Supporting Information for

The Dynamics of Copper-Containing Porous Organic Framework Catalysts Reveal Catalytic Behavior Controlled by Polymer Structure

Zhenwei Wu[†], Xu Zhang^{†,‡}, Emmett D. Goodman[†], Weixin Huang[†], Andrew Riscoe[†], Sara Yacob[⊥], Matteo Cargnello^{†,*}

[†]Department of Chemical Engineering and SUNCAT Center for Interface Science and Catalysis, Stanford University, Stanford, California 94305, United States [‡]School of Materials Science and Engineering, Tsinghua University, Beijing 10084, China [⊥]ExxonMobil Research and Engineering, Annandale, New Jersey 08801, United States

*Corresponding author: <u>mcargnello@stanford.edu</u>



Fig. S1. The FTIR spectra of the aldehyde and amine monomers used in the IPOF syntheses.



Fig. S2. N₂ physisorption isotherm of IPOF-tr-te (1) and IPOF-ph-py (2).



Fig. S3. a) TEM electron diffraction imaging and pattern of Cu-1_Air, and b) TEM image of Cu-2_Air.



Fig. S4. TEM images (a, b) and EDS analysis (c, d) of samples $Cu-1_N_2$ and $Cu-2_N_2$, respectively.



Fig. S5. CO oxidation reaction rate versus time on stream for Cu-1_N₂ and Cu-1_Air with a reaction mixture containing $CO:O_2 = 1$ for 12 hours.



Fig. S6. The real part and magnitude of Fourier transform of k^2 weighted chi(k) of EXAFS of the Cu-1_Air, Cu-1_N₂, Cu-2_Air, Cu-2_N₂.

Cu-2_Air







Cu-1_Air



Fig. S7. k^2 weighted chi(k) of *in situ* EXAFS of the Cu-IPOF catalysts measured at room temperature in air, 200 °C in H₂ after reduction for 1 hour, 200 °C in CO and O₂ (1:1).



Fig. S8. The real part and magnitude of Fourier transform of k^2 weighted chi(k) of *in situ* EXAFS of the Cu-**1**_Air catalysts measured at room temperature in air, 200 °C in H₂ after reduction for 1 hour, 200 °C in CO and O₂ (1:1) and corresponding fits.



Fig. S9. a) magnitude of the Fourier transform of k^2 -weighted Cu K edge EXAFS spectra of Cu-1_N₂ measured at room temperature in air, 200 °C in H₂ after reduction for 1 hour, 200 °C in CO and O₂ (1:1) right after the reaction starts and 200 °C in CO and O₂ after 4 hours, b) the same spectra for Cu-2_N₂; c) Cu K edge XANES spectra and d) magnitude of the Fourier transform of k^2 -weighted Cu K edge EXAFS spectra of Cu-2_Air measured at room temperature in air, 200 °C in H₂ after reduction for 1 hour, 200 °C in CO and O₂ (1:1) right after the reaction starts and 200 °C in CO and O₂ after 4 hours.



Fig. S10. Imaginary part of the Fourier transform of k^2 weighted chi(k) of *in situ* EXAFS of the Cu-2_N₂ catalysts measured at room temperature in air, 200 °C in H₂ after reduction for 1 hour, 200 °C in CO and O₂ (1:1).

Sample	C (*)	Ν	0 (*)	Cu	Cl
IPOF-tr-te (1)	91	6.2	3.0	-	-
Cu-1_N ₂	81	5.4	4.8	3.6	3.6
Cu-1_Air	70	2.5	14	7.4	2.5
IPOF-ph-py (2)	85	12	3.1	-	-
Cu- 2 _N ₂	76	15	4.4	2.4	1.9
Cu-2_Air	71	8.3	9.1	5.2	4.9

Table S1. Surface elemental composition in mol. % measured from XPS survey scan.

* The carbon surface concentration includes adventitious carbon. The oxygen surface concentration is significantly higher than the bulk concentration due to terminal aldehyde groups on the IPOF or also formation of oxidized copper nanoparticles.

Table S2. The catalyst Cu weight loading determined by ICP and the corresponding Cu: N molar ratio.

Sample	Cu (wt. %)	Cu:N
Cu-1_N ₂	18.2	0.30
Cu-1_Air	27.6	0.54
Cu- 2 _N ₂	9.7	0.06
Cu-2_Air	32.1	0.27

Catalyst	Scattering Pair	\mathbf{S}_0^2	CN	R (Å)	$\Delta E_0 (eV)$	$\sigma^2({\rm \AA}^2)$
Cu-1_Air	Cu-O	0.85 *	3.6 ± 0.6	1.98 ± 0.02	2.6 ± 1.4	0.006 ± 0.003
Cu-2_Air	Cu-O	0.85 *	3.0 ± 0.3	1.99 ± 0.01	3.1±1.3	0.007 ± 0.002
Cu-1_N ₂	Cu-N	0.85 *	0.8 ± 0.2	1.98 ± 0.03	8.1±2.9	0.008 ± 0.002
	Cu-Cl		1.9 ± 0.4	2.27 ± 0.02	-3.2 ± 1.1	0.008 ± 0.003
Cu- 2 _N ₂	Cu-N	0.85 *	2.3 ± 0.6	2.02 ± 0.04	7.7 ± 2.4	0.009 ± 0.004
	Cu-Cl		0.8 ± 0.2	2.24 ± 0.02	-2.7 ± 0.8	0.006 ± 0.002

 Table S3. EXAFS fitting results of the fresh catalysts.

* The amplitude reduction factor S_0^2 is fixed at the value (0.85) obtained by fitting the Cu metal foil.

Condition	Scattering Pair	S_0^2	CN	R (Å) #	$\Delta E_0 (eV) \#$	σ^2 (Å ²) #
RT He	Cu-O	0.85 *	3.6 ± 0.6	1.98 ± 0.02	2.6 ± 1.4	0.006 ± 0.003
200 °C H ₂	Cu-O	0.85 *	0.8 ± 0.2	1.98 ± 0.04	7.9 ± 4.5	0.005 ± 0.002
	Cu-Cu		3.4 ± 0.7	2.51 ± 0.02	-3.0 ± 3.2	0.012 ± 0.002
$\begin{array}{c} 200 \ ^{\circ}\text{C} \\ \text{CO} + \text{O}_2 \ \text{Oh} \end{array}$	Cu-N/O	0.85 *	2.0 ± 0.3	1.97 ± 0.02	7.0 ± 1.6	0.008 ± 0.003
200 °C $CO + O_2 4h$	Cu-N/O	0.85 *	2.4 ± 0.3	1.99 ± 0.01	7.8 ± 1.3	0.006 ± 0.002

 Table S4. In situ EXAFS fitting results for Cu-1_Air.

* The amplitude reduction factor S_0^2 is fixed at the value (0.85) obtained by fitting the Cu metal foil.