Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

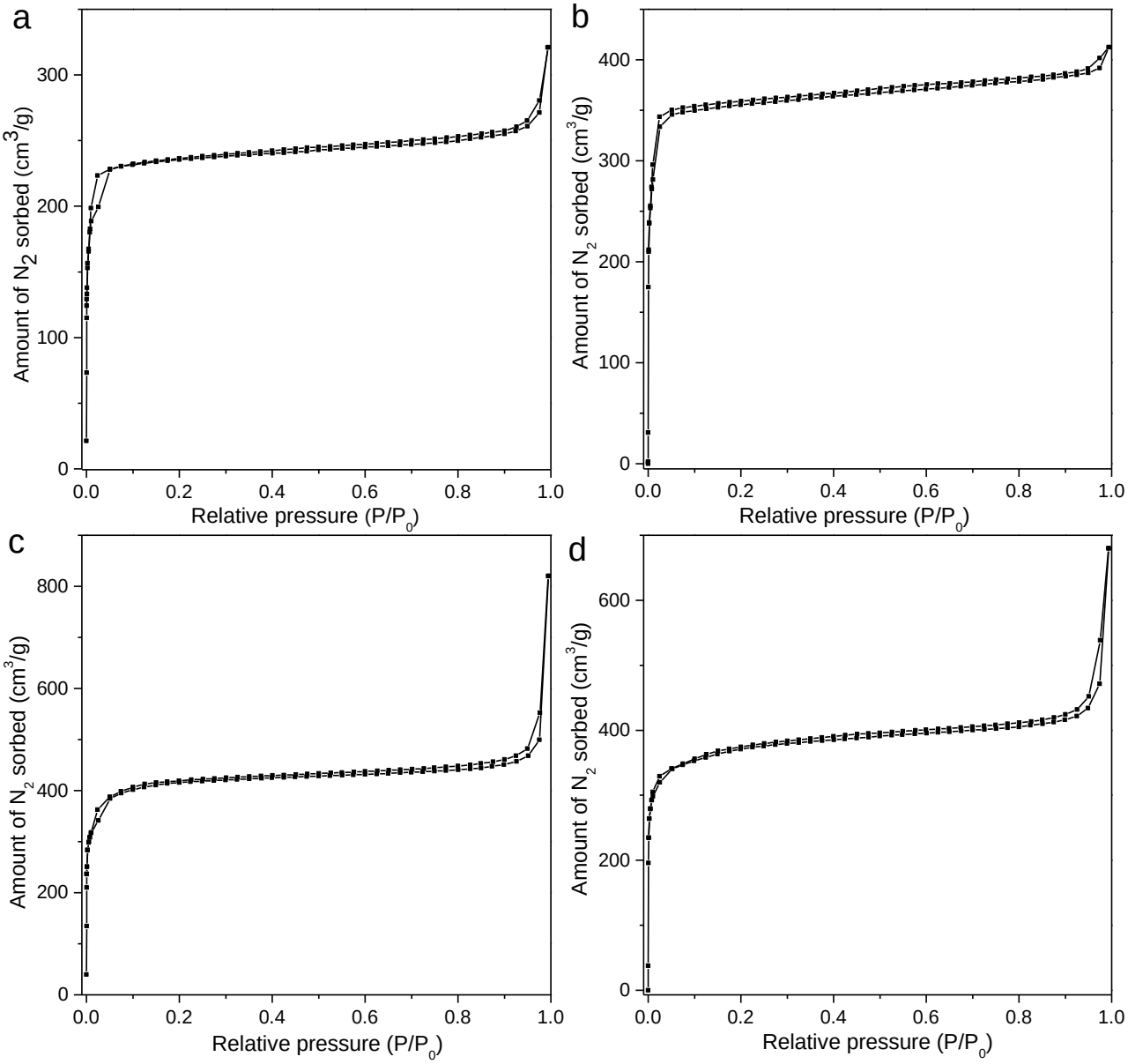

Figure S1 N_2 adsorption/desorption curves at 77 K for Cu/ZIF-8 crystals doped with (a) 0%, (b) 25%, (c) 55%, (d) 85%Cu.

