Supporting information

Aerobic oxidation of C-H bond under ambient conditions using highly dispersed Co over highly porous N-doped carbon

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Experimental section

Materials

All chemicals and solvents were obtained from commercial suppliers and used as received: $Zn(NO_3)_2\cdot 6H_2O$ (99%, Sigma-Aldrich), $Co(NO_3)_2\cdot 6H_2O$ (99%, Sigma-Aldrich), 2-methylimidazole (99%, Sigma-Aldrich), methanol (99%, Sigma-Aldrich), ethylbenzene (99%, Sigma-Aldrich), TBHP (70 wt. % in water, Sigma-Aldrich), ultrapure water (Millipore, 18.2 MΩ cm) was used throughout all experiments.

Characterization

Powder X-ray diffraction (PXRD) patterns of the samples were acquired by a STOE Stadi P powder diffractometer using Cu Kα radiation (40 kV, 40 mA, λ=0.1541 nm). N_2 physisorption experiments were conducted by using Micromeritics 3 Flex surface characterization analyzer at 77 K. All the samples were activated at 150 ˚C for 12 h under vacuum (<10^{-5} torr) before measurements. Transmission electron microscopy (TEM) images were acquired by using a Tecnai G2 F20 electron microscope operated at 200 kV. Inductively coupled plasmon-mass spectrometry (ICP-MS, X Series II, Thermo Scientific) was performed to determine the actual metal content. Samples were digested by boiled aqua regia before ICP analysis. X-ray photoelectron spectroscopy

(XPS) spectra were measured by a PHI 5500 Multi-technique system (Physical Electronics, Chanhassen, MN) equipped with a monochromatized Al *K*α X-ray source (1486.6 eV). The binding energies were calibrated based on the C1s peak at 284.6 eV as a reference.

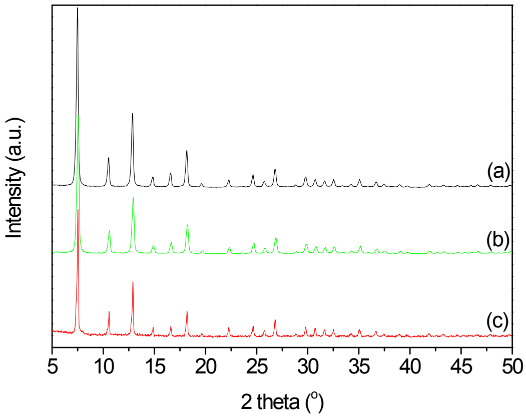


Fig. S1 XRD patterns of (a) ZIF-8, (b) Co_1Zn_{99}-ZIF and (c) ZIF-67.

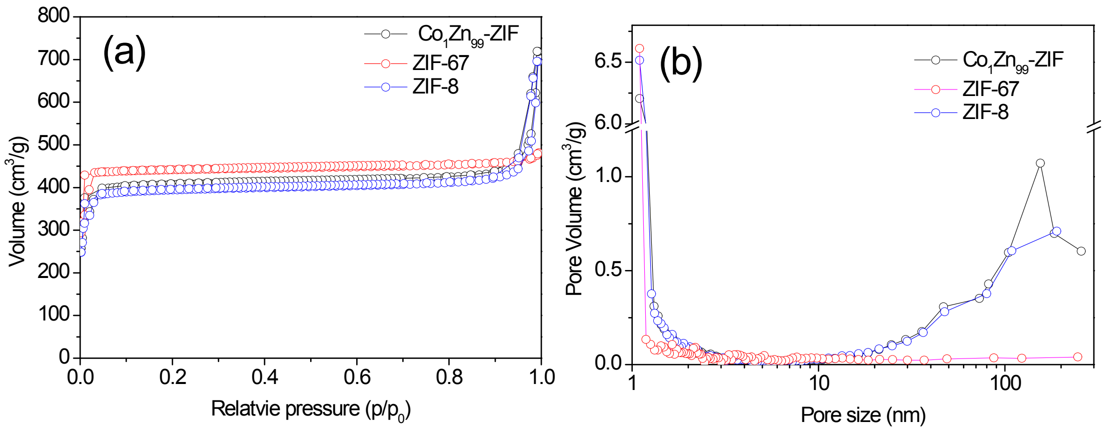


Fig. S2 (a) Nitrogen sorption isotherms and (b) pore size distribution of Co_xZn_{100-x}-ZIF materials.

