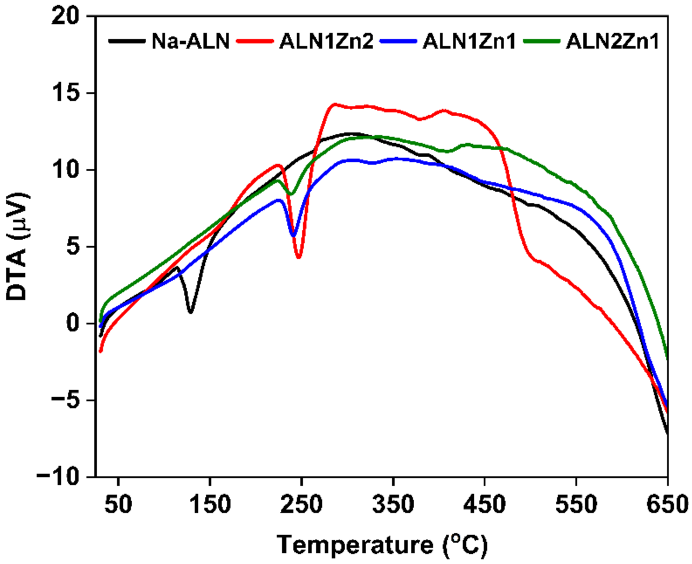


Figure S1. DTA graph of catalysts

5. FESEM-EDS images

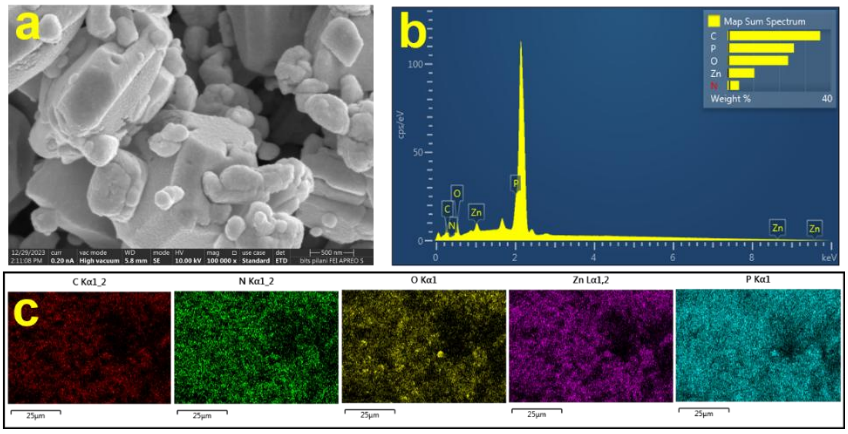


Figure S2. Na-ALN FESEM image and elemental analysis

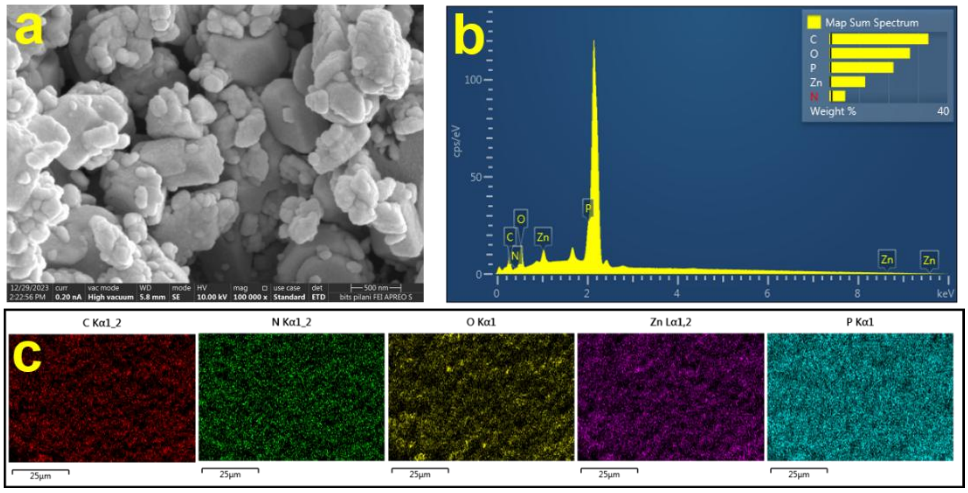


Figure S3. ALN1Zn1 FESEM image and elemental analysis

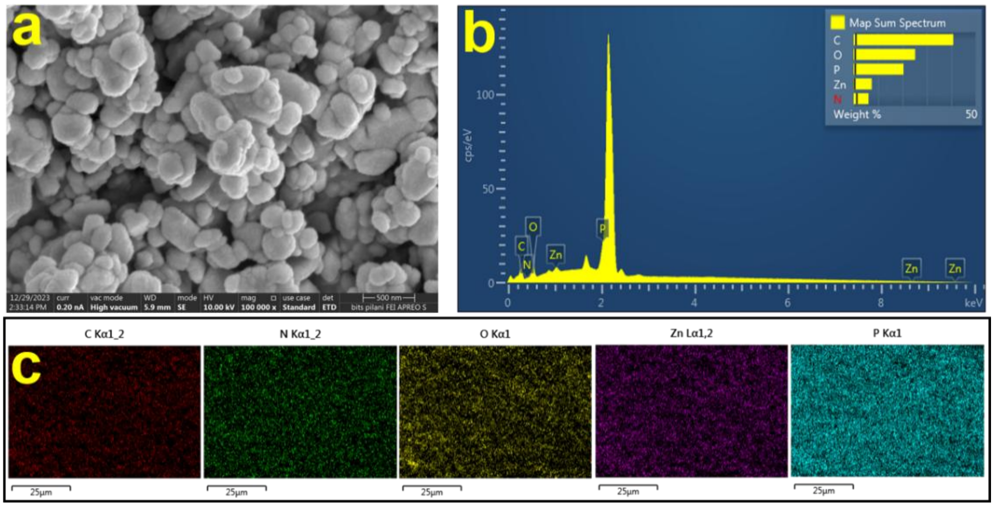


Figure S4. ALN2Zn1 FESEM image and elemental analysis

6. HR-TEM images of catalysts

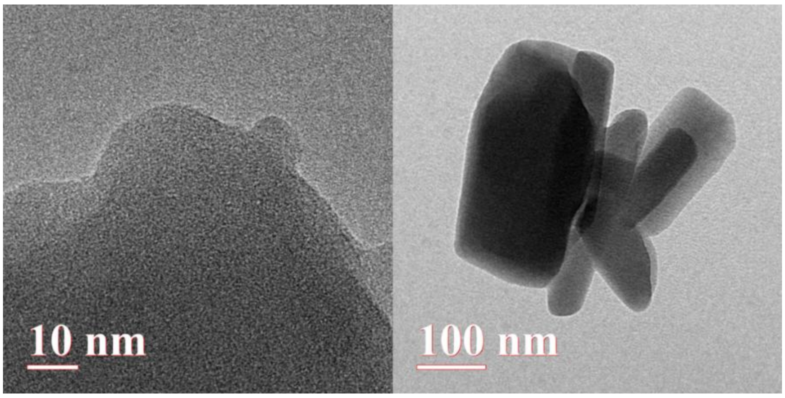


Figure S5. ALN1Zn1 HR-TEM images

