Amberlyst-15 supported zirconium sulfonate as an efficient catalyst for Meerwein-Ponndorf-Verley reductions.

Zixin Wang, Chao Xie,* Xun Li, Jiabao Nie, Hanmin Yang* and Zehui Zhang*

Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, South-Central Minzu University, Wuhan, China.

E-mail: xiechao14@iccas.ac.cn; yanghanmin@sina.com; zehuizh@mail.ustc.edu.cn

Materials.

$NiCl_2 \cdot 6H_2O$ (98%), $CoCl_2 \cdot 6H_2O$ (99%), methanol (99%), ethanol (99%), isopropanol (99%), triethylamine (99%), ammonia solution (28% in water), *tert*-butanol (98%), *N,N*-dimethylformamide (99%) and 4-cyanobenzaldehyde (98%) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. $ZnCl_2$ (98%) was received from Shanghai Macklin Biochemical Co., Ltd. Levulinic acid (98%), methyl levulinate (98%), ethyl levulinate (98%), butyl levulinate (98%), furfural (99%), 2-thiophenecarboxaldehyde (98%), cinnamaldehyde (95%), ethylbenzene(99%), benzaldehyde (99%), citronellal (96%), *p*-anisaldehyde (99%), *p*-methylbenzaldehyde (97%), *p*-nitrobenzaldehyde (97%), *p*-bromo benzaldehyde (99%), 4-acetylpyridine (98%), 2-pentanone (99%), cyclohexanone (99%), acetophenone (98%), 4-nitroacetophenone (97%), 4-methylacetophenone (98%), 2-acetonaphthone (98%), *sec*-butanol (99%), 2-chloroacetophenone (97%), 2-methylacetophenone (98%), 2-benzofuranyl methyl ketone (99%), ZrO_2 (99%), $ZrCl_4$ (98%), $AlCl_3$ (98%), amberlyst-

15, phytic acid solution (70% in water), cyanuric acid (98%), tannic acid (98%) and chitosan were purchased from Aladdin Industrial Co., Ltd.

Preparation of Zr-AIER.

The Zr-AIER was synthesized from $ZrCl_4$ and amberlyst-15 in ethanol. Typically, 442 mg amberlyst-15 was initially dispersed into 10 mL of ethanol solution of $ZrCl_4$ (0.15 mmol/mL) with stirring. Then, the pH was adjusted to 9 with 28% aqueous ammonia. After that, the mixture was continuously stirred at 60 ℃ for 7 h. The obtained brown precipitate was filtrated and thoroughly washed with DMF and ethanol to remove the uncoordinated Zr complex. Finally, the obtained Zr-AIER was dried in a vacuum oven at 60 °C for 6 h. The preparation of other metal-based catalysts ($CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$, $AlCl_3$) with amberlyst-15 was the same as that of Zr-AIER, and some other Zr based catalysts with different ligands (phytic acid, cyanuric acid, tannic acid and chitosan) are prepared according to the relevant literature.

Catalyst characterization

The scanning electron microscopy (SEM) measurements were performed on Hitachi S-4800 scanning electron microscope. The transmission electron microscopy (TEM) measurements were obtained on the FEI Talos F200X instrument. X-ray powder diffraction (XRD) patterns were conducted on a Bruker advanced D8 powder diffractometer using Cu Kα radiation. N_2 adsorption/desorption isotherms were determined using V-Sorb 2800P instrument. X-ray photoelectron spectroscopy (XPS) was conducted on Thermo VG scientific ESCA MultiLab-2000 spectrometer. The

content of Zr in Zr-AIER and the reaction solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, VISTA-MPX), and the NH_3-TPD and CO_2-TPD were performed on MicrotracBEL BELCAT II. FT-IR spectra were collected by the KBr pellet method with a Nicolet Nexus 470 Fourier transform infrared spectrometer (FTIR). The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (NETZSCH STA 449C) over the temperature range of 30 °C to 800 °C under N_2 atmosphere with a heating rate of 20 °C/min and were provided technical support by Ceshigo Research Service "www.ceshigo.com".

Catalytic reaction.