Table S1 the pore structure of Co_xZn_{100-x}-ZIF.

Samples	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_p (nm)
ZIF-8	1410	0.83	<1

ZIF-67	1560	0.71	<1
Co_1Zn_{99}-ZIF	1450	0.87	<1
Co_1Zn_{99}-ZIF-800-Ar	610	0.40	<1, 110
$Co_{10}Zn_{90}$-ZIF-800-Ar	350	0.51	-
ZIF-67-800-Ar	260	0.44	-
Co_1Zn_{99}-ZIF-800-H_2	1090	0.89	1.2, 110
Co_1Zn_{99}-ZIF-900-H_2	1100	0.88	1.3, 80
Co_1Zn_{99}-ZIF-700-H_2	830	0.55	<1, 110
Co_1Zn_{99}-ZIF-600-H_2	530	0.32	<1, 110
Spent Co_1Zn_{99}-ZIF-800-H_2	980	0.83	1.2, 80

Table S2 ICP-MS tests of different Co_xZn_{100-x}-ZIF materials.

Samples	Co content (wt %)	Zn content (wt %)
Co_1Zn_{99}-ZIF	0.24	25.09
Co_1Zn_{99}-ZIF-400-H_2	0.28	26.13
Co_1Zn_{99}-ZIF-600-H_2	0.54	24.02
Co_1Zn_{99}-ZIF-700-H_2	0.78	11.45
Co_1Zn_{99}-ZIF-800-H_2	0.93	6.24
Co_1Zn_{99}-ZIF-900-H_2	1.21	2.82
ZIF-67	25.5	-
ZIF-67-800-Ar	41.85	-
$Co_{50}Zn_{50}$-ZIF-800-Ar	25.75	-
$Co_{10}Zn_{90}$-ZIF-800-Ar	5.59	-
Co_5Zn_{95}-ZIF-800-Ar	3.35	-
$Co_{2.5}Zn_{97.5}$-ZIF-800-Ar	1.23	-
Co_1Zn_{99}-ZIF-800-Ar	0.65	9.53
$Co_{0.2}Zn_{99.8}$-ZIF-800-Ar	0.17	-

Table S3 Elemental analysis of Co_xZn_{100-x}-ZIF catalysts.[a]

Catalysts	Elemental percentage (at. %)				
	C	N	O	Zn	Co
Co_1Zn_{99}-ZIF	62.9	26.4	2.4	8.3	-
Co_5Zn_{95}-ZIF	63.0	26.1	3.3	7.4	0.23
Co_1Zn_{99}-ZIF-800-H_2	84.7	8.5	5.7	0.66	0.49

[a] Determined by XPS.

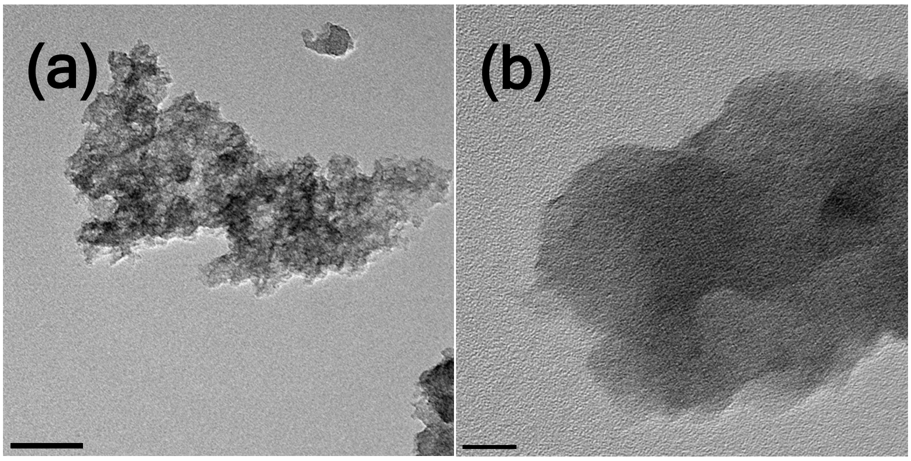


Fig. S3 TEM images of Co_1Zn_{99}-ZIF-800-H_2.

