1	Electronic Supplementary Information
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3	Optimization of a heterogeneous Pd-Cu/zeolite Y Wacker catalyst
4	for ethylene oxidation
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1 Supplementary Methods

2 Catalyst preparation and characterization. Sodium ions in zeolite Y ($SiO_2/Al_2O_3 = 5.1$, 3 Zeolyst International) were exchanged with 0.01 M solution of Cu(NO₃)₂·3H₂O (>99%, Sigma-Aldrich) at room temperature with a solid/liquid ratio of 1 g/L, mixed continuously for 4 24 hr. Removal of nitrate ions were done by washing with deionized water. The remaining 5 sodium ions were then exchanged with a Pd(NH₃)₄(CH₃COO)₂ (>99%, Alfa-Aesar) precursor, 6 7 denoted with Pd(a)Cu(b)-Y label (a,b=wt%). All samples were washed with deionized water 8 to remove the acetate ions; filtered; and dried at 373 K overnight. The dried zeolite powder was 9 then pelletized, crushed and sieved to fractions between 100-150 µm.

Catalytic performance test. Wacker oxidation of ethylene was carried out in a quartz tube 10 (internal diameter=6 mm) fixed bed plug flow reactor using CATLAB (Hiden Analytical) with 11 standard operating conditions of 378 K, 1 atm and space-time (W/F₀) of 0.86 kg s mol⁻¹ unless 12 13 stated otherwise. The standard gas feed is composed of 2.3 mol% oxygen, 0.2 mol% ethylene, 1.4 mol% water and 96.1 mol% helium. Water was added to the feed by reacting hydrogen and 14 oxygen using an external home-made reactor bearing a Pt/cordierite catalyst. The gas outlet 15 16 was analyzed by an online gas chromatograph (MicroGC-MS, SRA). All catalysts are pre-17 treated in oxygen at 378 K for 1 hr unless otherwise specified.

18 The kinetics of the reaction was investigated by determining the overall reaction rates under 19 low conversions (<10%) to assume differential reactor conditions so that there will be minimal 20 concentration gradients from entrance to exit of the catalyst bed.

Elemental Analysis. The amount of Cu and Pd were determined via atomic absorption
spectroscopy (AAS, SpectrAA 220FS). Twenty milligrams of the zeolite-supported catalysts
were digested in a solution consisting of 2 mL HF and 3 mL HNO₃, diluted 50 times. The
carbon content of the catalysts was estimated through the combustion products of carbon (CO₂)
by means of infrared spectroscopy (LECO TruSpec Micro).

Surface Area and Pore Volume Determination. The metal-exchanged zeolite samples were
 evacuated at 523 K to less than 0.02 mbar in vacuum prior to N₂ physisorption experiments
 (Micromeritics Tristar II 3020 analyzer) at liquid nitrogen temperature (77 K).

4 In situ XAS. In situ XAS measurements were performed in a custom-made quartz capillary reactor cell with quartz wool on both ends of the catalyst to secure the bed. The reactor was 5 6 heated with two hot air blowers. The controlled gas flows were directed to the reactor with a 7 gas feed consisting of C₂H₄:H₂O:O₂ at a 1:7:10 molar ratio. The quickXAS spectra were collected at the SuperXAS beamline of the Swiss Light Source (SLS, Villigen, Switzerland) 8 9 in transmission mode at the Pd (E₀=24.35 keV) and Cu (E₀=8.979 keV) K-edges. The polychromatic beam of the 2.9 Tesla superbend was collimated by a Si-coated (for copper) or 10 a Pt-coated (for palladium) collimating mirror and subsequently monochromatized by a 11 12 Si(111) channel-cut crystal of the monochromator, which oscillated at 1 Hz frequency (2 MHz sampling frequency). The beam was then focused to the sample using a Rh-coated or 13 Pt-coated toroidal mirror to a spot size of 1 x 0.2 mm. 14





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XAS Data Treatment. Energy calibration was performed by consideration of the maximum
 derivative of Cu and Pd foils, which were measured simultaneously. Edge step normalization
 was performed using a 1st order polynomial pre-edge function and a Victoreen post-edge
 function:¹

 $y = \frac{af^3}{F^3} - \frac{bf^4}{F^4} + c$

where E is the energy, *a*, *b* and *c* are Victoreen coefficients, and *f* = 1.23986 × 10⁴ / ÅV.
To reduce data-point density from extreme oversampling, a localised radial basis function
interpolation was performed with a constant energy step in the XANES region of 0.25 eV for
Cu and 0.5 eV for Pd K-edge data and a constant k-step of 0.025 Å⁻¹ in the EXAFS region for
both edges.