In a typical reaction procedure, 10 mL isopropanol, 200 mg catalyst, and 1 mmol substrate were added into a 50 mL stainless steel reactor. After the reactor was sealed, the reaction mixture was stirred at the desired temperature for desired time. When the reaction was completed, the reactor was cooled to room temperature, and 0.5 mmol ethylbenzene was added as the internal standard. The product was quantitatively analyzed by gas chromatography (GC, Agilent 7820A) equipped with the FID detection. Identification of reaction products was done by GC-MS (Agilent 7890A GC/5973 MS).

Reusability of the prepared Zr-AIER.

For the recyclability tests, the reactions were performed under the same reaction conditions as described above, except using the recovered catalyst. Each time, the

catalyst was recovered by centrifugation and thoroughly washed with ethanol for 5 times (5 × 10 mL). After drying under vacuum at 60 °C for 7 h, the recovered catalyst was reused for the next run. For the GVL yield kinetics plot of the recycling tests, each data point was gathered as a separate reaction.

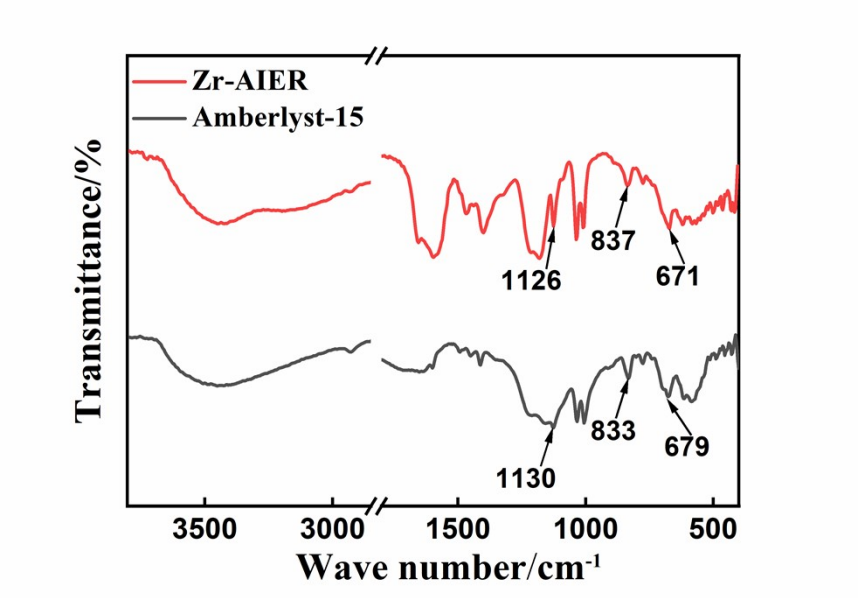


Figure S1. FT-IR spectra of Zr-AIER and amberlyst-15.