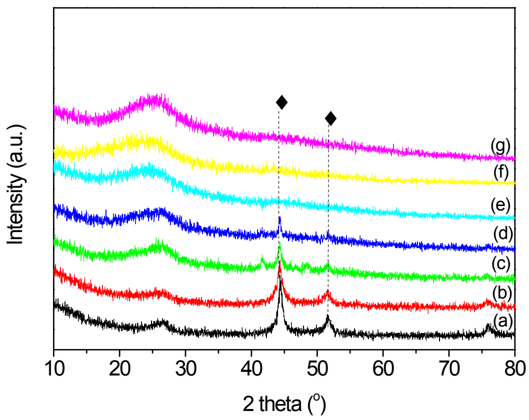


Fig. S4 XRD patterns of (a) ZIF-67-800-Ar, (b) $Co_{50}Zn_{50}$-ZIF-800-Ar, (c) $Co_{10}Zn_{90}$-ZIF-800-Ar, (d) Co_5Zn_{95}-ZIF-800-Ar, (e) $Co_{2.5}Zn_{97.5}$-ZIF-800-Ar, (f) Co_1Zn_{99}-ZIF-800-Ar and (g) $Co_{0.2}Zn_{99.8}$-ZIF-800-Ar.

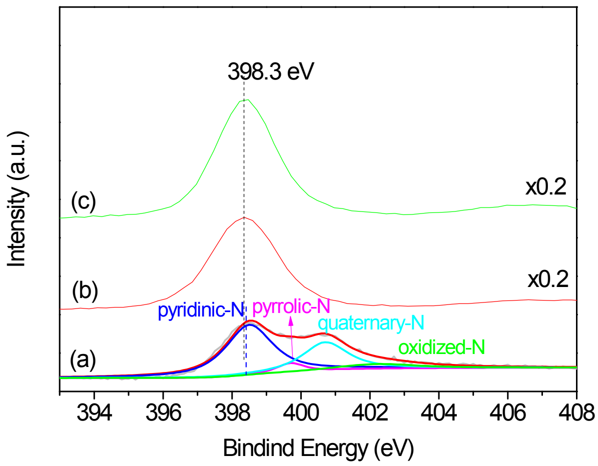
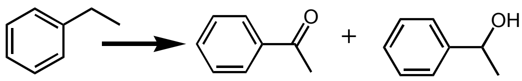
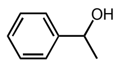
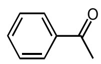


Fig. S5 N1s XPS spectra of (a) Co_1Zn_{99}-ZIF-800-H_2, (b) Co_1Zn_{99}-ZIF and (c) Co_5Zn_{95}-ZIF.

Table S4 Selective oxidation of EB with TBHP over Ar-treated Co_xZn_{100-x}-ZIF catalysts.[a]

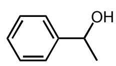
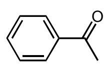


Entry	Catalysts	Conv/%			TOF/h^{-1} [b]
1	ZIF-8	0.9	80.3	19.7	-
2	ZIF-67	22.3	10.5	89.5	1.3
3	Co_1Zn_{99}-ZIF	1.6	32.2	67.8	9.8
4	$Co_{0.2}Zn_{99.8}$-ZIF-800-Ar	1.5	8.4	91.6	13.0
5	Co_1Zn_{99}-ZIF-800-Ar	14.2	19.7	80.3	32.2
6	$Co_{2.5}Zn_{97.5}$-ZIF-800-Ar	21.3	19.3	78.1	25.5
7	Co_5Zn_{95}-ZIF-800-Ar	27.0	18.1	81.9	11.9
8	$Co_{10}Zn_{90}$-ZIF-800-Ar	38.2	18.5	81.5	10.1
9	$Co_{50}Zn_{50}$-ZIF-800-Ar	75.6	12.5	87.5	4.3
10	ZIF-8-800-Ar	4.1	15.5	84.5	-
11	ZIF-67-800-Ar	62.5	16.9	83.1	2.2
12	Co_1Zn_{99}-ZIF-800-H_2	57.4	12.9	87.1	90.9
13	Co_1Zn_{99}-ZIF-400-H_2	1.0	20.4	79.6	5.3
14	Co_1Zn_{99}-ZIF-600-H_2	1.1	34.0	66.0	3.0
15	Co_1Zn_{99}-ZIF-700-H_2	40.9	21.2	78.8	77.2
16	Co_1Zn_{99}-ZIF-900-H_2	59.3	17.1	82.9	72.2