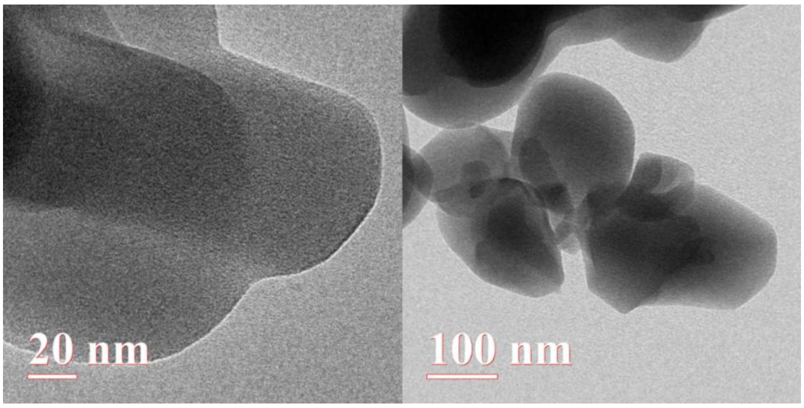


Figure S6. ALN2Zn1 HR-TEM images

7. FT-EXAFS analysis table

Table S1. Quantitative results of X-ray absorption spectroscopy model analysis at Zn K-edges of experimental samples.

Catalyst	**Zn K-edge**		
	Bond pair	CN	R (Å)
ALN1ZN2	Zn-O	2.40	1.874
	Zn-Zn	1.20	3.277
	Zn-P	1.98	3.221
	Zn-OH	1.90	3.805
ALN1ZN1	Zn-O	1.80	1.930
	Zn-Zn	1.30	3.195
	Zn-P	1.90	3.139
	Zn-OH	2.73	4.905
ALN2ZN1	Zn-O	1.84	1.929
	Zn-Zn	1.22	3.143
	Zn-P	1.94	2.996
	Zn-OH	2.55	3.874

