

Supporting Information

One “Click” to Controlled Bifunctional Supported Catalysts for the Cu/TEMPO-Catalyzed Aerobic Oxidation of Alcohols

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Reagents were obtained from commercial sources and used without further purification. All reactions were carried out under N₂. Spherical silica gel (40-75 μm, 100 Å) was purchased from Sorbtech Technologies. Milli-Q water (resistivity 18.2 MΩ.cm) was obtained from a Millipore system (Elga Purelab Ultra). FT-IR was measured on a Thermo Scientific FTIR 6700 spectrometer. TGA was measured on a TA Q5000 instrument. Physisorption measurements were done on a Quantachrome Autosorb-iQ system. AAS was performed on a Agilent 200 Series AA spectrometer equipped with a GTA 120 graphite tube atomizer. Prior to AAS analysis, the samples were treated with ultrapure aqua regia (3:1 concentrated HCl:HNO₃) and the resulting solution diluted 500 times before analysis. **(Caution! Aqua regia is a very corrosive oxidizing agent, which should be handled with great care).** NMR spectra were recorded on a Bruker-400 spectrometer. XPS was performed on a Physical Electronics Phi5000 Versaprobe II instrument. EPR spectra were obtained using a Bruker EMX spectrometer. GC was performed on a Hewlett Packard HP 6890 Series equipped with a FID and MS detector.

Synthetic procedure

Preparation of azide-functionalized silica 1

Commercially available spherical silica gel (Sorbtech Technologies, 40-75 μm , 100 \AA) was activated by boiling in HCl 6 M for 1 day. The silica was filtered and washed with deionized water until neutral pH and dried in oven for 2 days at 120 $^{\circ}\text{C}$. The resulting silica was then placed in a round-bottom flask and heated at 120 $^{\circ}\text{C}$ under vacuum for 2 hours. The flask was then allowed to cool to room temperature and toluene (20 mL/g) was added together with AzPTMS¹ (2 mmol/g) and the resulting mixture refluxed overnight. The silica was then filtered, washed with toluene, CH_2Cl_2 and finally extracted using a CH_2Cl_2 soxhlet for 1 day. The obtained azide functionalized silica was placed in a round-bottom flask and dried under vacuum at 60 $^{\circ}\text{C}$ overnight. The flask was then cooled with liquid nitrogen and HMDS (1.5 mL/g) was added under vacuum. The resulting mixture was finally heated at 80 $^{\circ}\text{C}$ for 8 hours. The silica was filtered, washed with CH_2Cl_2 and finally extracted using a CH_2Cl_2 soxhlet for 1 day to give **1**.

General procedure for the CuAAC ligation

Azide-functionalized silica **1** was suspended in degassed DMF (15 mL/g). Alkyne(s) (1.4 equiv.) was added followed by Et_3N (5 equiv.) and CuI (10 mol%). The reaction was stirred at 50 $^{\circ}\text{C}$ for 2 days and monitored by FT-IR. The functionalized silica was recovered by filtration, washed with CH_3CN , Na_2EDTA (0.05 M), water, CH_3CN , CH_2Cl_2 and finally extracted using a CH_3CN soxhlet for 1 day.

General procedure for Cu complexation

Pyta-functionalized silica **4** and **6a-e** were suspended in a degassed solution of $\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf}$ in CH_3CN (0.02 M, 20 mL/g of silica) and the reaction stirred 1 day at room temperature. The suspension was then filtered and washed thoroughly with CH_2Cl_2 .

Representative procedure for the aerobic oxidation of alcohols

The catalyst was added to a solution of alcohol (0.26 mmol) and dodecane (0.26 mmol) in toluene (0.2 M) and heated at 80 $^{\circ}\text{C}$ under O_2 bubbling (5.5 mL/min). Aliquots (10 μL) were periodically taken and analyzed by GC.