[a] Reaction condition: EB (0.25mmol), catalyst (5mg), H_2O (3mL), TBHP (7 equiv.), 23^oC, 2h.

[b] TOF = moles of converted substrate per mole of Co atoms per hour.

Table S5 Selective oxidation of EB with TBHP over Co_1Zn_{99}-ZIF-800-H_2 catalyst.

Catalysts	t/h	T/^oC	Conv/%		
Co_1Zn_{99}-ZIF-800-H_2	4	60	97.4	5.1	94.9

Reaction condition: EB (0.25mmol), catalyst (5mg), H_2O (3mL), TBHP (7 equiv.).

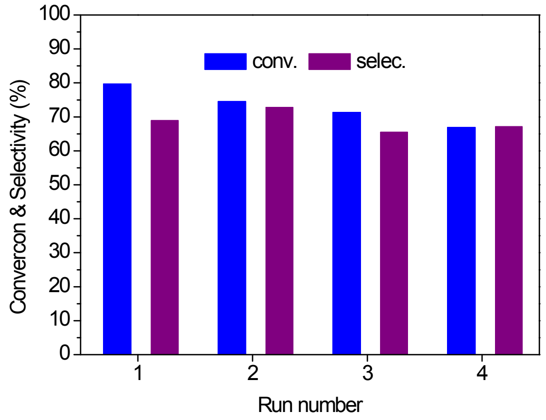


Fig. S6 Recycle of Co_1Zn_{99}-ZIF-800-H_2 for selective oxidation of EB with O_2 at high conversion.

Reaction condition: EB (0.25mmol), catalyst (5mg), H_2O (3mL), TBHP (0.28 equiv.), O_2 (1 atm), 60°C, 4 h.

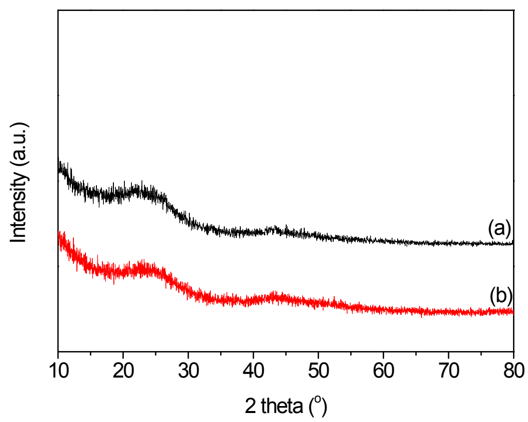


Fig. S7 XRD patterns of (a) fresh Co_1Zn_{99}-ZIF-800-H_2 and (b) 4 times reused Co_1Zn_{99}-ZIF-800-H_2.