CN: Coordination number, R(Å): Radial distance in angstrom

8. XPS profile of catalysts

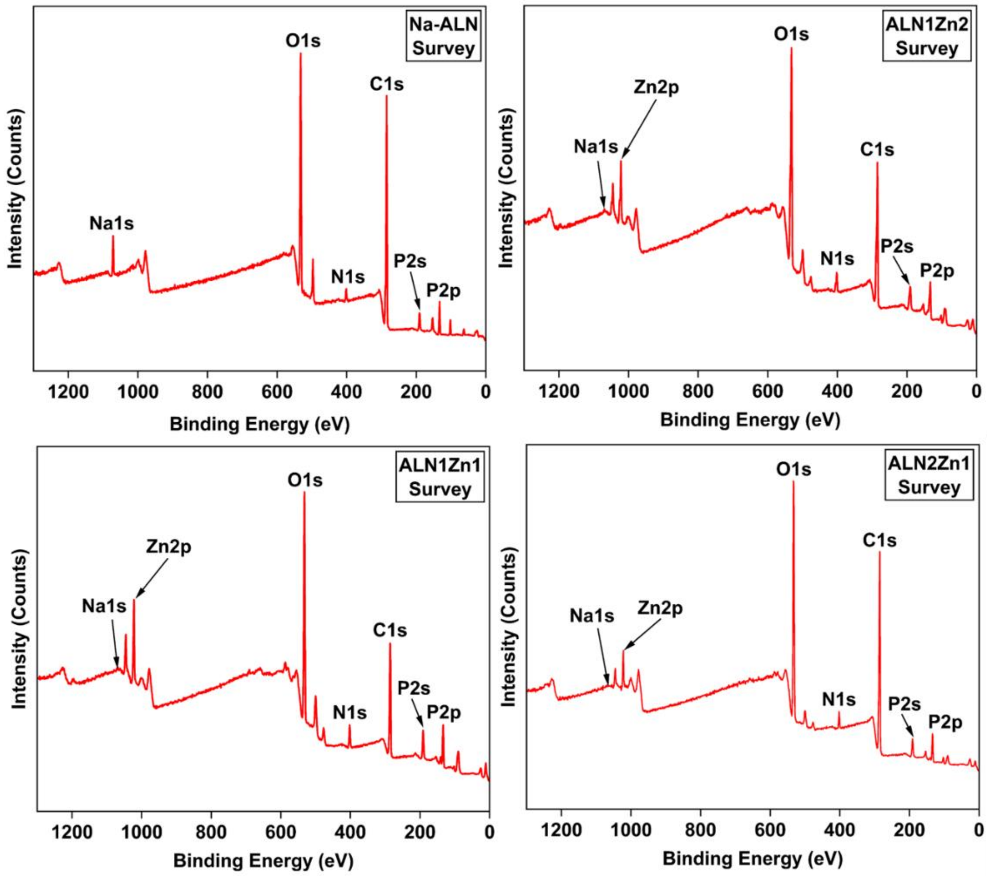


Figure S7. XPS survey spectra of catalysts

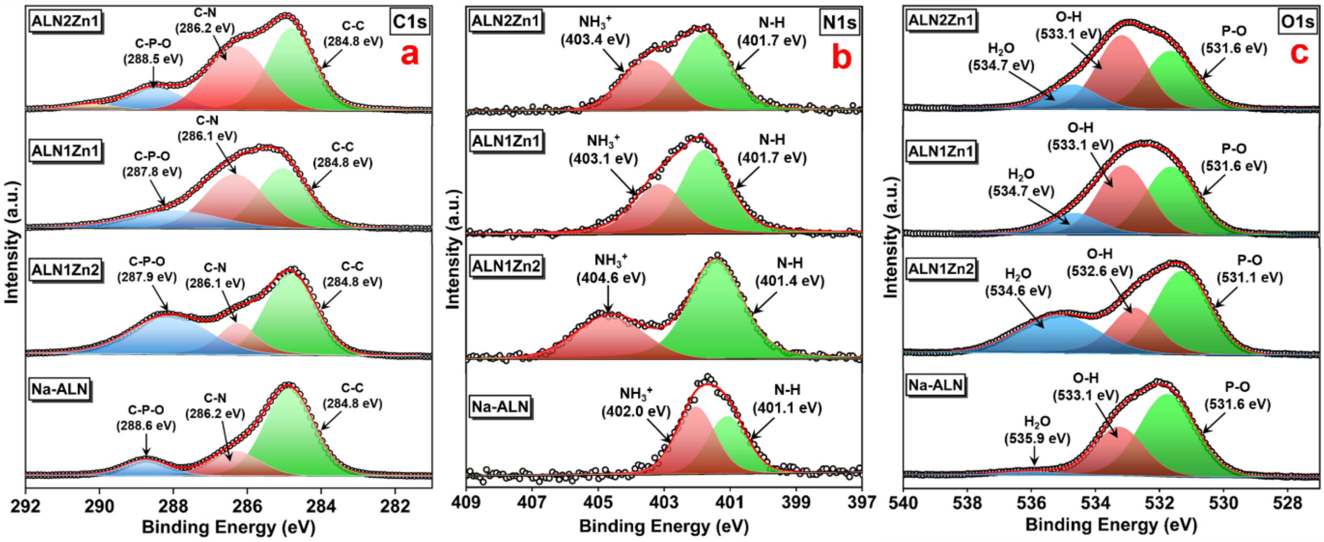


Figure S8. A) C1s, b) N1s and c) O1s XPS spectra of different ossified zinc alendronate catalysts including Na-ALN