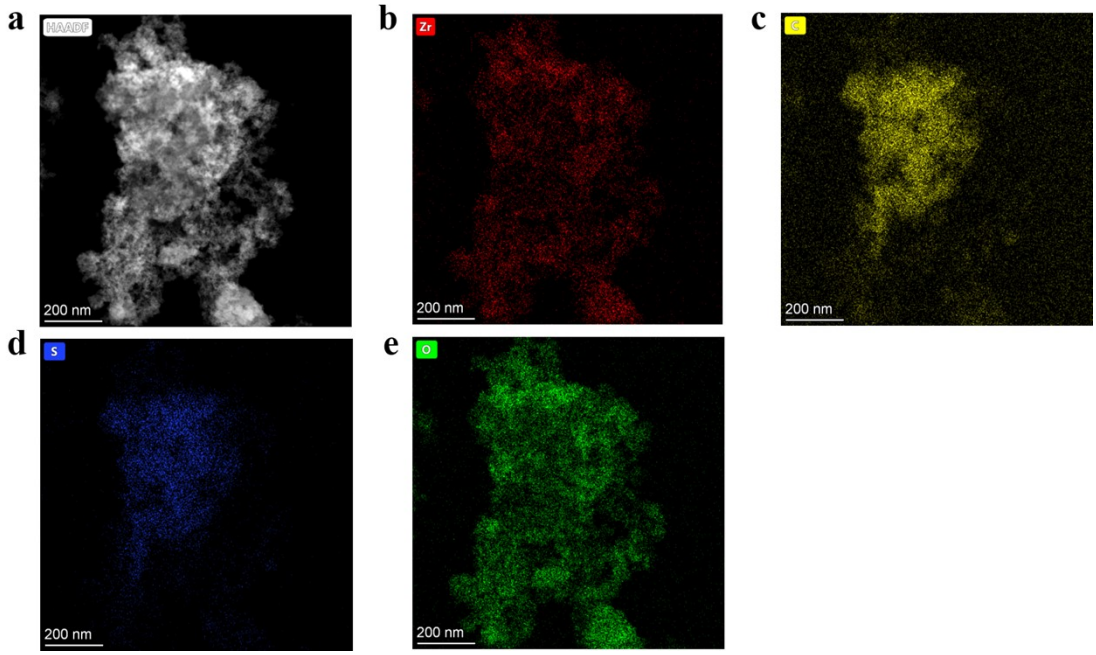


Figure S2. EDS mapping of the distribution of Zr, C, S, and O elements in Zr-AIER.

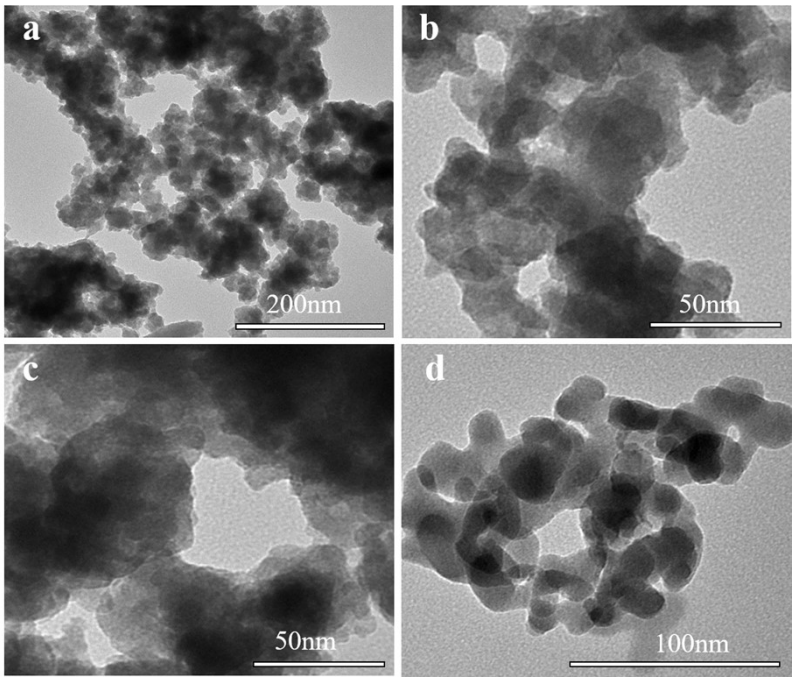


Figure S3. TEM images of (a) Zr-PhyA, (b) Zr-CA, (c) Zr-Tannin, and (d) Zr-Chitosan.