FT-IR

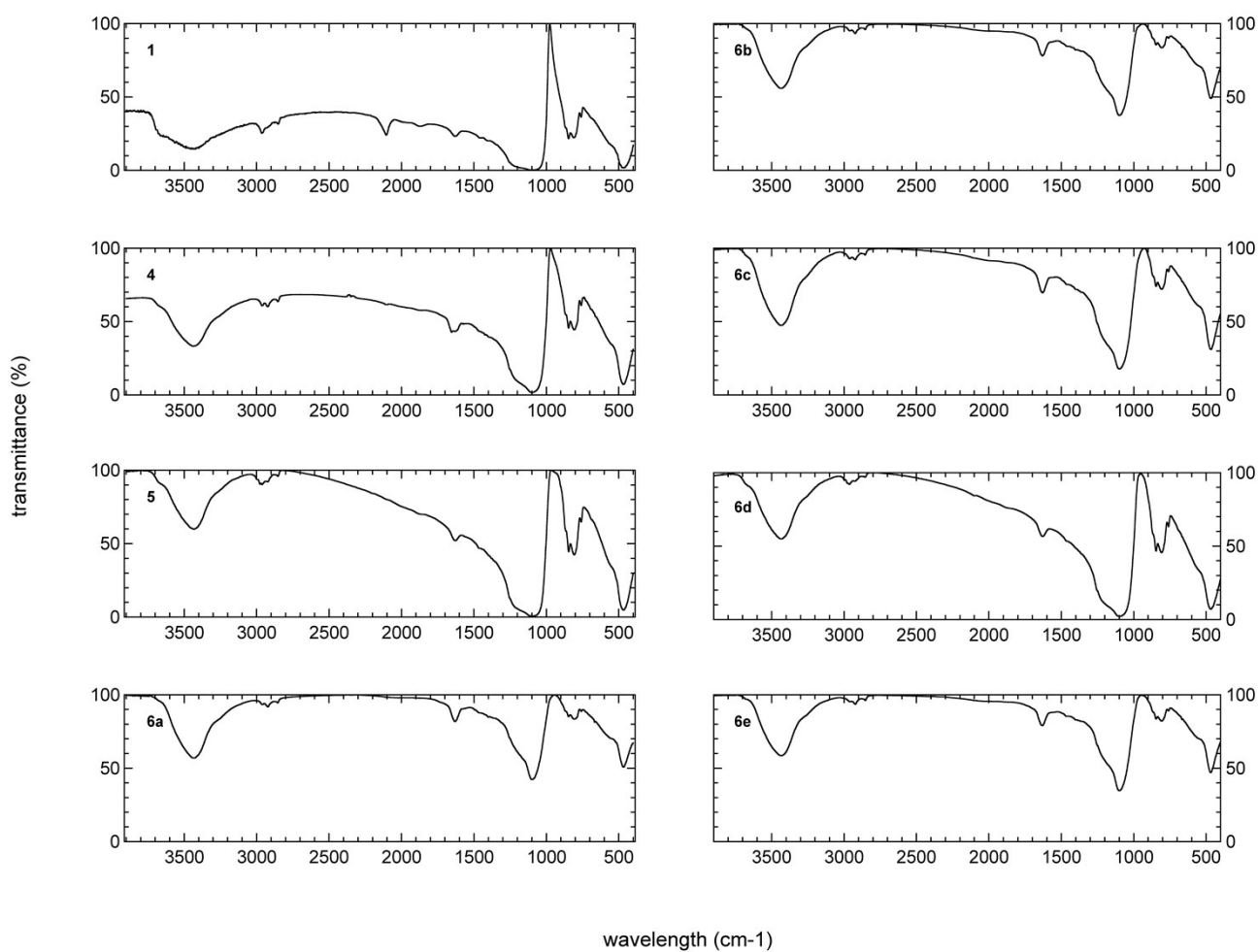


Figure S1. FT-IR spectra of **1**, **4**, **5** and **6a-e**.

TGA

Thermogravimetric analysis was done at a temperature ramp rate of 10 °C/min under N₂.

