Supplementary Information

Synthesis of a Sustainable and Robust Heterogeneous TEMPO Catalyst based on Activated Carbon for Aerobic Alcohol Oxidation

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Characterization apparatus and setups

The materials were investigated by scanning electron microscopy in a HITAKI Regulus8100. The samples were sputter-coated with gold before the analysis. Elemental analysis was performed with the CHN-analyzer Flash EA-1112 (Vario Miro Cube, German). Thermogravimetric analysis (TGA) was performed under Ar flow (50 ml min^{-1}) in the temperature range 40-810 °C with a heating rate of 10 °C min^{-1} on a NETZSCH STA 409 PC/PG instrument. The specific surface areas were determined by N_2 physisorption using Micromeritics ASAP2460 and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum ($<1\times10^{-5}$ bar) in the Micromertics system at 120 °C for 8 h before N_2 physisorption. The electron paramagnetic resonance (EPR) tests were executed on an EPR spectrometer at room temperature with microwave frequency of 9.85 GHz and microwave power of 200 mW (EMXplus, Bruker Optics). For quantitative infrared-spectroscopy (IR) pressed KBr pellets made of 2 mg sample substance and 198 mg KBr were analyzed (Thermo IS10, Bruker Optics). The IR spectra were recorded in a measuring range of 400-4000 cm^{-1} with a resolution of 2 cm^{-1}. X-ray photoelectron spectroscopy (XPS) analysis was performed in a Thermo Fisher ESCALAB 250Xi photoelectron spectrometer using monochromatic Al K_α (1486.7 eV) X-ray irradiation with vacuum degree of the analysis chamber is 8×10^{-10} Mbar. The binding energy of the photoemission spectra was calibrated to adventitious carbon C 1s peak with a binding energy of 284.8 eV.

The liquid products from the outlet of micro-packed bed reactor were collected when the system reached a steady state, then the samples were diluted with acetonitrile to the mass fraction of substrates below 5wt% and analyzed by GC. GC analyses were performed using a Hp-5 column (30m × 320μm × 0.25μm) installed in the Agilent 8860 GC system equipped with a FID detector. The column flow rate 1.5ml/min of N_2 with a split ratio of 30:1. The column temperature started at 60 °C, ramped at 20 °C/min to 280 °C (11 min), maintained 200 °C for 5 min, and the detector was held at 300 °C. 2 mol% toluene was used as internal standard.

Titration was conducted by an automatic acid-base titration equipment. Samples were washed by deionized water for 3 times at first. After drying at room temperature, samples were accurately weighed (around 1.0 g) and stirred in 10.00 mL standard $NaHCO_3$ solution at room temperature for 2 days (surface-carboxyl groups would be consumed). After filtration, the filtrate was titrated by standard HCl solution (Marked with $NaHCO_3$) to determine the remaining $NaHCO_3$. Finally, the number of surface-carboxyl groups was derived by subtraction.

Mass balance for the experimental setups

Inlet Stream: benzyl alcohol ($C_{BnOH,s}$) in MeCN (0.3 mL/min) and O2 (30 mL/min)

Outlet Stream: benzyl alcohol ($C_{BnOH,p}$) and benzaldehyde ($C_{BzH,p}$) in MeCN and O2 (approx. 30 mL/min, assumed as constant because it is excess)

We used Gas Chromatograph to calculate the $C_{BnOH,s}$, C_{BnOH} and C_{BzH}. If they satisfy:

$$C_{BnOH,p} + C_{BzH,p} = C_{BnOH,s}$$

the mass balance is valid, and the results are as follows:

Samples	$C_{BnOH,s}$(mol/L)	$C_{BnOH,p}$(mol/L)	$C_{BzH,p}$(mol/L)
inlet-1	1.02	n.a.	n.a.
outlet-1	n.a.	0.84	0.16
outlet-2	n.a.	0.88	0.13
outlet-3	n.a.	0.66	0.42
outlet-4	n.a.	0.83	0.17
outlet-5	n.a.	0	0.97

Catalysts pretreatment steps

All the samples undergo the following washing procedure for characterization or catalytic activity testing to eliminate the influence of physically adsorbed TEMPO molecules:

1. The samples are washed three times with water and three times with methanol;

2. Washed samples would be filtered and air-dried at 120°C for 12 hours;

3. Samples are flushed by a high flow rate (5 mL/min) solvent (MeCN) for 10 minutes to remove residual adsorbed TEMPO.

Table S1. B mode: elemental analysis results.