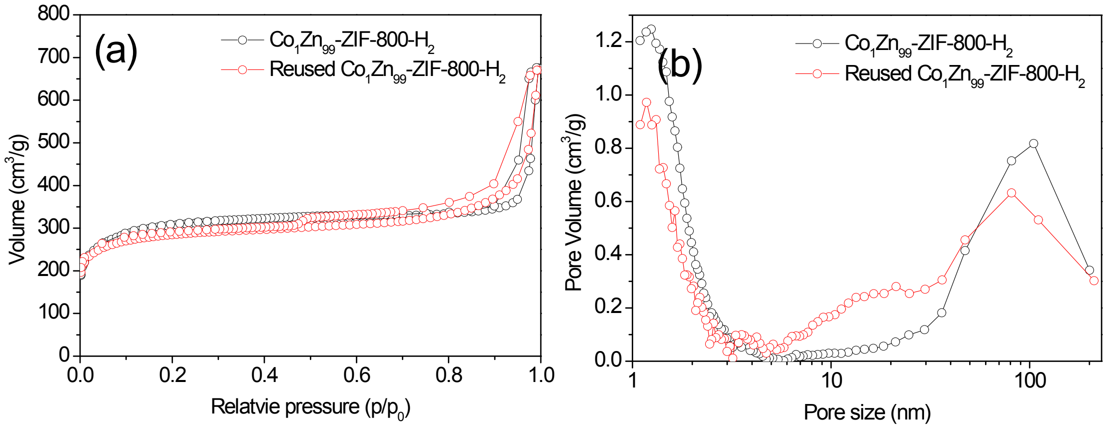
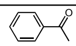
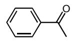
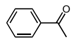
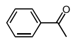
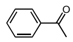
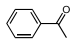
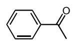
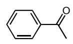
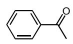
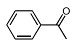
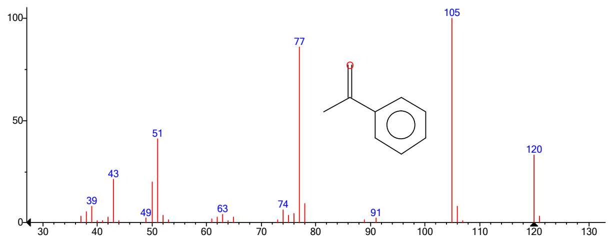


Fig. S8 (a) Nitrogen sorption isotherms and (b) pore size distribution of fresh and 4 times reused Co_1Zn_{99}-ZIF-800-H_2.

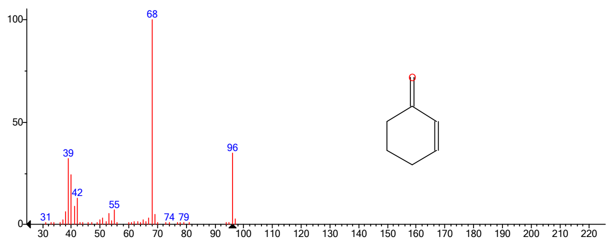
Table S6 Representative works for the oxidation of ethylbenzene (EB) using heterogeneous catalysts.

catalyst	Reaction conditions	Product	Conv./ %	Selec./%	Ref.
Co_1Zn_{99}-ZIF-800-H_2	60 °C, H_2O solvent, TBHP (28 mol%) +1 atm O_2, 0.008mol% Co.		57.0	93.5	This study
Mn-N-C@SiO_2	120 °C, solvent-free, 0.8 MPa O_2, 0.17mol% Mn.		12.8	73.6	[1]
Co–N–C/CeO_2	120 °C, solvent-free, 0.8 MPa O_2, 0.35mol% Co.		33.1	74.8	[2]
Fe-N-C	25 °C, H_2O solvent, TBHP (2-6 equiv.), 0.6 mol% Fe.		99	99	[3]
Au/LDH hybrid	140 °C, TBHP (3mol%) + 3 MPa O_2, 0.002mol% Au.		39	91	[4]
Co/AC-salen-400	80 °C, CH_3CN solvent, TBHP (0.4 equiv.), 0.76 mmol% Co.		20.8	76.8	[5]
Pd@C-Glu_A-550	120 °C, 20 h, solvent-free, 1 atm air, 0.003 mmol% Pd.		14.2	94	[6]
$Ce_{0.5}Mn_{0.5}O_x$@500	120 °C, CH_3CN solvent, 1 MPa O_2, 10 mmol substrate, 30 mg catalyst.		20.3	87	[7]
GSCN-20	150 °C, CH_3CN solvent, 1 MPa O_2, 10 mmol substrate, 50 mg catalyst.		12	99	[8]
N-doped graphene	80 °C, H_2O solvent, TBHP (3 equiv.), 1 mmol substrate, 10 mg catalyst.		98.6	91.3	[9]