Table S1 Comparison of BET surface area, pore size and pore volume for ZIF-8 and Cu doped ZIF-8 nanocrystals

Materials	Surface area(m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
ZIF-8	1751	0.97	1.30
Cu25%ZIF-8	1618	0.92	1.27
Cu55%ZIF-8	1445	0.74	1.23
Cu85%ZIF-8	1322	0.74	1.15

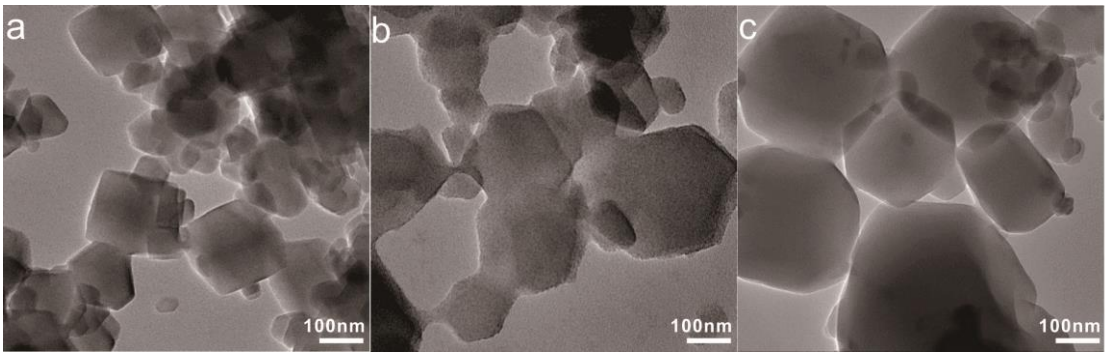

Figure S2 TEM images of Cu ion doped ZIF-8 nanocrystals with different doping percentage of Cu (a) 25%, (b) 55%, (c) 85%.

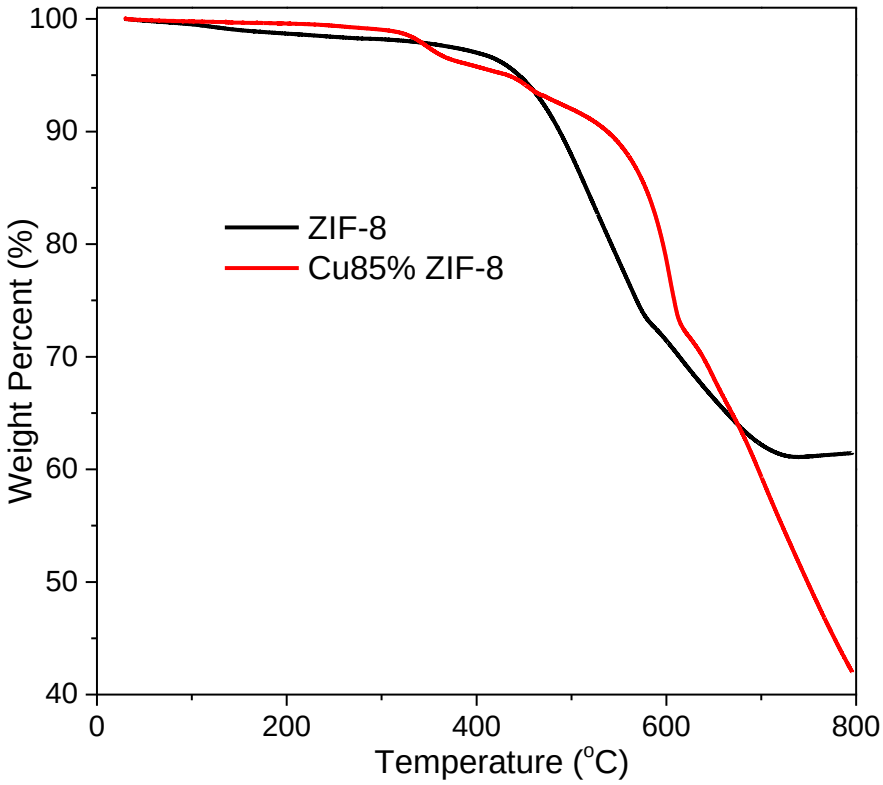

Figure S3 TG plots of Cu85%ZIF-8 nanocrystals and ZIF-8 nanocrystals.