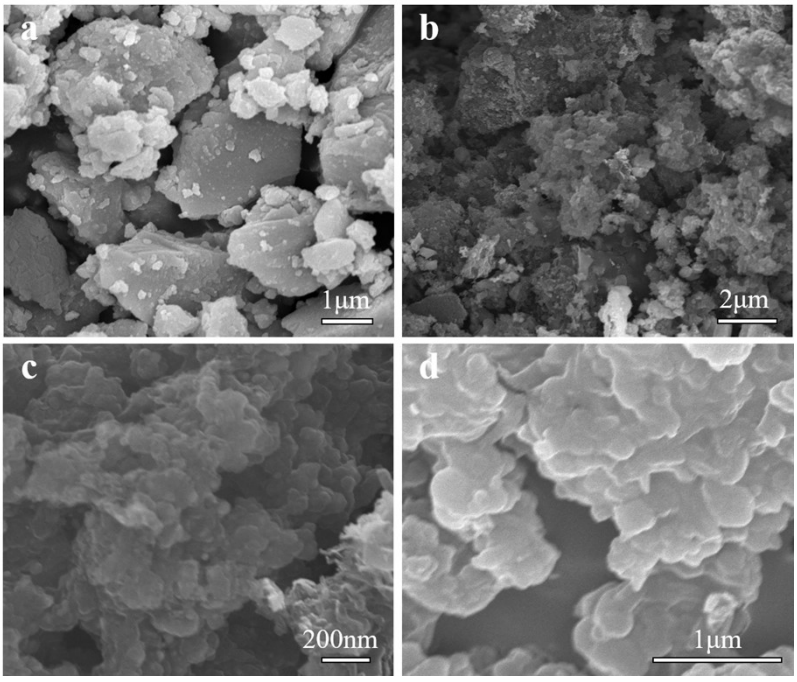


Figure S4. SEM images of (a) Zr-PhyA, (b) Zr-CA, (c) Zr-Tannin, and (d) Zr-

Chitosan.

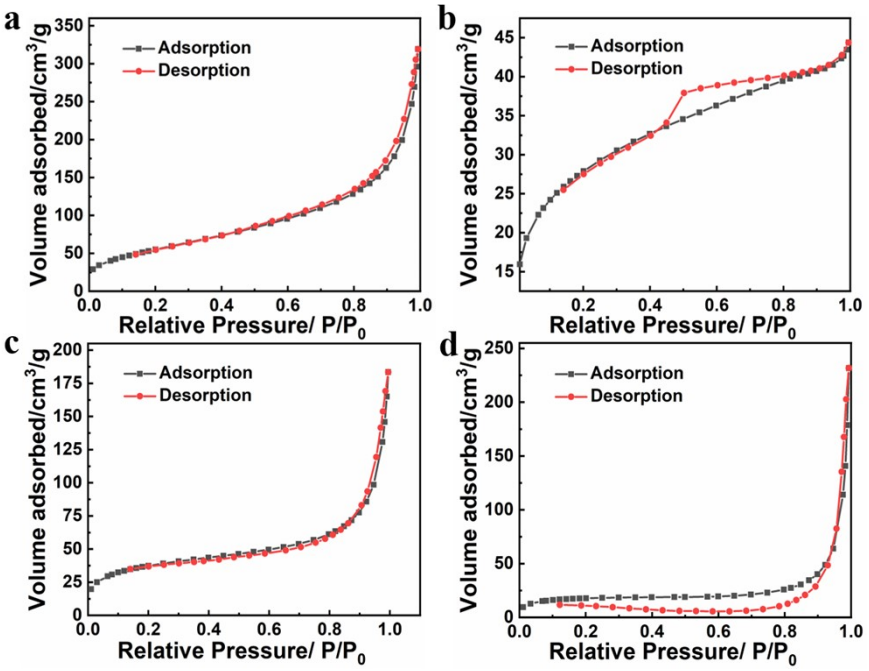


Figure S5. Nitrogen adsorption-desorption isotherms of (a) Zr-PhyA, (b) Zr-CA, (c) Zr-Tannin, and (d) Zr-Chitosan.

Table S1 the Zr content and BET surface area of those used catalysts.

Entry	Catalyst	Zr loading wt %	BET surface area m^2/g
1	Zr-AIER	18.63	159.42
2	Zr-AIER-reused	18.12	137.23
3	Zr-PhyA	28.2	205.2
4	Zr-CA	38.3	100.04
5	Zr-Tannin	21.6	135.1
6	Zr-Chitosan	9.1	62

Table S2 MPV reduction of EL to GVL over different catalysts.[a]