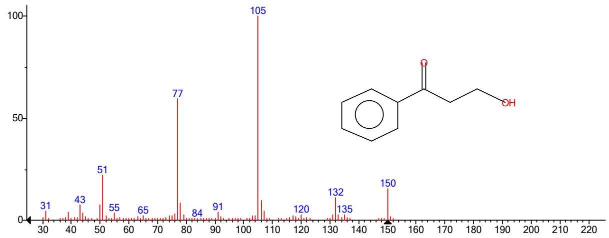
3 Mass spectrogram of some ketones (aldehydes) (9 largest peaks based on EI)



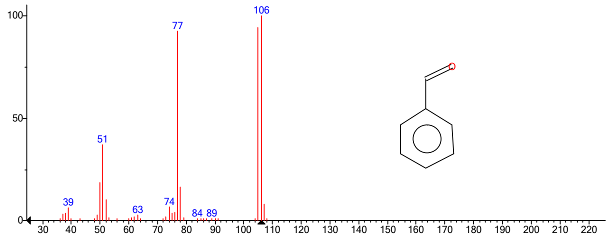
(replib) Acetophenone



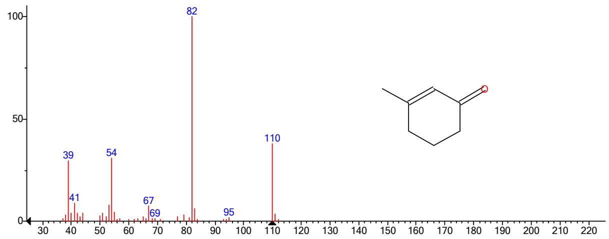
(replib) 2-Cyclohexen-1-one



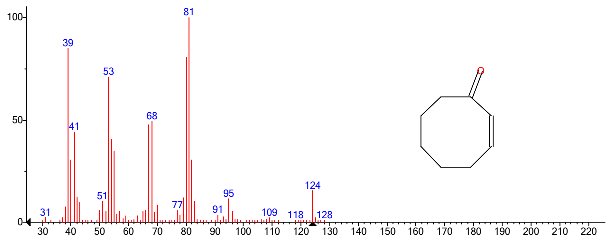
(mainlib) 1-Propanone, 3-hydroxy-1-phenyl-



(replib) Benzaldehyde



(mainlib) 2-Cyclohexen-1-one, 3-methyl-



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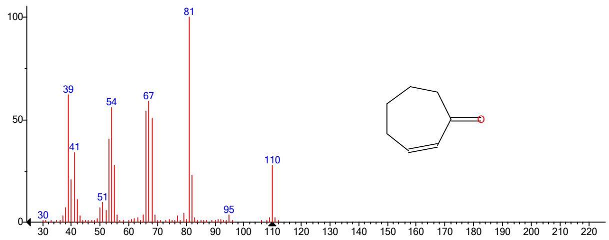

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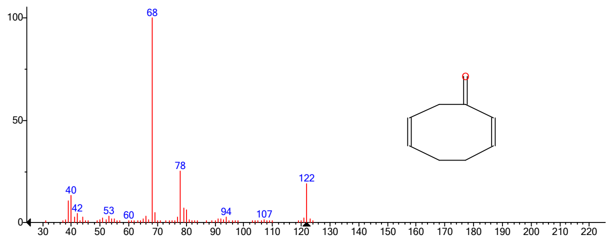

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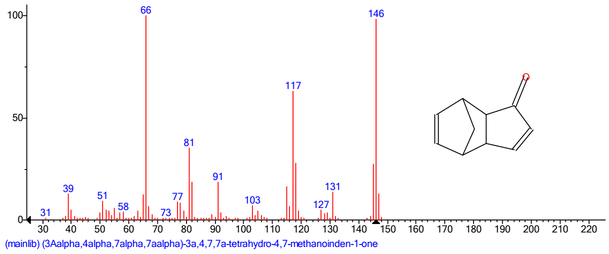

References

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