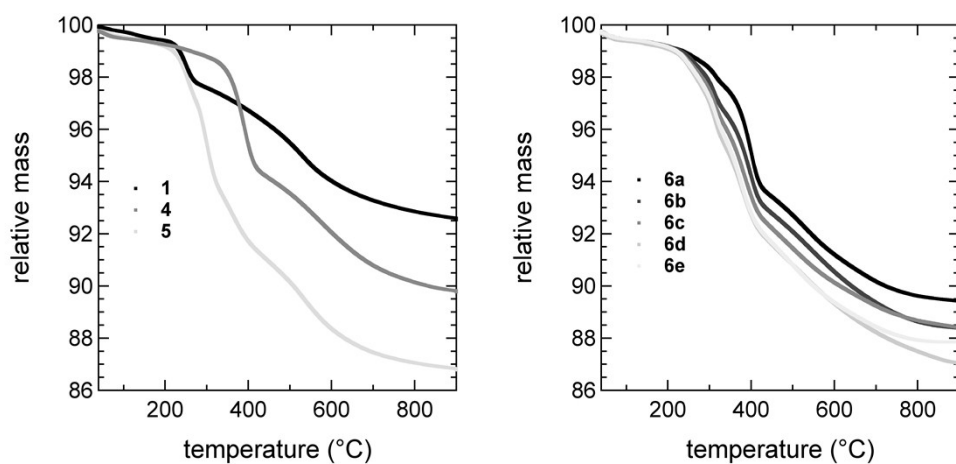


Figure S2. TGA of **1**, **4**, **5** and **6a-e**.

