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Fabrication of Hierarchical Composite Microspheres of Copper-doped Fe_3O_4@P4VP@ZIF-8 and Their Aerobic Oxidation Application

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Table S1 Surface elements percentage by ICP-AES.

Sample	Cu (wt%)	Zn (wt%)
$CuNO_3$-ZIF-8	20.8	21.8
CH_3COOCu-ZIF-8	1.62	27.3
$CuSO_4$-ZIF-8	8.42	18.5
Cu-FPZ	5.45	13.6
$Cu_3(BTC)_2$	17.6	-
Cu-BDC	15.2	-
Cu-TDPAT	14.1	-

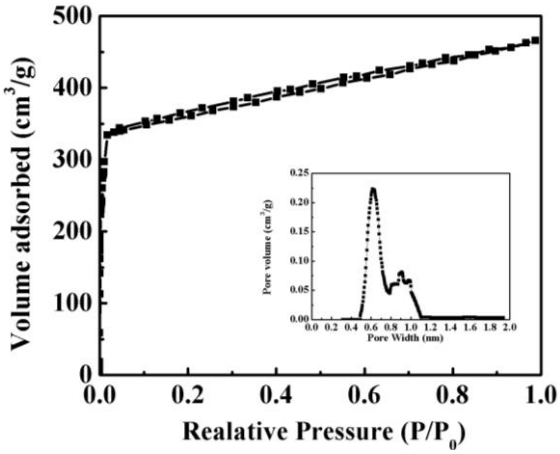


Fig. S1 Nitrogen adsorption–desorption isotherms and the pore size distribution of the pure ZIF-8.

Table S2 Nitrogen adsorption-desorption data for the ZIF-8 and the Cu-FPZ catalyst.

Samples	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_p (cm^3/g)
ZIF-8	1560	0.47	0.72
Cu-FPZ	743	0.23	0.58

S_{BET}, BET surface area; V_{micro}, microporous volume; V_p, total pore volume.

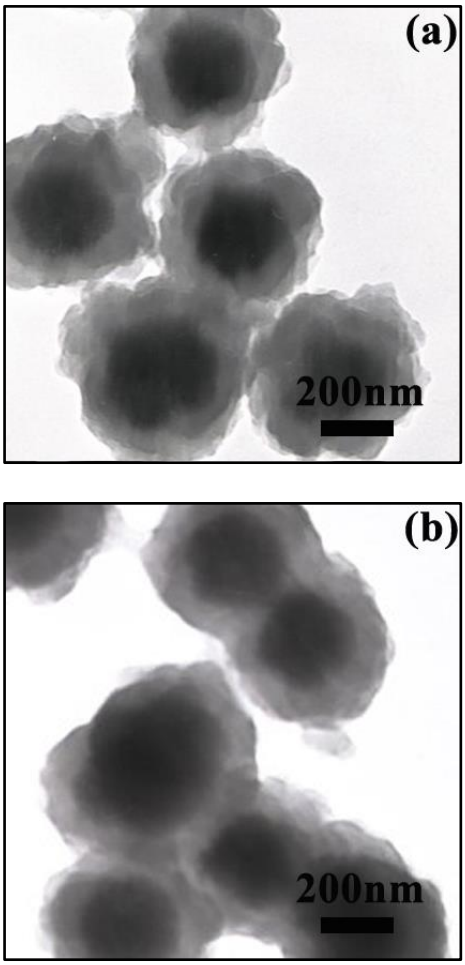


Fig. S2 TEM images of the Fe_3O_4@P4VP@ZIF-8 (FPZ) (a) and the core-shell Cu-FPZ catalyst cycled 15 times (b).

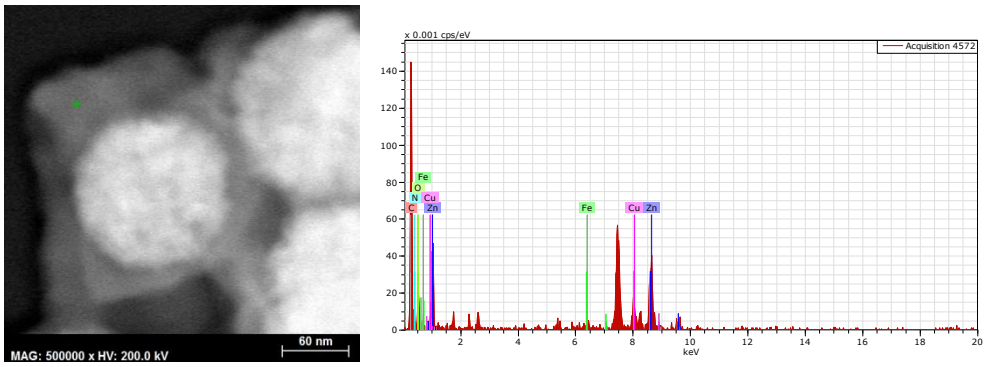


Fig. S3 TEM images (left) and EDS specrta (right) of the Cu-FPZ catalyst.