Table S2. Binding energies of different ossified zinc alendronate catalysts including Na-ALN

		C1s (Binding Energy (eV))		
Catalyst	Adventitious carbon	C – N	C – P – O	
Na-ALN	284.8	286.2	288.6	
ALN1Zn2	284.8	286.1	287.9	
ALN1Zn1	284.8	286.1	287.8	
ALN2Zn1	284.8	286.2	288.5	290.2
		N1s (Binding Energy (eV))		
	N – H bonding	NH_3^+ or metal coordination		
Na-ALN	401.1	402.0		
ALN1Zn2	401.4	404.6		
ALN1Zn1	401.7	403.1		
ALN2Zn1	401.7	403.4		
		O1s (Binding Energy (eV))		
	P – O	O – H	H_2O	
Na-ALN	531.6	533.1	535.9	
ALN1Zn2	531.1	532.6	534.6	
ALN1Zn1	531.6	533.1	534.7	
ALN2Zn1	531.6	533.1	534.7	
		P2p (Binding Energy (eV))		
Catalyst	$2p_{3/2}$	$2p_{1/2}$	Extended phosphates	Zn3s
Na-ALN	132.8	133.8		
ALN1Zn2	132.8	133.9	135.8	140.7
ALN1Zn1	133.2	134.4	135.6	140.9
ALN2Zn1	133.2	134.5	135.7	141.0
		Zn2p (Binding Energy (eV))		
Catalyst	$2p_{3/2}$ (td)	$2p_{3/2}$ (oh)	$2p_{1/2}$ (td)	$2p_{1/2}$ (oh)
ALN1Zn2	1021.8	1025.8	1044.9	1049.1
ALN1Zn1	1022.4	1024.2	1045.4	1047.2
ALN2Zn1	1022.1	1023.8	1045.3	1047.0