Table S2 Anisotropic parameters deduced from EPR spectra of Cu ion doped ZIF-8 nanocrystals

Sample	**g⊥**	**g||**
Cu25%ZIF-8	2.082	2.310
Cu55%ZIF-8	2.095	2.316
Cu85%ZIF-8	2.095	2.321

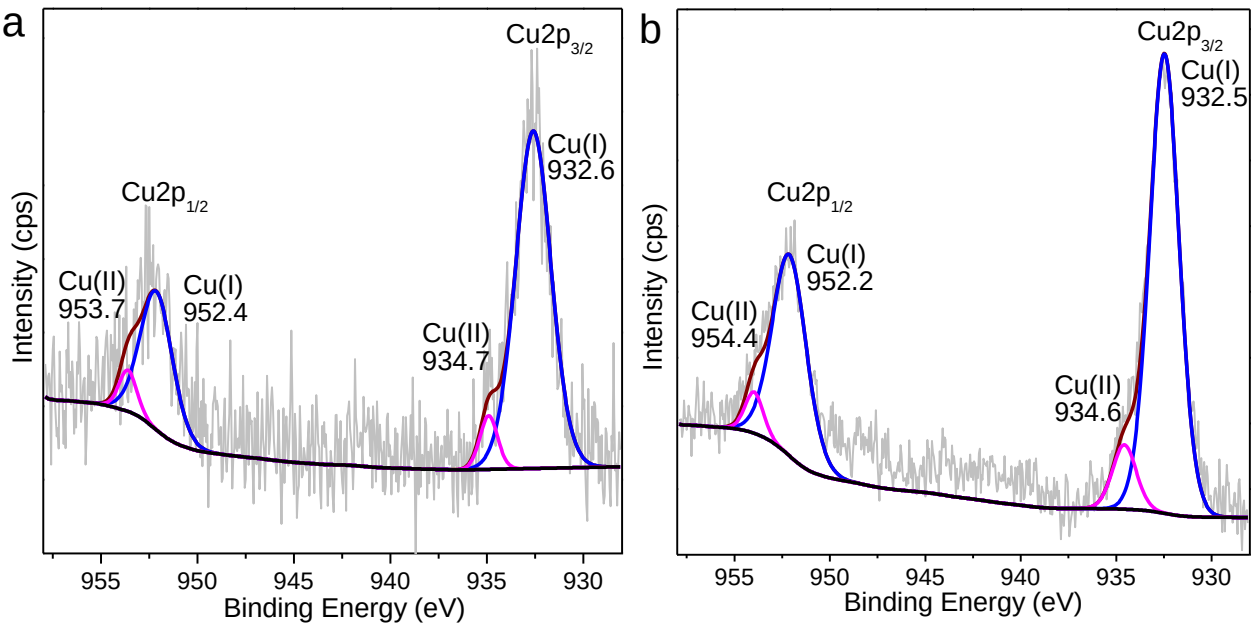

Figure S4 Cu 2p XPS spectrum for (a) Cu25%ZIF-8 and (b) Cu55%ZIF-8. (gray line: raw data; wine line: fitted peak plot; blue line: fitted Cu(I) peak plot; magenta line: fitted Cu(II) peak plot and black line: background).