EXAFS data were fitted using the Demeter software.² The Fourier transformation of the k³weighted Cu and Pd K-edge EXAFS data was done between 3-11 Å⁻¹ and fitted in R space in the range of 1-3.5 Å for Cu and 1-4 Å for Pd. The theoretical phase shifts and scattering amplitudes of the Cu-O, Cu-Cu (oxide), Pd-O and Pd-Pd (metallic and oxide) shells were calculated by the FEFF6 code.³ These references were used for the initial guess of the EXAFS fit for the following shells:

17 ICSD-16025 (CuO): Cu-O, Cu-(O)-Cu

18 ICSD-257583 (PdO): Pd-O, Pd-(O)-Pd

- 19 ICSD-77885 (Pd): Pd-Pd
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Supplementary Figures







Supplementary Figure 2. IR-ATR spectra of parent zeolite Na-Y and pre-treated (378 K, O₂) 2 and spent (after 4 hours under Wacker conditions) Pd1Cu5-Y. The weak band at 1310 cm⁻¹ 3 4 associated to symmetric N-H deformation is indicative of the presence of ammine coordinated to Pd(II).⁴ Loss of palladium-ammine coordination is evident from the decrease in the intensity 5 6 of this band in the spectrum of spent Pd1Cu5-Y (after 4 hours under Wacker conditions). The weak band at 1450 cm⁻¹ in the spectrum of the spent catalyst suggests the presence of 7 ammonium ions.^{4,5} In the spectrum of the regenerated catalyst (623 K, O₂), the bands at 1310 8 and 1450 cm⁻¹ disappeared, signifying the total loss of Pd-ammine coordination and the 9 subsequent release and oxidation of ammonia. 10



Supplementary Figure 3. k³-weighted Fourier transform magnitude (non-phase shift corrected) of the (a,b) Cu and (c,d) Pd K-edge EXAFS spectra of Pd1Cu5-Y in different reaction conditions, performed in the 3-11 Å⁻¹ range (black: magnitude of FT, red: best fit).
Wacker equilibration: 378 K, C₂H₄:H₂O:O₂ (1:7:10 molar ratio), 4 hr. The k³-weighted Cu and Pd K-edge EXAFS spectra are shown in Figure S8.



Supplementary Figure 4. k³-weighted Fourier transform magnitude (non-phase shift
corrected) of the (a,b) Cu and (c,d) Pd K-edge EXAFS spectra of Pd4Cu5-Y in different
reaction conditions, performed in the 3-11 Å⁻¹ range (black: magnitude of FT, red: best fit).
Wacker equilibration: 378 K, C₂H₄:H₂O:O₂ (1:7:10 molar ratio), 4 hr. The k³-weighted Cu and
Pd K-edge EXAFS spectra are shown in Figure S8.





- **Supplementary Figure 5.** (a) HAADF-STEM image and the corresponding (b-e) EDX-STEM
- 3 elemental maps of Pd4Cu5-Y after 4 hours under Wacker conditions.

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1 Supplementary Figure 6. Stability test of Pd1Cu5-Y under Wacker conditions. Ethylene

conversion and product selectivities vs time on stream over Pd1Cu5-Y. Standard reaction
conditions: 378K, 1 atm, W/F₀ = 0.86 kg_{cat} s mol^{-1.}





Supplementary Figure 7. k³-weighted Fourier transform magnitude (non-phase shift
corrected) of the (a,b) Cu and (c,d) Pd K-edge EXAFS spectra of Pd1Cu5-Y in different
conditions, performed in the 3-11 Å⁻¹ range (black: magnitude of FT, red: best fit).
Reactivation: 1st cycle, 623 K, O₂; Wacker conditions: 378 K, C₂H₄:H₂O:O₂ (1:7:10 molar
ratio), 4 hr. The k³-weighted Cu and Pd K-edge EXAFS spectra are shown in Figure S8.

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Supplementary Figure 8. k³-weighted (top) Cu and (bottom) Pd K-edge EXAFS spectra of
Pd1Cu5-Y and Pd4Cu5-Y in different reaction conditions. Pre-treatment: 378 K, O₂; Wacker
equilibration: 378 K, C₂H₄:H₂O:O₂ (1:7:10 molar ratio), 4 hr; Reactivation: 1st cycle, 623 K,
O₂.

1 Supplementary Tables

2 Supplementary Table 1. Cu and Pd contents (determined by AAS of totally dissolved as-

Sample	Cu (wt%)	Pd (wt%)	Cu/Pd
Cu7-Y	6.7	Not measured	
Pd2-Y	Not measured	1.9	
Pd1Cu5-Y	4.7	1.1	6.7
Pd2Cu5-Y	4.8	2.2	3.7
Pd4Cu5-Y	4.6	3.6	2.2
Pd1Cu1-Y	1.2	1.2	1.7
Pd1Cu3-Y	2.9	1.1	4.4
Pd1Cu6-Y	5.6	1.0	9.4

3 prepared catalysts) of catalysts used.

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5 Supplementary Table 2. Properties of the parent Na-Y zeolite and the ion-exchanged catalysts

6 before and after reaction.