9. Deconvoluted NH_3 and CO_2-TPD spectra

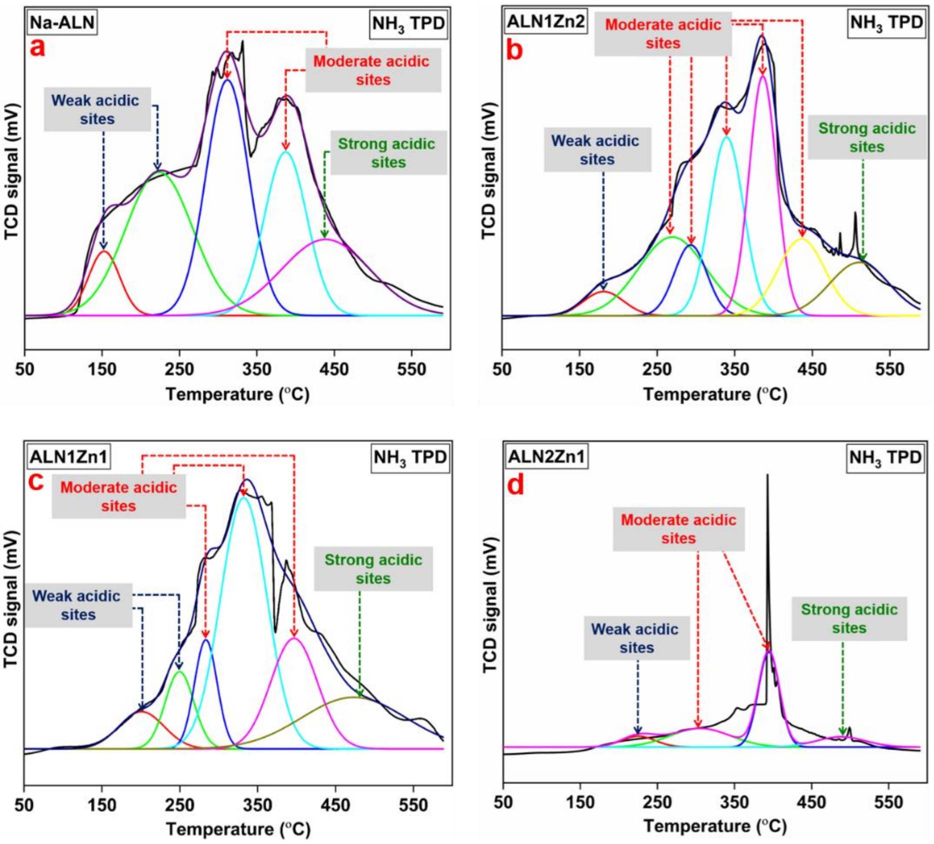


Figure S9. Deconvoluted NH_3 TPD profile of catalysts

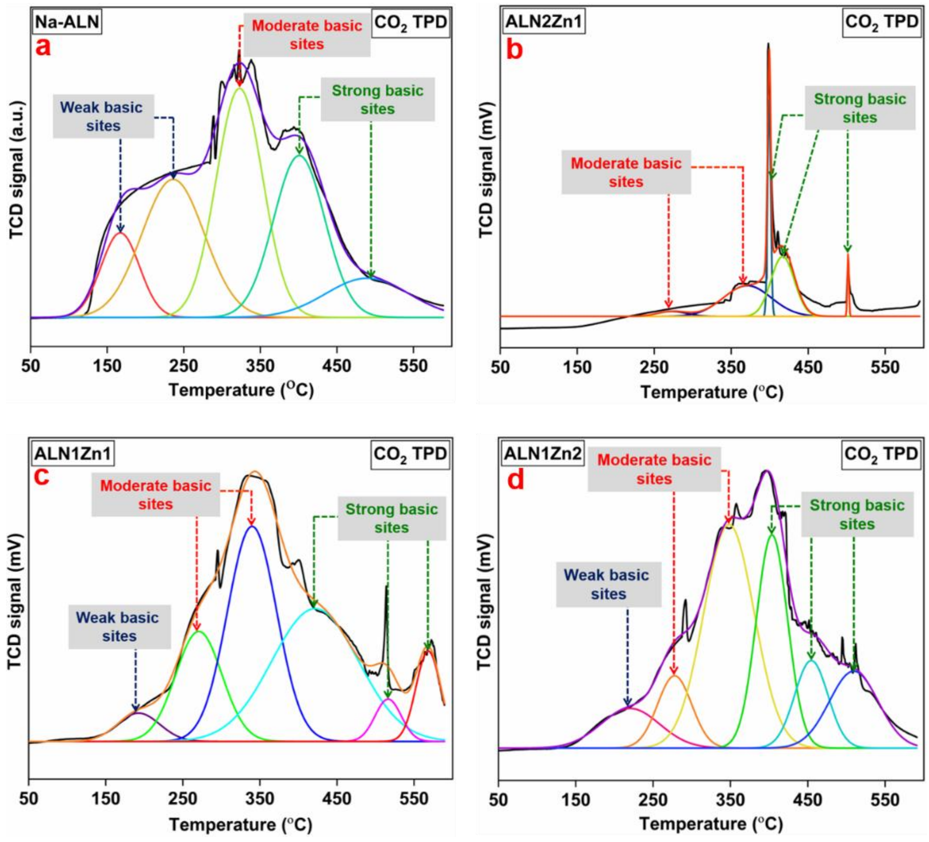


Figure S10. Deconvoluted NH_3 and CO_2 TPD profile of catalysts

10. Zinc Glycerolate FT-IR and PXRD

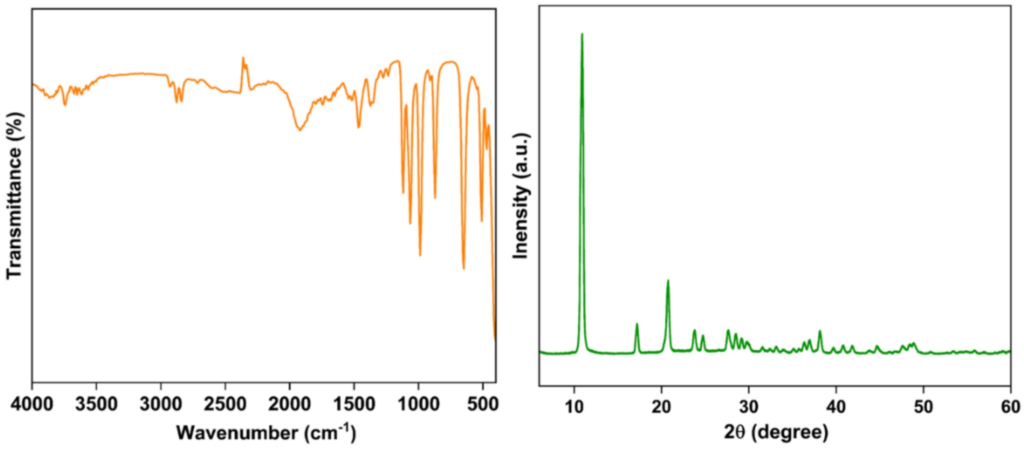


Figure S11. FT-IR and PXRD spectra of zinc nitrate white powder after reaction

11. Spent catalysis study experiment

The spent catalyst was filtered from the reaction mixture, followed by ethanol washing multiple times to remove adsorbed reaction mixture from the catalyst surface. The washed catalyst was dried at 80 °C overnight before reemployed in the catalytic tests under previously outlined reaction conditions.