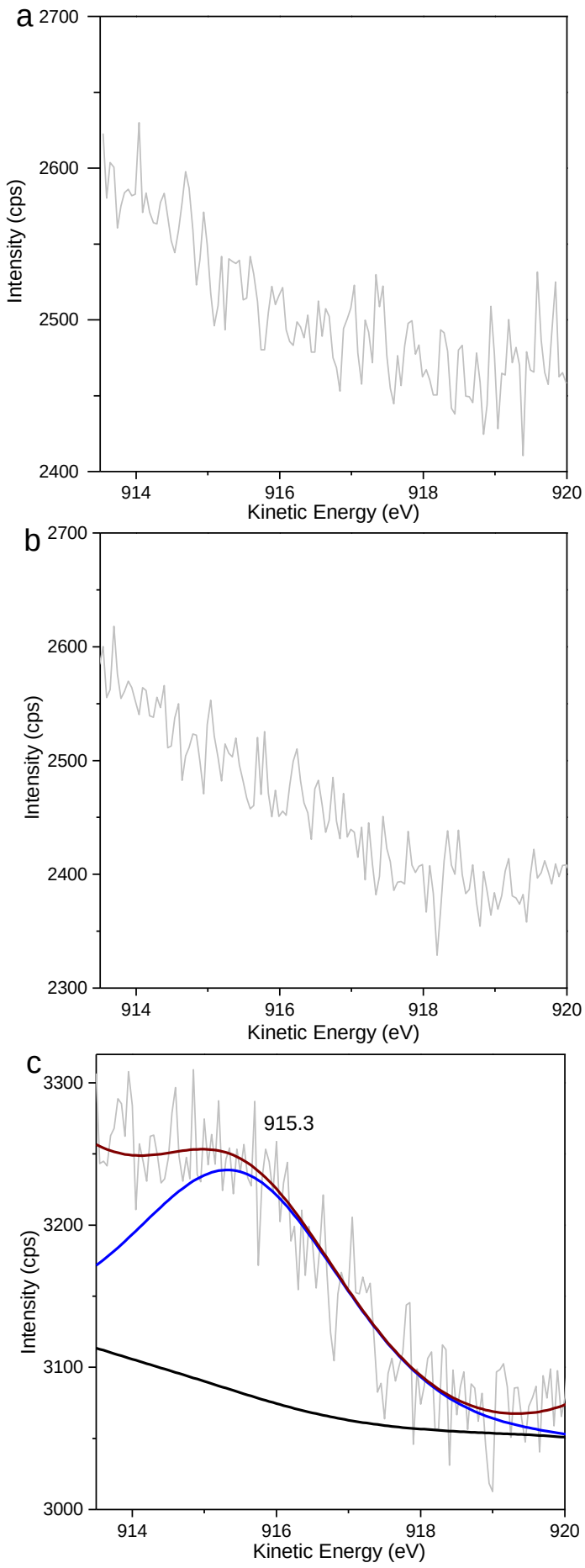

Figure S5 Cu LMM Auger spectrums of Cu ion doped ZIF-8 nanocrystals with different Cu doping percentage (a)25%, (b)55%, (c) 85%. (gray line: raw data; wine line: fitted peak plot; blue line: fitted Cu(I) peak plot and black line: background)

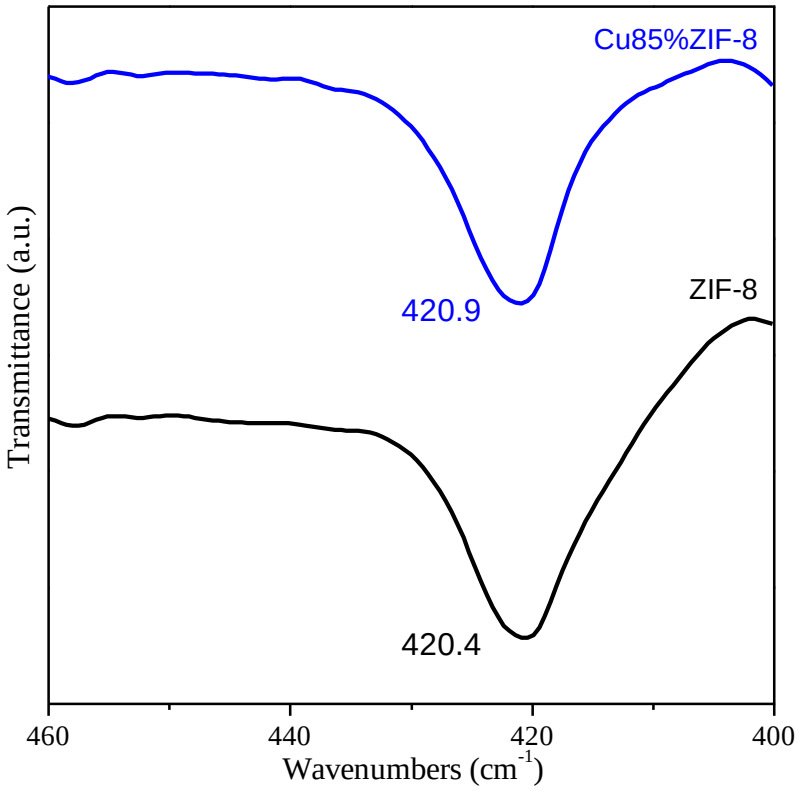

Figure S6 FT-IR spectra of ZIF-8 and Cu85%ZIF-8.

Table S3 Control experiments for dehydrogenative coupling of $PhMe_2SiH$ and n-butanol[a]

Entry	Catalyst	Time /h	Conv.[b] /%	Sel.[b] /%
1	blank[c]	14	1.0	100
2	ZIF-8[d]	14	4.4	100

[a] Reaction condition: $PhMe_2SiH$ (1.0 mmol), 2 mL of n-butanol, 70 °C. [b] Conversion of $PhMe_2SiH$ determined by GC analysis using anisole as the internal standard and the product was siloxane. [c] Without catalyst. [d] 50 mg ZIF-8 nanocrystals.