Sample	Sbet (m ² /g) ^a	$V_{total} (cm^3g^{-1})^b$	Vmicro (cm ³ g ⁻¹) ^c	Vmeso (cm ³ g ⁻¹) ^d	Carbon (wt%) ^e
Na-Y	660	0.34	0.32	0.019	Not measured
Pd1Cu5-Y (as- prepared)	612	0.31	0.31	0.007	0.1
Pd1Cu5-Y (spent) ^f	411	0.21	0.21	0.004	5.4
Pd4Cu5-Y (as- prepared)	588	0.29	0.28	0.009	0.2
Pd4Cu5-Y (spent) ^f	324	0.12	0.11	0.007	6.8

7 (a) S_{BET}: surface area determined by Brunauer-Emmett-Teller theory; (b) Total pore volume = adsorbed volume at $P/P_0 = 0.95$;

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8 (c) Micropore volume obtained by the t-plot method; (d) Mesopore volume = V_{total} - V_{micro}; (e) From IR spectroscopy; (f)
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9 Measured after 4 hr under Wacker conditions.

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1 Supplementary Table 3. Cu and Pd K-edge EXAFS curve fitting results for Pd-Cu/zeolite Y

2 in different reaction conditions.

Cu K-edge	Scattering pair	N ^a	R(Å ²) ^b	$\sigma^2(\text{\AA}^2)^c$	$\Delta E(eV)^d$	R-factor ^e
Pre-treated Pd1Cu5-Y	Cu-O	4.4(0.2)	1.94(0.004)	0.006(0.001)	3.1(0.9)	0.004
Wacker-equilibrated Pd1Cu5-Y	Cu-O	4.2(0.2)	1.95(0.004)	0.006(0.001)	1.3(0.5)	0.001
Pre-treated Pd4Cu5-Y	Cu-O	4.2(0.3)	1.94(0.004)	0.005(0.002)	1.0(0.6)	0.009
Wacker-equilibrated Pd4Cu5-Y	Cu-O	3.9(0.3)	1.96(0.002)	0.007(0.001)	1.3(0.9)	0.006
	Cu-O	3.9(0.3)	1.95(0.01)	0.008(0.001)	0.8(0.6)	0.008
Regenerated Policus-Y (first cycle)	Cu-(0)-Cu	3.2(1.9)	2.91(0.03)	0.018(0.004)	0.8(0.6)	
	Cu-O	3.2(0.2)	1.95(0.01)	0.007(0.001)	1.4(0.6)	0.006
Spent Regenerated Policus-Y (first cycle)	Cu-(0)-Cu	2.3(0.6)	2.93(0.01)	0.013(0.003)	1.4(0.6)	
Pd K-edge	Scattering pair	N ^a	$R(Å^2)^b$	$\sigma^2(\text{\AA}^2)^c$	$\Delta E(eV)^d$	R-factor ^e
Pre-treated Pd1Cu5-Y	Pd-O/N	3.5(0.2)	2.01(0.01)	0.004(0.001)	8.5(1.3)	0.010
Wacker-equilibrated Pd1Cu5-Y	Pd-O/N	3.1(0.3)	2.01(0.01)	0.004(0.001)	2.5(1.5)	0.009
·	Pd-Pd	1.5(0.9)	2.76(0.05)	0.018(0.003)	7.9(2.5)	
Pre-treated Pd4Cu5-Y	Pd-O/N	3.6(0.2)	2.01(0.01)	0.004(0.001)	5.7(2.1)	0.011
	Pd-O/N	2.9(0.5)	2.04(0.01)	0.006(0.001)	6.7(1.2)	0.017
Wacker-equilibrated Pd4Cu5-Y	Pd-Pd	2.6(0.7)	2.75(0.01)	0.006(0.001)	3.4(1.1)	
	Pd-0	3.5(0.7)	2.02(0.01)	0.004(0.001)	7.6(1.7)	0.027
Regenerated Pd1Cu5-Y	1. Pd-(0)-Pd	0.4(0.6)	3.04(0.01)	0.006(0.003)	7.6(1.7)	
	2. Pd-(0)-Pd	0.8(0.6)	3.43(0.03)	0.006(0.003)	7.6(1.7)	
	Pd-0	2.7(0.5)	2.03(0.01)	0.003(0.001)	4.3(1.8)	0.012
Spent Regenerated Pd1Cu5-Y	Pd-Pd (metallic)	1.2(0.9)	2.75(0.02)	0.008 ^f	0.5(0.2)	
	1. Pd-(0)-Pd	1.1(0.6)	3.03(0.08)	0.006(0.003)	4.3(1.8)	
	2. Pd-(0)-Pd	2.1(0.6)	3.42(0.09)	0.006(0.003)	4.3(1.8)	

3 (a) Number of nearest neighbors determined by fixing the amplitude reduction factor (S_0^2) values obtained from the fits to Cu

4 (0.82) and Pd (0.86) foil reference spectra

5 (**b**) Interatomic distance

6 (c) Pseudo Debye-Waller factor

7 (d) Shift of the energy threshold

8 (e) R-factor = $\sum_{i}^{N_{fit}} [X_i^{measured} - X_i^{model}(x)]^2 / \sum_{i}^{N_{fit}} [X_i^{measured}]^2$

9 (f) Set from the Debye model of metallic Pd-Pd

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