XPS

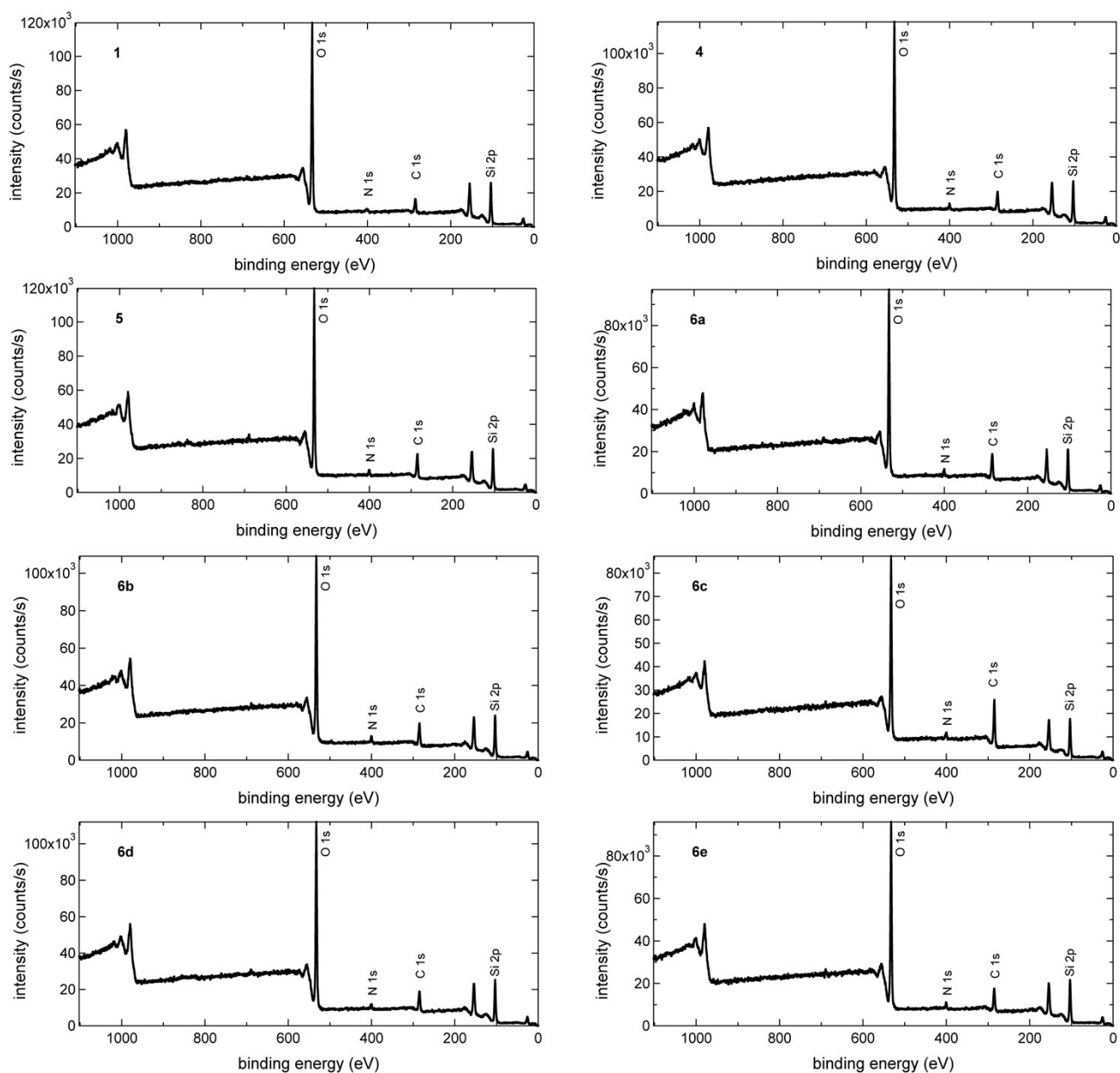


Figure S3. XPS survey scan of 1, 4, 5 and 6a-e.