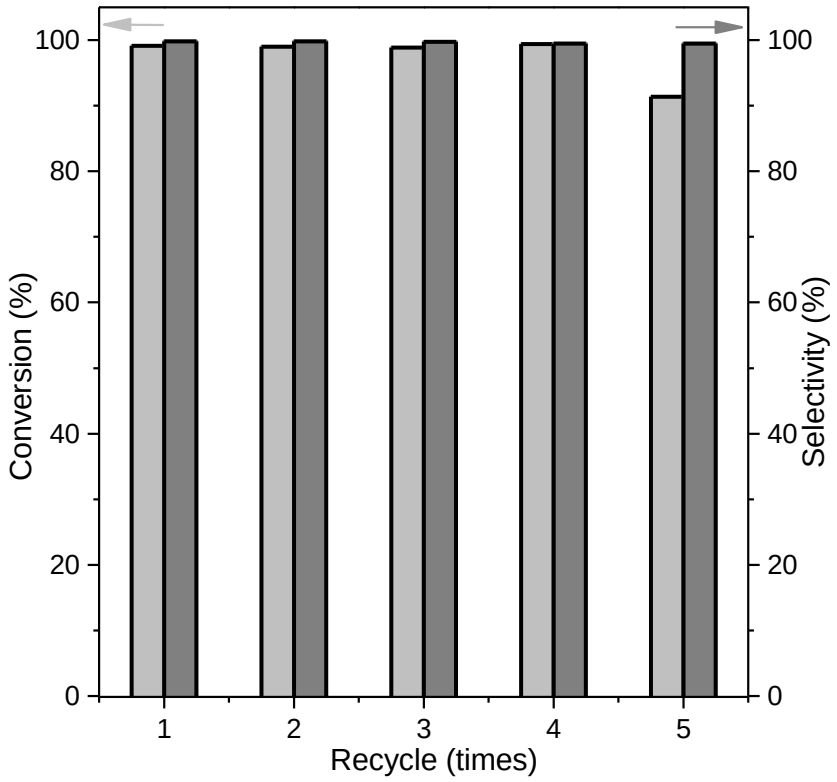

Figure S7 Reusability of Cu85%ZIF-8 nanocrystals for dehydrogenative coupling of $PhMe_2SiH$ with n-butanol. Reaction condition: $PhMe_2SiH$ (1.0 mmol), 2 mL of n-butyl alcohol, 50 mg Cu85%ZIF-8 nanocrystals at 70 ^oC for 14 h.

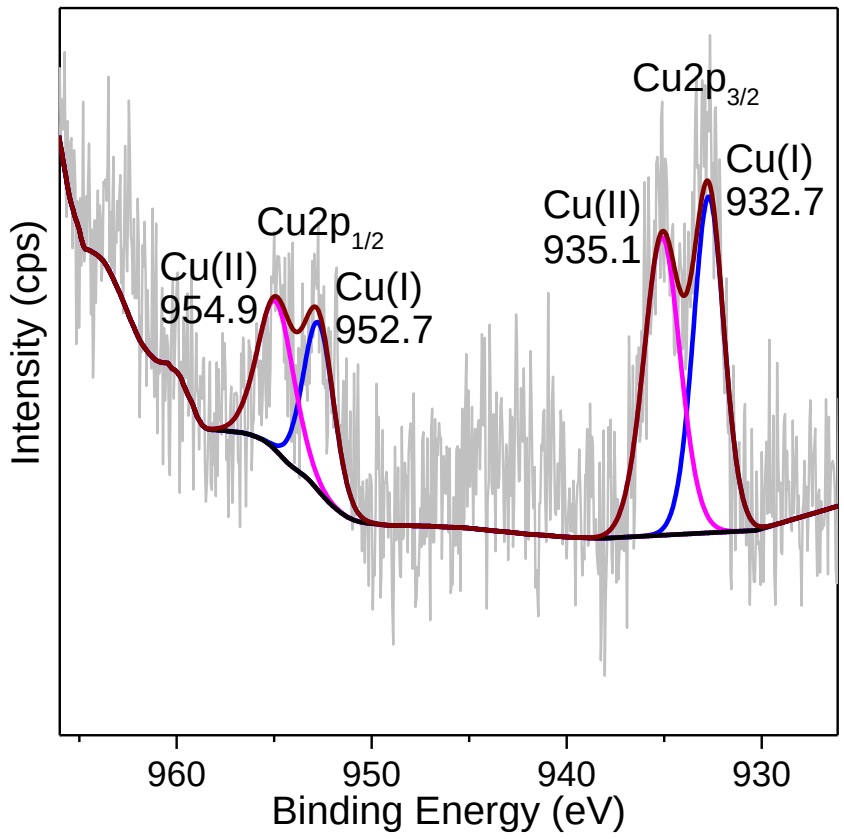

Figure S8 Cu 2p XPS spectrum of Cu85%ZIF-8 after five cycles reaction. (gray line: raw data; wine line: fitted peak plot; blue line: fitted Cu(I) peak plot; magenta line: fitted Cu(II) peak plot and black line: background).