Entry	Catalyst	t/h	C/%	Y/%	S/%	TON	TOF/h^{-1}
1[b,c]	Zr-AIER	1	46	40	87	0.98	0.98
2[b]	Zr-PhyA	1	17	11	67	0.27	0.27
3[b]	Zr-CA	1	32	25	83	0.61	0.61
4[b]	Zr-Tannin	1	16	12	75	0.29	0.29
5[b]	Zr-Chitosan	1	35	28	80	0.68	0.68
6[b]	Zr-AIER	8	97	95	96	2.32	0.29
7[b]	Zr-PhyA	8	52	44	85	1.08	0.14
8[b]	Zr-CA	8	81	68	84	1.66	0.21
9[b]	Zr-Tannin	8	53	47	89	1.15	0.14
10[b]	Zr-Chitosan	8	88	79	90	1.93	0.24
11[c]	Zr-AIER	8	97	95	96	2.32	0.29
12[c]	Zr-PhyA	8	78	59	76	0.95	0.12
13[c]	Zr-CA	8	97	82	85	0.97	0.12
14[c]	Zr-Tannin	8	67	55	82	1.15	0.14
15[c]	Zr-Chitosan	8	51	45	88	2.25	0.28
16[c]	$ZrCl_4$	8	80	49	61	0.72	0.09

Reaction conditions: [a]EL 1 mmol, isopropanol 10 mL, reaction temperature 150 °C; [b]40.9 mol% catalyst was used, which was marked in blue; [c]200 mg catalyst was used, which was marked in green; t = time, C = Conversion, Y = Yield and S = Selectivity.

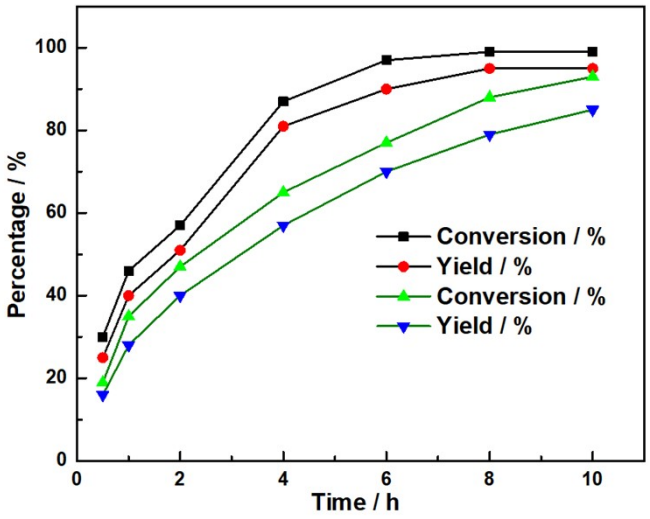


Figure S6. The Time-Yield plot comparison of Zr-AIER and Zr-Chitosan. Black line for Zr-AIER and oliver for Zr-Chitosan.

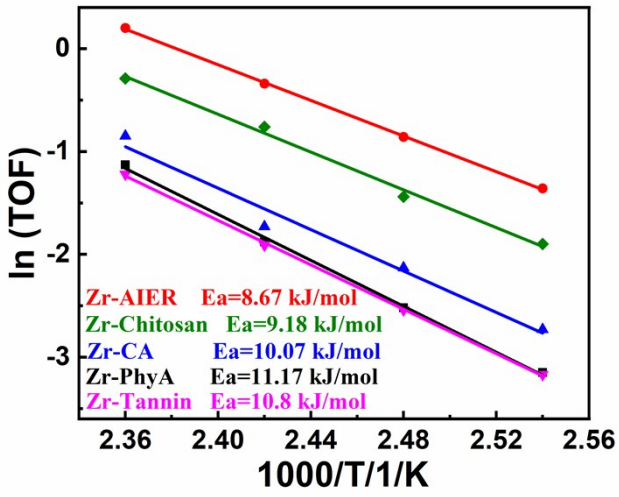


Figure S7. Natural logarithm of TOF versus inversed temperature for apparent activation energy.

Table S3 The gram-scale reaction and low catalyst dosage tests on MPV reduction of EL to GVL.[a]

Entry	Dosage	Zr/mol%	t/h	C/%	Y/%	S/%	TON	TOF/h^{-1}
1[b]	200 mg	40.9	8	97	95	96	2.32	0.29
2[c]	200 mg	4.09	4	31	27	87	6.6	1.65
3[c]	200 mg	4.09	72	97	90	93	22	0.31
4[b]	20 mg	4.09	4	21	18	86	4.4	1.1
5[b]	20 mg	4.09	100	96	88	92	21.52	0.22
6[d]	41 mg	4.09	100	64	53	83	12.96	0.13

Reaction conditions: [a]isopropanol 10 mL, reaction temperature 150 °C; [b]EL 1 mmol, Zr-AIER was used as catalyst; [c]EL 10 mmol, Zr-AIER was used as catalyst; [d]EL 1 mmol, 41 mg Zr-Chitosan (4.09 mol% Zr) was used as catalyst; t = time, C = Conversion, Y = Yield and S = Selectivity.