12. Characterization of spent catalyst

11.1 FT-IR analysis

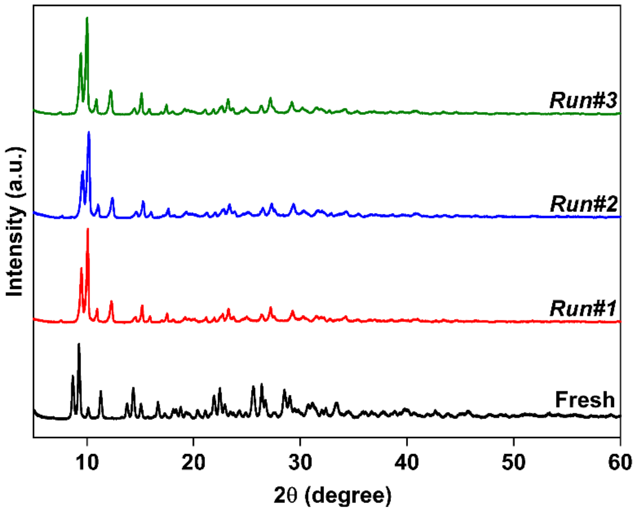


Figure S12. FT-IR spectra of spent catalysts

11.2 PXRD analysis

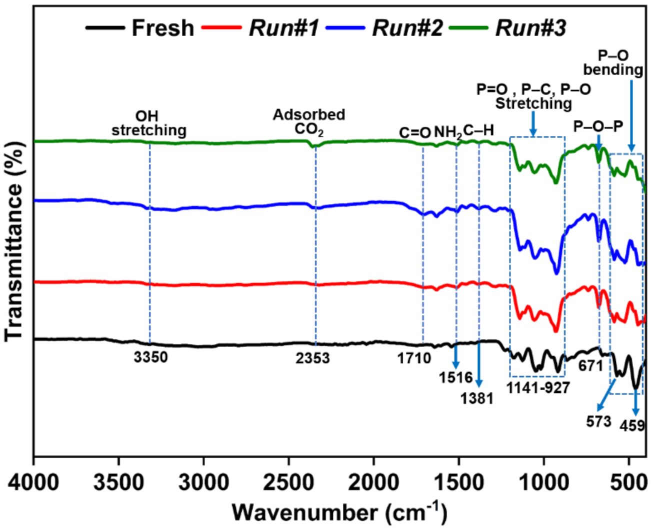


Figure S13. PXRD spectra of spent catalysts

11.3 XPS analysis

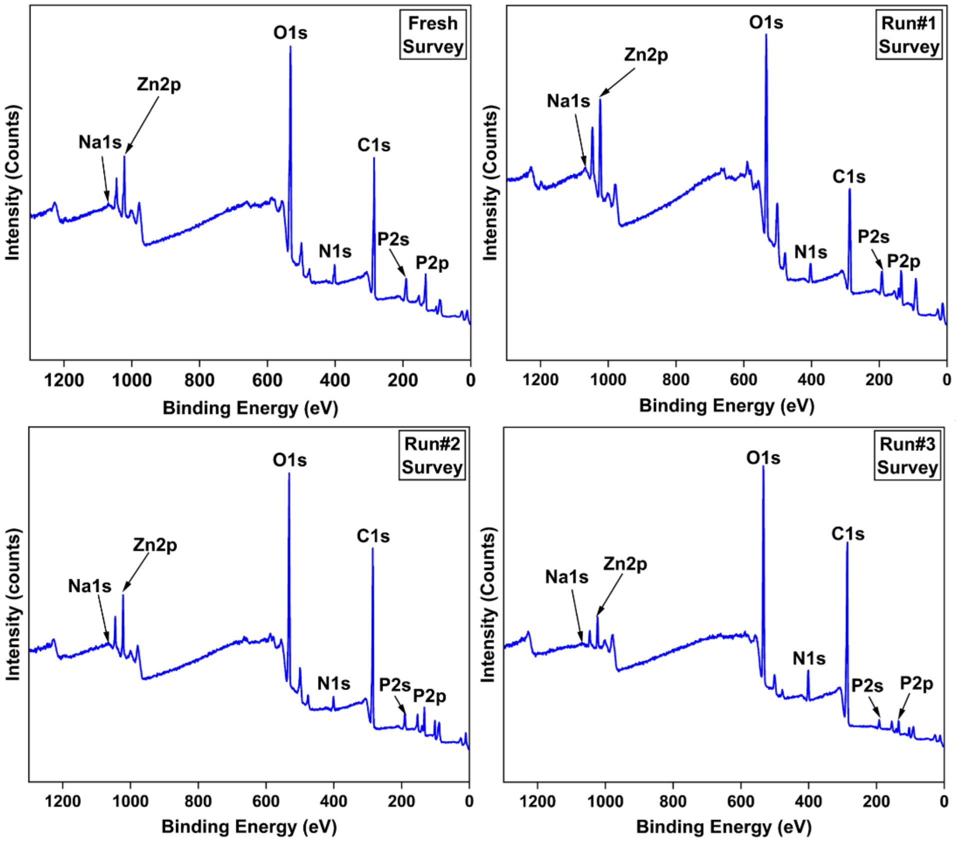


Figure S14. XPS survey of spent catalysts

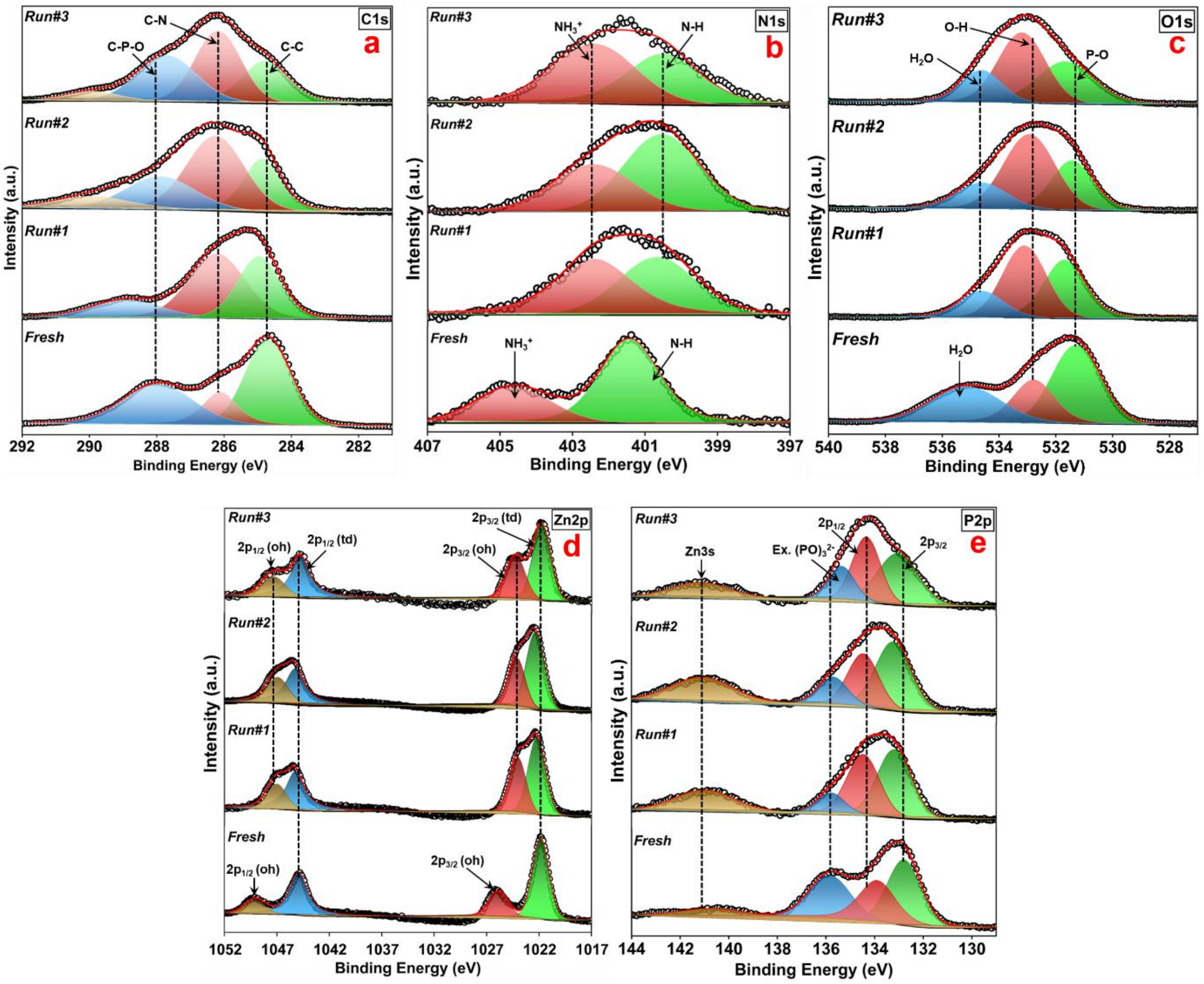


Figure S15. C1s, N1s, O1s, Zn2p and P2p XPS spectra of spent catalysts

11.4 AAS analysis

Table S3. AAS analysis of spent catalysts

	Zn loading (%)
Fresh	11.28
Run#1	10.94
Run#2	10.60
Run#3	10.43

13. Experimental set up to study the reaction progress using FT-IR