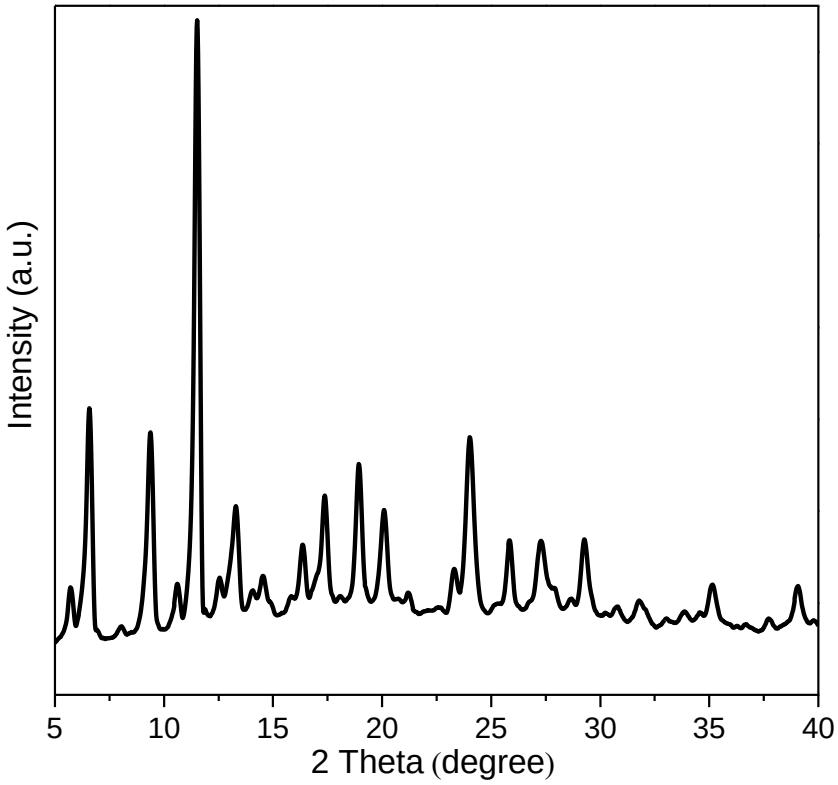

Figure S9 XRD pattern of HKUST-1.