Table S3. EDS elemental composition of Cu-FPZ.

Element	C(K)	Zn(K)	Cu(L)	O(K)	N(K)	Fe(K)
Weight %	58.79	23.87	8.83	4.95	2.82	0.74
Atomic %	82.65	6.16	2.35	5.22	3.40	0.27

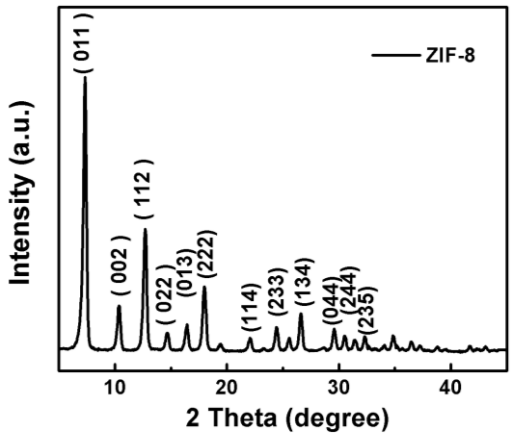


Fig. S4 PXRD patterns of the pure ZIF-8.

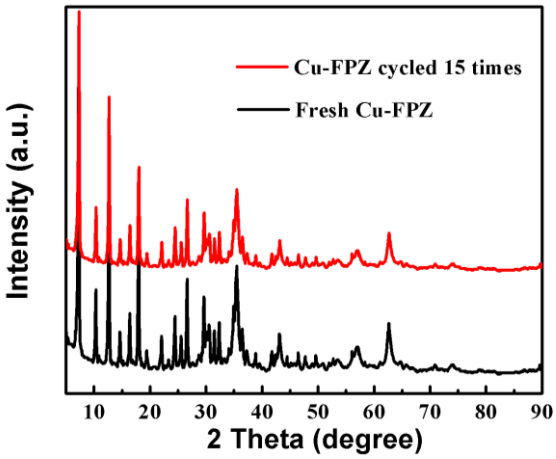


Fig. S5 PXRD patterns of the fresh Cu-FPZ catalyst and the Cu-FPZ catalyst cycled 15 times.

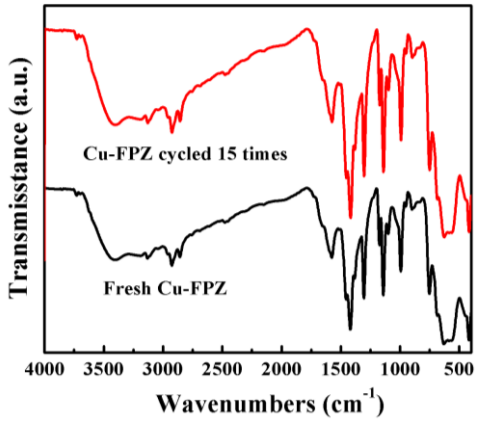


Fig. S6 FT-IR spectra of the fresh Cu-FPZ catalyst and the Cu-FPZ catalyst cycled 15 times.

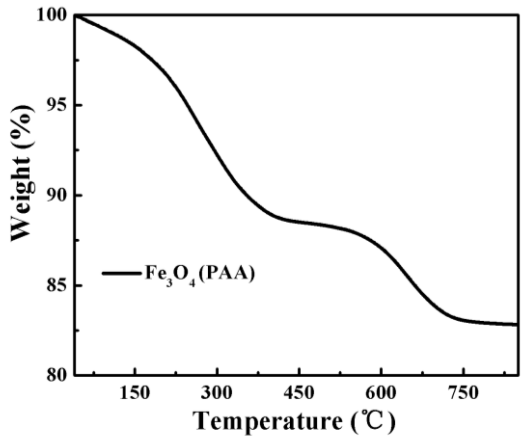


Fig. S7 TG spectra of the Fe_3O_4(PAA)