To study the reaction progress, optimized reaction parameters were used. In 50 mL two neck round bottom flask, 2 g (22 mmol) of glycerol was added and heated to 150 °C under constant agitation. Following this, 0.2 g of ALN1Zn2 was introduced into heated glycerol. Once catalyst was evenly dispersed throughout the glycerol, 1.3 g (22 mmol) urea was added to the reaction mixture. The reaction proceeded under a continuous N_2 flow (20 mL min^{-1}) to remove NH_3 generated during the reaction. To study the reaction mechanism, required amount of reaction mixture (5 μL) was collected from the round bottom flask using micropipette at particular time interval. Collected samples were dissolved in methanol and centrifuge to separate the solid catalyst. Aliquot was collected after centrifugation and methanol was evaporated using rotary evaporator to collect the dense products mixture. FT-IR of the product mixtures, collected at particular time interval were performed and analyzed to propose the reaction mechanism.

**The expected products, including unreacted urea, are soluble in methanol. Consequently, methanol is utilized as a solvent.*

14. 2 dimentional FT-IR spectra of reaction progress

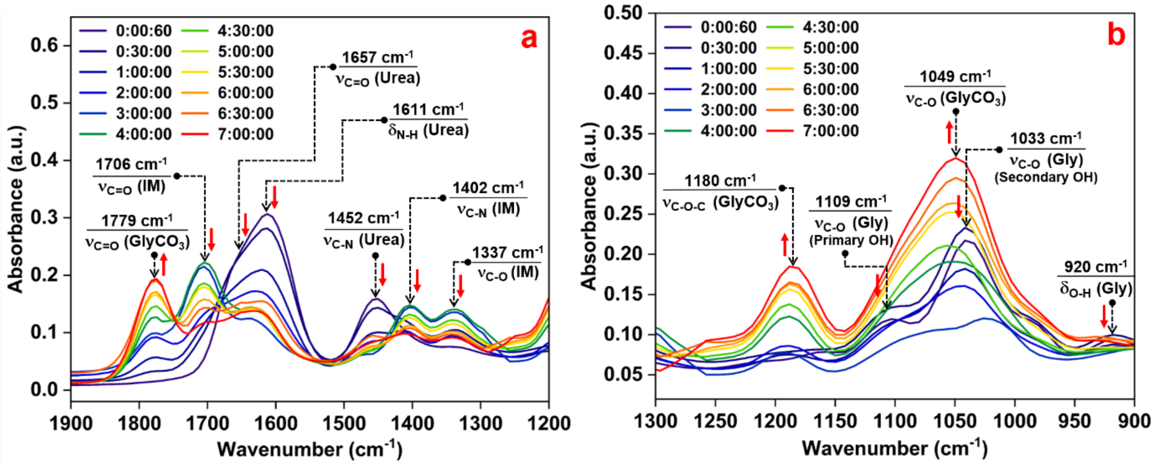


Figure S16. 2D FT-IR spectra of reaction progress

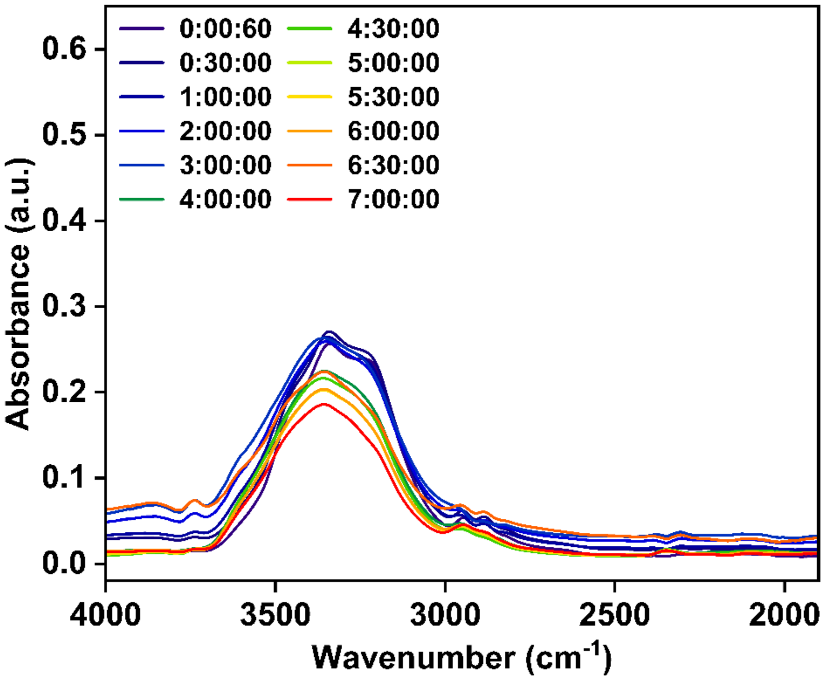


Figure S17. 2D FT-IR spectra of reaction progress between 4000-2000 cm^{-1}