Entry [a]	Temp.	Time (h)	Element content			
			C (wt%)	H (wt%)	N (wt%)	O^b (wt%)
0 [c]	r.t.	0	94.1	0.97	1.06	3.91
1	r.t.	2	88.0	1.82	1.00	9.18
2	r.t.	5	89.0	1.61	0.88	8.56
3	r.t.	13	89.1	1.65	0.91	8.34
4 [d]	ice bath	2	88.1	1.94	0.90	9.06

a. Conditions: 10 g activated carbon, 100 mg/L O_3/O_2 gas, 70 mL/min gas flow rate.

b. O contents were derived by (100%-C%-H%-N%), only for reference.

c. Crude activated carbon, without ozone treatment.

d. This sample was chosen to represent the **B** mode ozone treatment results, namely **B-ozo-AC**.

Table S2. P mode: elemental analysis results.

Entry [a]	Time (h)	Element content			
		C (wt%)	H (wt%)	N (wt%)	O^b (wt%)
0 [c]	0	94.1	0.97	1.06	3.91
5	2.5	90.7	1.51	1.52	6.22
6 [d]	5	89.3	1.64	1.87	7.21
7	10	87.2	2.08	2.51	8.21
8	20	90.9	1.28	1.55	6.26
9	30	91.3	1.27	0.87	6.59
10	60	91.4	1.28	0.91	6.37
11	90	91.3	1.30	0.90	6.54

a. Conditions: 7.2 g activated carbon, 80 mg/L O_3/O_2 gas, 50 mL/min gas flow rate, 2.5 mL/min liquid (water or saturated sodium sulfite solution) flow rate, 0°C (ice bath).

b. O contents were derived by (100%-C%-H%-O%), only for reference.

c. Crude activated carbon, without ozone treatment.

d. This sample was chosen to represent the **P** mode ozone treatment results, namely **P-ozo-AC**.
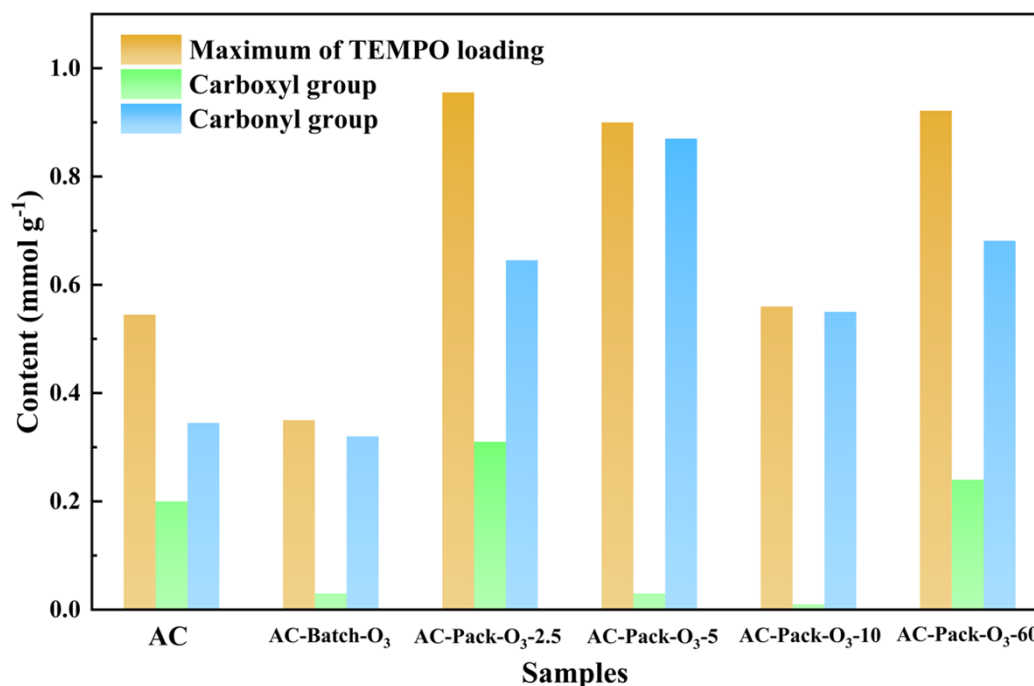
Figure S1. Titration and elemental analysis results (functional groups)