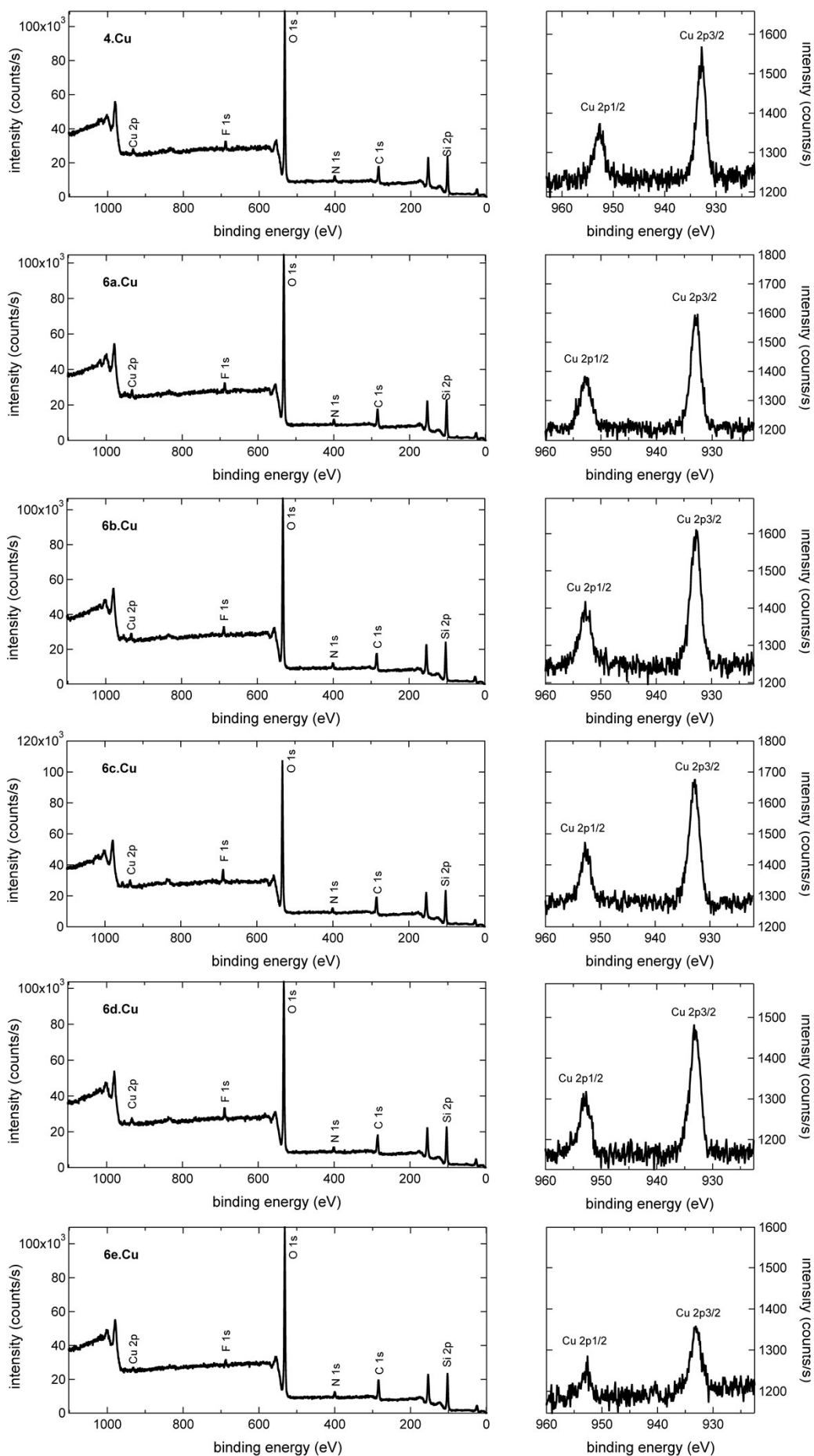


Figure S4. XPS survey scan and Cu 2p HR region of **4.Cu** and **6a-e.Cu**.

Physisorption

Sample	S_{BET} (m ² /g)	Pore volume (BJH, desorption) (cm ³ /g)	Pore diameter (BJH, desorption) (nm)
1	293	0.66	6.80
4	250	0.54	6.26
5	269	0.58	5.76
6a	231	0.53	5.82
6b	238	0.54	5.80
6c	213	0.52	5.42
6d	249	0.54	5.80
6e	222	0.46	6.26

Table S1. Physisorption analysis of **1,4,5** and **6a-e**.

EPR

EPR calibration curve was prepared by mixing TEMPO with pristine mesoporous spherical silica.

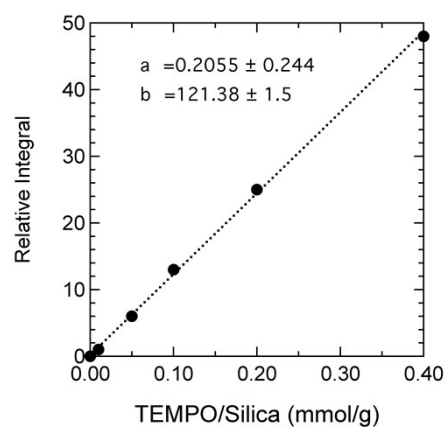


Figure S5. EPR calibration curve of TEMPO/silica.

Catalysis

Catalyst	% of 2	k ($\times 10^{-5} \text{ s}^{-1}$)
6a.Cu	75	1.01
6b.Cu	50	1.92
6c.Cu	25	2.25
6d.Cu	12.5	2.66
6e.Cu	6.25	1.07
4.Cu/TEMPO	-	n.d.
4.Cu + 5	-	n.d.

Table S2. Pseudo-rate constants k . Conditions: BnOH (0.26 mmol), dodecane (0.26 mmol) in toluene (0.2 M), O₂, 80 °C.

Reference

- 1 L. Deiana, L. Ghisu, S. Afewerki, O. Verho, E. V. Johnston, N. Hedin, Z. Bacsik and A. Córdova, *Adv. Synth. Catal.*, 2014, **356**, 2485.