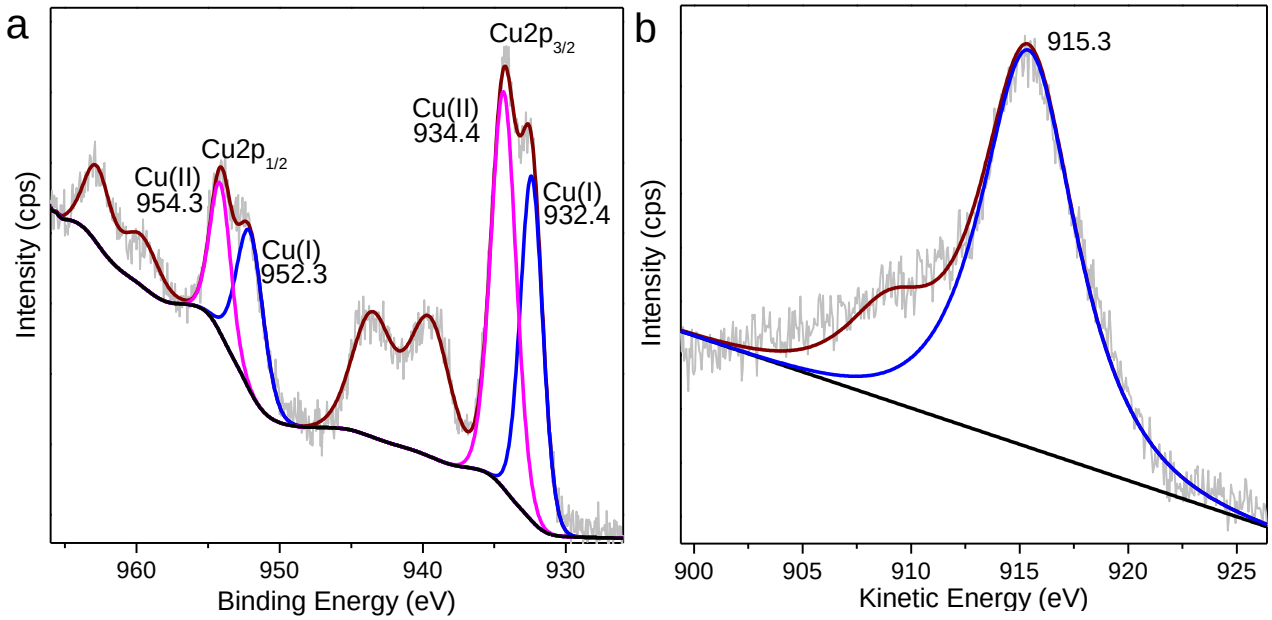

Figure S10 (a) Cu 2p XPS spectrum for HKUST-1 (gray line: raw data; wine line: fitted peak plot; blue line: fitted Cu(I) peak plot; magenta line: fitted Cu(II) peak plot and black line: background). (b) LMM Auger spectrum of HKUST-1. The peak at 915.3 eV was assigned to Cu(I).

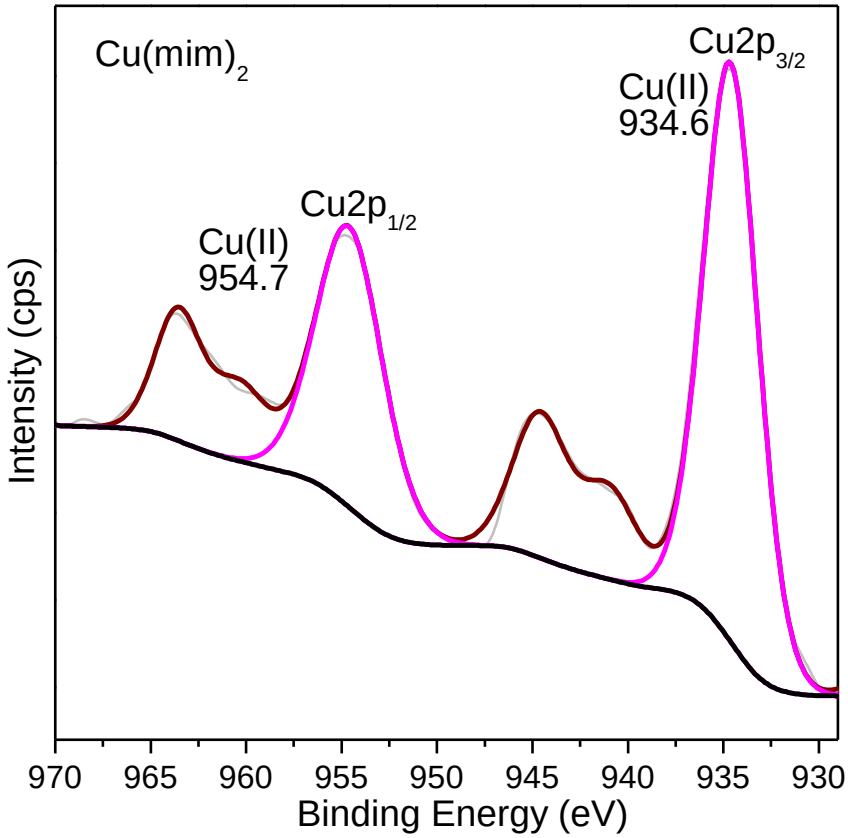

Figure S11 Cu 2p XPS spectrum for Cu(2-MeIm)$_2$ (gray line: raw data; wine line: fitted peak plot; magenta line: fitted Cu(II) peak plot and black line: background).