for sample screening.

Since the elemental content of each sample obtained from Bubbly Batch ozone treatment (**B** mode) treatment was almost identical, this may be due to the limitation of ozone transfer under bubbly treatment conditions, and the ozone concentration in water could not reach a high level. Therefore, the sample from Entry 4 was chosen as a representative sample and named AC-Batch-O_3 or **B-ozo-AC**; however, the samples obtained from Micro-Packed Bed continuous ozone treatment (**P** mode) had significant differences with treatment time and needed further optimization. As shown in **Figure S1**, the number in the sample name "AC-Pack-O_3-(Number)" represents the treatment time (min). Among them, the sample treated with ozone for 5 min could achieve a TEMPO loading of about 0.90 mmol/g with less carboxylate content, which indicates the optimal carbonylation conditions. Therefore, the sample of Entry 6 was chosen as representative and named AC-Pack-O_3-5 or **P-ozo-AC**.
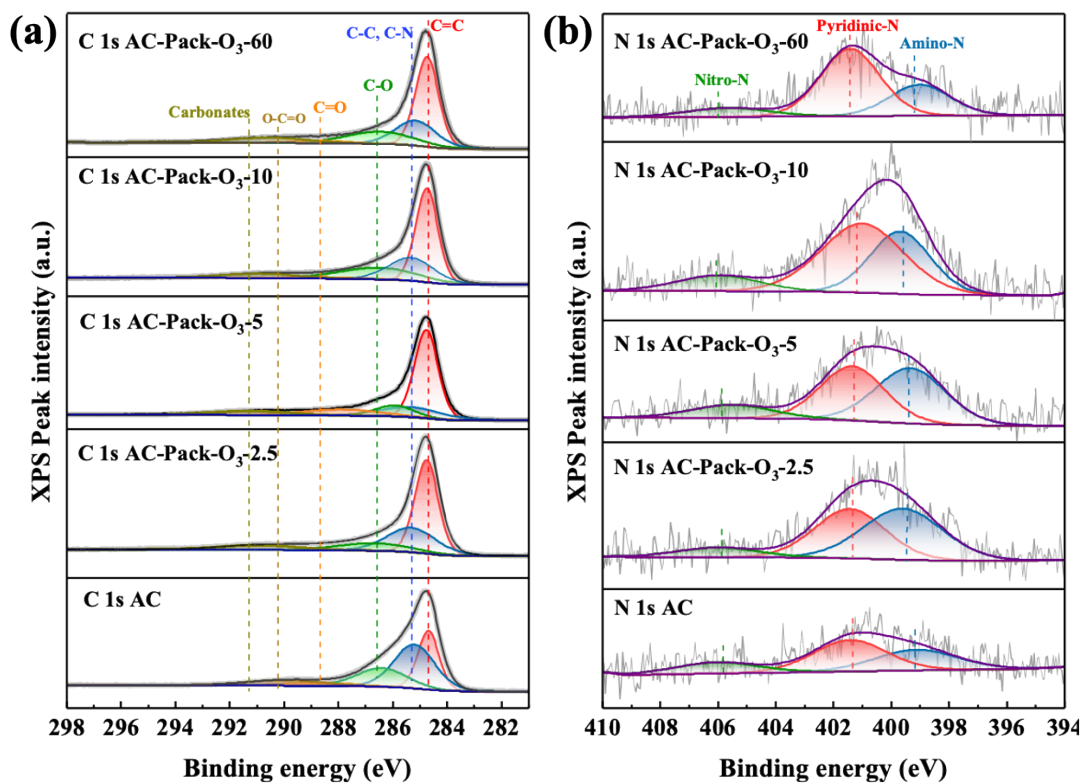
Figure S2. XPS of all **P** mode treated samples (include peak fitting):

(a) C 1s spectra; (b) N 1s spectra.