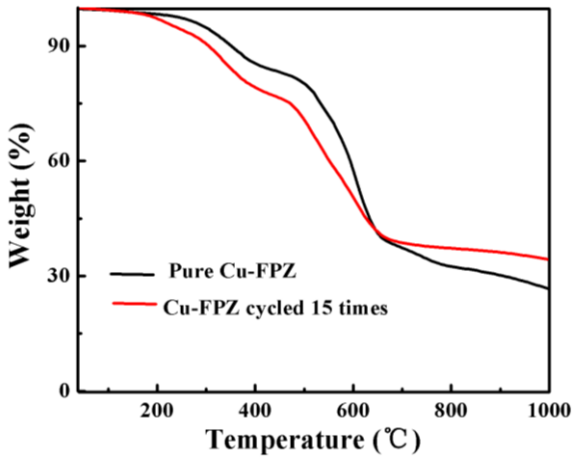


Fig. S8 TG spectra of the fresh Cu-FPZ catalyst and the Cu-FPZ catalyst cycled 15 times.

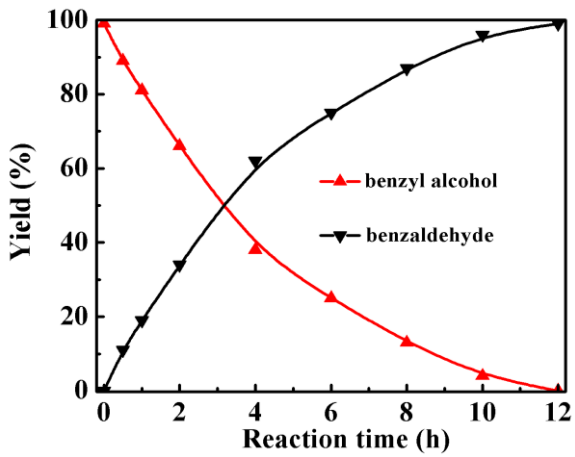


Fig. S9 Yields vs time employing the Cu-FPZ catalyst for the aerobic oxidation of benzyl alcohol.

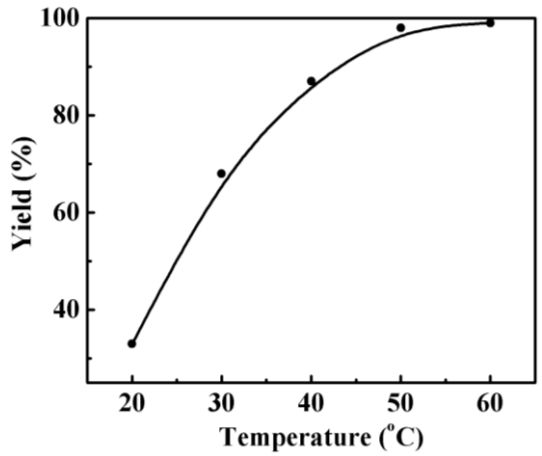


Fig. S10 Yields vs temperature employing the Cu-FPZ catalyst for the aerobic oxidation of benzyl alcohol.

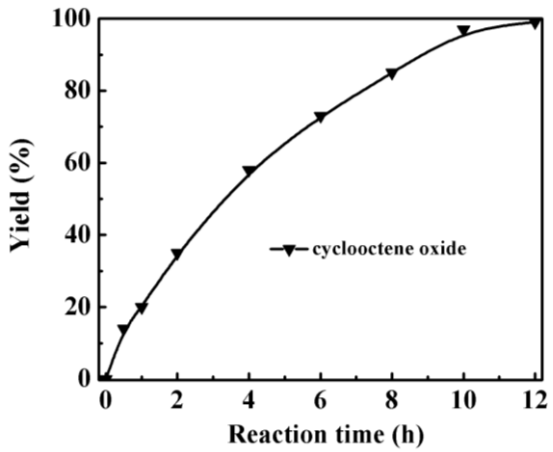
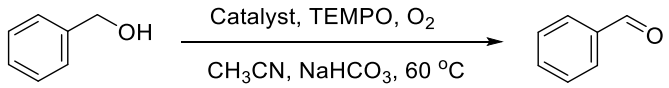


Fig. S11 Yields vs time employing the Cu-FPZ catalyst for the aerobic oxidation of cyclooctene

Table S4 Optimization of selective aerobic oxidation of benzyl alcohol [a]