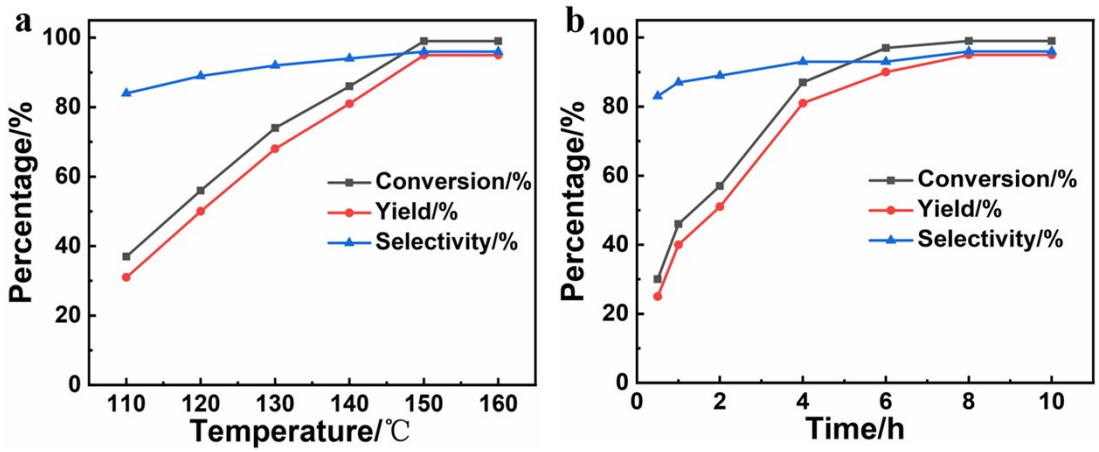


Figure S8. The effects of (a) reaction temperature and (b) reaction time on the performances of Zr-AIER. Reaction conditions: EL 1 mmol, isopropanol 10 mL, catalyst 200 mg, 8 h for (a) and 150 °C for (b).

Table S4 Influence of alcohols as the hydrogen donor on MPV reduction of EL to GVL over Zr-AIER.[a]

Entry	Solvent	C/%	Y/%	S/%
1	methanol	79	74	94
2	ethanol	60	54	90
3	isopropanol	99	95	96
4	*sec*-butanol	96	80	83
5	*tert*-butanol	9	5	56

[a]Reaction conditions: EL 1 mmol, isopropanol 10 mL, catalyst 200 mg, reaction temperature 150 °C, reaction time 8 h. C = Conversion, Y = Yield and S = Selectivity.

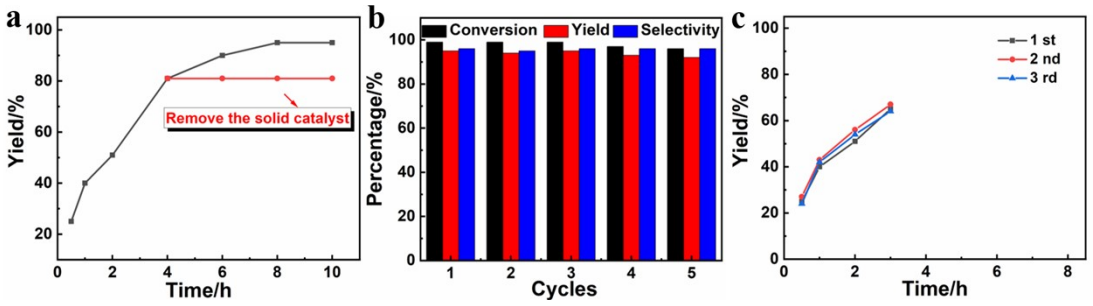


Figure S9. (a) Leaching tests, (b) recycle tests, and (c) kinetics plot of GVL yield at low conversion as a function of time for each recycling step by Zr-AIER catalyst. Reaction conditions: EL 1 mmol, isopropanol 10 mL, catalyst 200 mg, reaction temperature 150 °C, 8 h for (b).