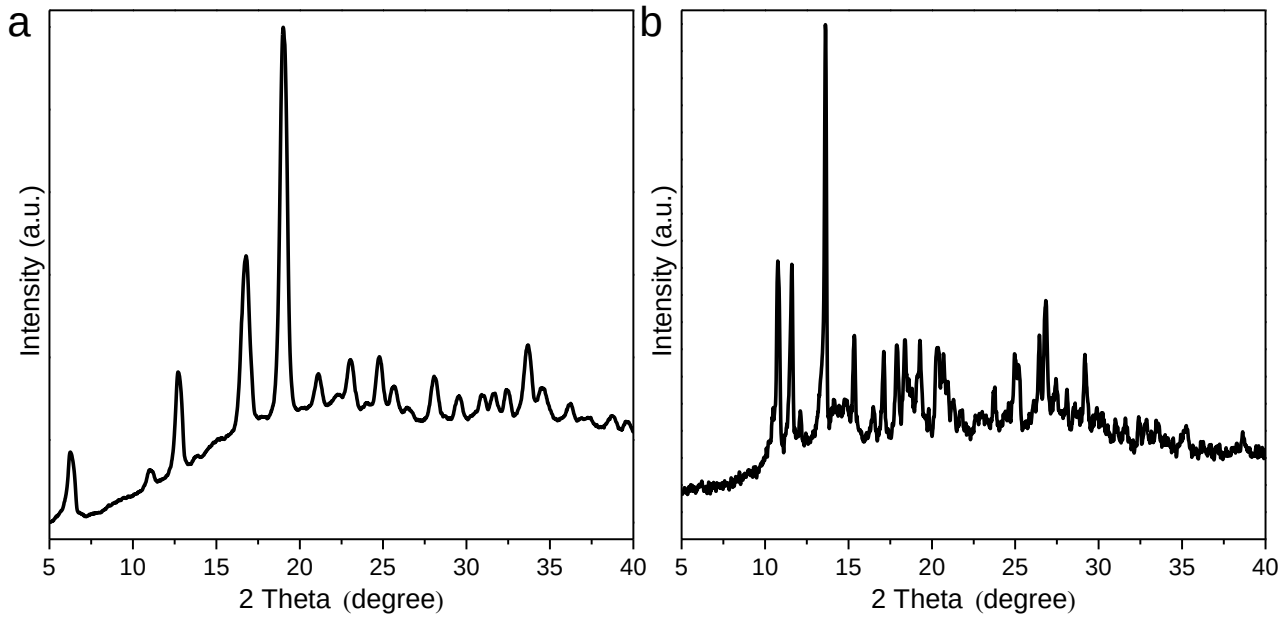

Figure S12 XRD patterns of (a) Cu(Im)$_2$ and (b) Cu(2-MeIm)$_2$.

Table S4 The dehydrogenative coupling of silanes with alcohols over different catalysts

Catalyst	T /°C	Time /h	Conv. /%	Sel.[e] /%	TOF[f] /h^{-1}	n (S:C)[g]	Atmo-sphere	Reference
Cu85%ZIF-8[a]	70	14	100	100	34.9	25	air	This work
HKUST-1[a]	70	0.25	100	100	20	3.7	Ar	Chem. Commun., 2016, 52, 2725
Cu-(B)G[a]	100	48	>99	>99	-	200	Ar	Angew. Chem. Int. Ed., 2014, 53, 12581.
oriented (2.0.0) Cu_2O/fl-G[a]	110	-	-	-	22700	451729	Ar	Nat. Commun., 2015, 6, 8561.
Co SAs/2D N–C[b]	R.T.	2	100	100	3858	7851	Ar	Chem. Commun., 2019, 55, 6563
Au/HAP_{nano}[a]	25	1	>99	>99	-	667	air	Chem. Eur. J., 2013,19, 14398.
Au-SiO_2[a]	50	5	>99	>99	97	500	air	Rsc Advances, 2016, 6, 102102.
1.0 wt % Pd/XC-72-700-Ar[c]	25	0.05	>99	>99	208100	10000	air	ACS. Catal., 2017, 7, 1720.
HPNSC[a,d]	120	16	100	99.6	-	-	air	Chem. Commun., 2017, 53, 13019.

The corresponding substrates were as follow: [a] $HSiMe_2Ph$ and n-butanol, [b] $HSiMe_2Ph$ and ethanol, [c] $HSiEt_3$ and n-butanol. [d] HPNSC was hierarchically porous N and S co-doped carbon, [e] The selectivity for siloxane, [f] TOF was based on total metal atoms, [g] n (S:C) was n (substrate: moles of metal in catalyst).

Table S5 Surface ratio of Cu(I) to Cu(II) calculated based on the XPS spectrums

Sample	Cu(I):Cu(II)
Cu25%ZIF-8	93: 7
Cu55%ZIF-8	90:10
Cu85%ZIF-8	92: 8
HKUST-1	31:69