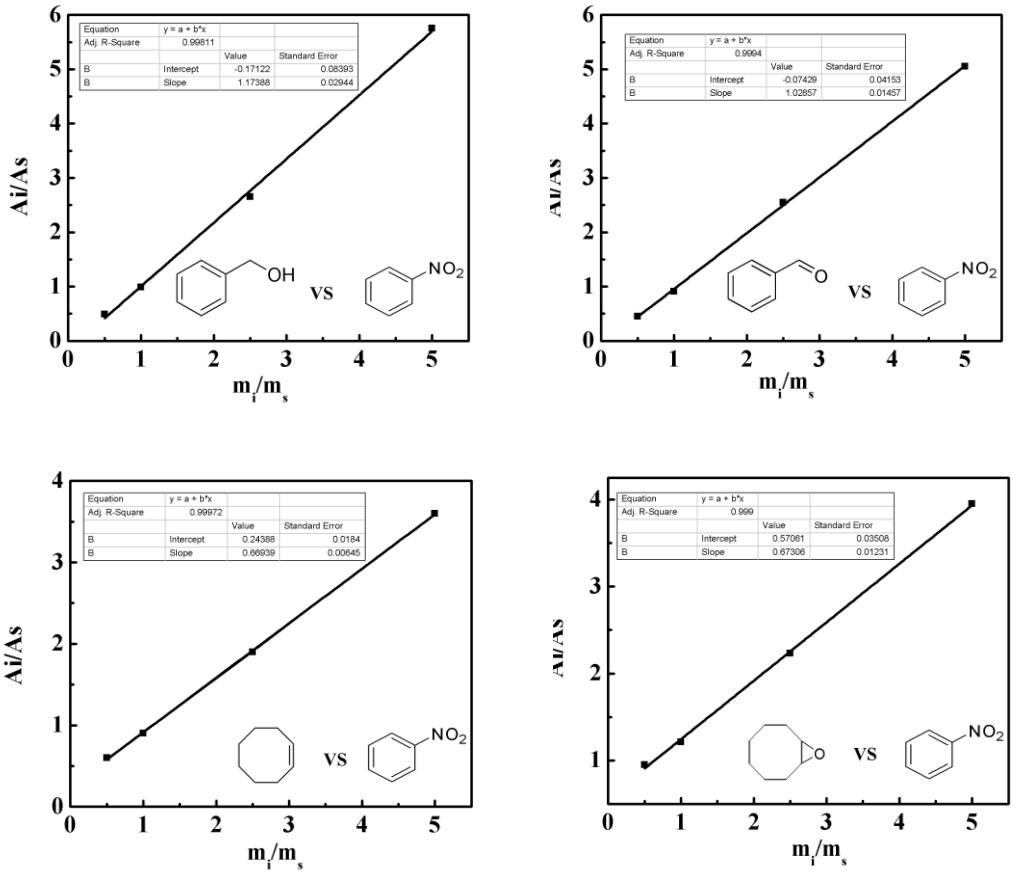


Entry	Catalyst	Solvent	Base	Conv. [b] (%)	Sel. [b] (%)	TON	TOF (h^{-1})
1	$CuNO_3$-ZIF-8	CH_3CN	$NaHCO_3$	63	99	63	5.25
2	CH_3COOCu-ZIF-8	CH_3CN	$NaHCO_3$	17	99	17	1.42
3	$CuSO_4$-ZIF-8	CH_3CN	$NaHCO_3$	79	99	79	6.58
4	$Cu_3(BTC)_2$ [1]	CH_3CN	$NaHCO_3$	16	99	16	0.29
5	Cu-BDC [2]	CH_3CN	$NaHCO_3$	18	99	18	1.50
6	Cu-TDPAT [3]	CH_3CN	$NaHCO_3$	12	99	12	1.00
7	Cu-FPZ [c]	CH_3CN	$NaHCO_3$	99	99	99	8.25
8 [d]	Cu-FPZ	CH_3CN	$NaHCO_3$	5.2	99	208	208

[a] Reaction conditions: benzyl alcohol (0.5 mmol), 1 mol% catalyst based on copper, solvent (2.5 mL), base, TEMPO (0.25 mmol), 60 °C for 12 h under 1 atm O_2. [c] Copper doped Fe_3O_4@P4VP@ZIF-8. [d] benzyl alcohol (20 mmol), 0.005 mmol catalyst, solvent (25 mL), base, TEMPO (0.25 mmol), 60 °C for 1 h under 1 atm O_2.

[b] Determined by GC-MS using nitrobenzene as the internal standard.

Fig. S12 Compound vs. nitrobenzene internal standard for GC analysis.



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