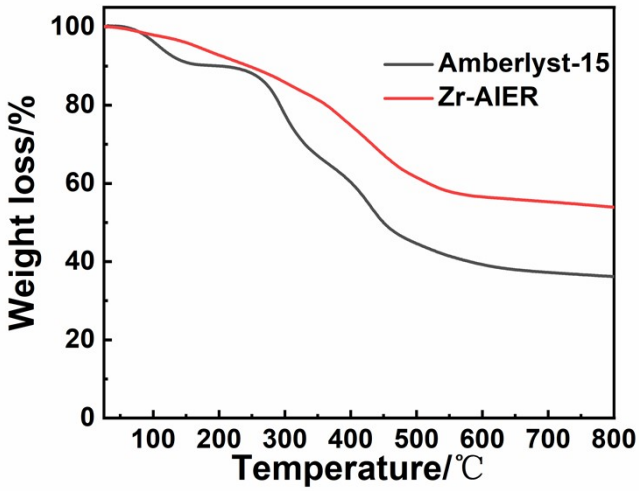


Figure S10. Thermogravimetric analysis image of Zr-AIER and Amberlyst-15 under N_2 atmosphere.

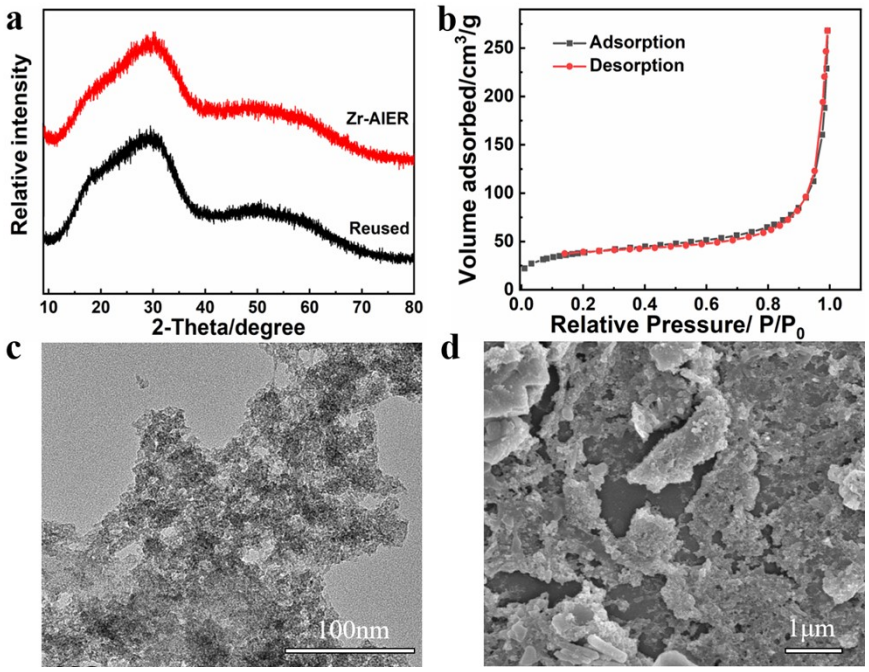
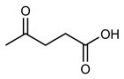
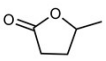
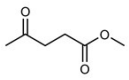
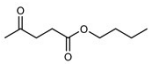
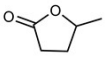


Figure S11. (a) XRD pattern, (b) Nitrogen adsorption-desorption isotherm, (c) TEM image, and (d) SEM image of Zr-AIER reused.

Table S5 MPV reduction of LA and its esters over Zr-AIER.[a]

Entry	Substrate	Product	T/°C	t/h	C/%	Y/%
1			130	8	99	84
2			150	6	99	88
3			150	12	99	90

[a]Reaction conditions: EL 1 mmol, isopropanol 10 mL, catalyst 200 mg. T = Temperature, t = time, C = Conversion and Y = Yield.