Table S3. XPS-based atomic percentage of species on the surface of AC, ozone-treated AC, and TEMPO-functionalized AC.

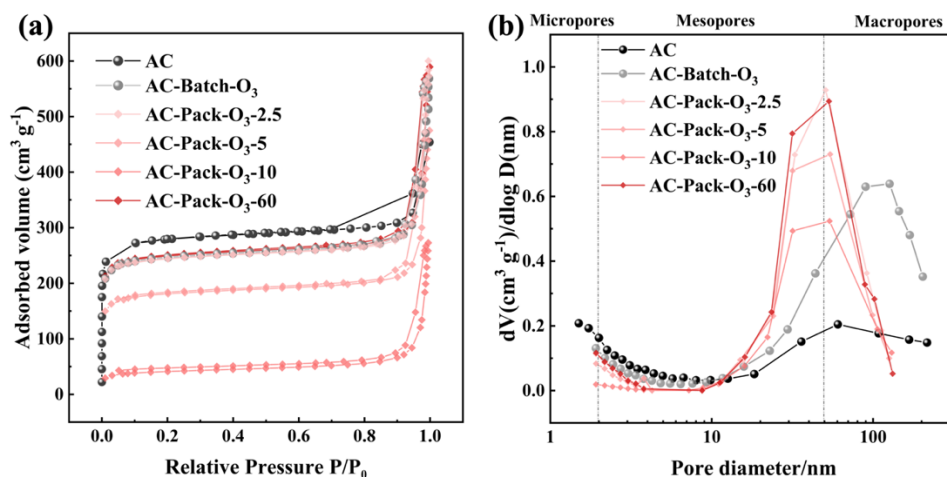| Species	Samples				
	AC	B-ozo-AC	P-ozo-AC	B-ozo-AC-TEMPO	P-ozo-AC-TEMPO
C=C	27.0%	48.4%	51.0%	39.2%	40.6%
C-C, C-N	36.4%	21.0%	15.1%	30.7%	27.0%
C-O	21.6%	9.70%	10.5%	13.7%	14.9%
C=O	3.66%	8.25%	11.9%	2.64%	3.27%
O-C=O	6.67%	6.54%	7.81%	10.5%	6.74%
Carbonates	~0	~0	~0	~0	~0
Amino-N	0.83%	1.44%	1.65%	1.21%	2.71%
Pyridinic-N	3.24%	3.90%	1.49%	1.52%	3.45%
Nitro-N	0.55%	0.75%	0.47%	0.34%	0.68%
Nitroxyl-N	~0	~0	~0	0.17%	0.68%

Figure S3. BET analysis of all samples:

(a) adsorption-desorption curves; (b) pore size distributions.

Table S4. Structural parameters of all ozone treated samples.

Samples	Average pore diameter (nm)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
AC	2.52	1064.7	0.67
AC-Batch-O_3	3.53	907.5	0.48
AC-Pack-O_3-2.5	3.46	936.1	0.48
AC-Pack-O_3-5	3.77	693.5	0.38
AC-Pack-O_3-10	9.54	150.1	0.35
AC-Pack-O_3-60	3.46	956.2	0.49

Table S5. Elemental analysis results of B-ozo-AC-TEMPO(freshly

prepared), B-ozo-AC-TEMPO(used)

Samples	Element content (%) [a]		
	C	H	N
B-ozo-AC-TEMPO(freshly prepared)	90.6	1.8	1.9
B-ozo-AC-TEMPO(after 80 hours usage)	90.3	1.6	1.4

a. it has an error around ±0.1% inevitably.