

Supporting Information

for

Ryu et al., “Fully Copper-Exchanged High-Silica LTA Zeolites as Unrivaled Hydrothermally Stable NH₃-SCR Catalysts”

Catalyst synthesis

Three LTA zeolites with Si/Al ratios of 11, 16, and 23 were synthesized by heating an aluminosilicate synthesis mixture with the chemical composition $0.5\text{ROH}\cdot x\text{TMAOH}\cdot 0.49\text{HF}\cdot 1.0\text{SiO}_2\cdot 0.5x\text{Al}_2\text{O}_3\cdot 5.0\text{H}_2\text{O}$, where ROH stands for 1,2-dimethyl-3-(4-methylbenzyl)-imidazolium hydroxide and x is 0.1, 0.067, or 0.05, at 175 °C for a given time. The synthesis of zeolites with Si/Al = 11 and 16 also included the use of a small amount (4 wt% of the silica in the synthesis mixture) of calcined LTA with Si/Al = 23 as seed crystals. More details can be found in our recent work.^[S1] An SSZ-13 zeolite with Si/Al = 16 was synthesized according to the procedure described elsewhere.^[S2]

As-made LTA zeolites were converted into the ammonium form following the two steps, i.e., calcination at 600 °C for 8 h in air to remove the occluded organic structure-directing agent, and refluxing twice in 1.0 M NH₄NO₃ (2.0 g solid per 100 mL solution).^[S1,S3] Copper-exchanged zeolites were prepared by ion exchange of their ammonium form using 0.01 M Cu(CH₃COO)₂ (97%, Aldrich) solutions at room temperature, where the number of ion exchange and time were properly adjusted, followed by drying at 90 °C overnight and calcining at 550 °C in air for 8 h. If required, copper-exchanged zeolites were hydrothermally aged under flowing air containing 10% H₂O at 750 - 900 °C for up to 24 h. Here we denoted Cu-LTA catalysts with different Si/Al and Cu/Al ratios as Cu-LTA- x - y , where x and y are the Si/Al and Cu/Al ratios, respectively. For catalytic comparison, three Cu-SSZ-13 with Si/Al = 16 and Cu/Al = 0.15 – 0.49 were prepared according to the procedures similar to the Cu-LTA preparation.

Catalysis

The activity test over the catalysts employed here was conducted in a continuous fixed-bed flow reactor system.^[S1] For each test, the powder type catalysts in 20/30 mesh size were

charged into a 3/8-in.-od aluminum tube reactor, heated from room temperature to 500 °C at a heating rate of 10 °C min⁻¹ under 21% O₂/N₂ flow (2,000 mL min⁻¹), and held at the final temperature for 2 h. The NO conversion was collected over the temperature range 150 - 600 °C and with a reactor space velocity of 100,000 h⁻¹. The standard feed gas composition containing 500 ppm NH₃, 500 ppm NO, 5% O₂, 10% H₂O, and N₂ was supplied through mass flow controllers.

To investigate the effects of propylene (C₃H₆) on the deNO_x activity of catalysts, 2000 ppm C₃H₆ was continuously injected into the standard feed gas stream under the reaction conditions described above. We also examined the influence of sulfur dioxide (SO₂) on the catalyst deactivation. 20 ppm SO₂ was injected into the mixing zone containing glass beads located just above the catalyst in order to avoid the formation of sulfur-like species, and the deNO_x performance was recorded at 270 °C for every 2 h. Then, the used catalyst was regenerated under air flow at 500 °C for 2 h. This procedure was repeated twice. NH₃ oxidation was conducted under the identical reaction conditions described above, except that the NO feed was excluded. The concentrations of the inlet and outlet gas composition were determined online by a ThermoNicolet 6700 FT-IR spectrometer equipped with a 2 m gas cell.

Catalysts characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert diffractometer (Cu K_α radiation) with an X'Celerator detector. Data were collected with a fixed divergence slit (0.50°) and Soller slits (incident and diffracted = 0.04 rad). Elemental analysis for Si, Al, and Cu was carried out by a Jarrell-Ash Polyscan 61E inductively coupled plasma spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. The N₂ sorption experiments performed on a Mirae SI nanoPorosity-XG analyzer. Prior to the experiments, each zeolite sample was evacuated for 6 h at 250 °C.

The ²⁷Al MAS NMR spectra were performed on a Bruker Avance II spectrometer at spinning rate of 24.0 kHz. The ²⁷Al MAS NMR spectra were recorded at a ²⁷Al frequency of 130.318 MHz with a π/6 rad pulse length 1.0 μs, a recycle delay of 2.0 s and an acquisition of ca. 1000 pulse transients. The ²⁷Al chemical shifts are referenced to an Al(H₂O)₆³⁺ solution. The variable-temperature infrared spectra in the 1000-4000 cm⁻¹ region were measured on a Nicolet 6700 FT-IR spectrometer using self-supporting zeolite wafers of approximately 13 mg (1.3 cm diameter). Prior to infrared measurements, the zeolite wafers were pretreated

under vacuum at 550 °C for 2 h inside a home-built infrared cell with CaF₂ windows. Then, the infrared spectra were recorded under vacuum (10⁻⁵ Pa) at room temperature. The X-ray absorption near edge structure (XANES) spectra at the Cu K-edge were obtained at the 8C beamline of the Pohang Accelerator Laboratory (PAL) using a Si (111) crystal monochromator. Cu foil was employed for the energy calibration ($E_0 = 8979.0$ eV). The X-ray intensity was monitored using ionization chambers purged with pure N₂ gas at room temperature for the incident (I_0) and transmitted (I) beam in the Cu K-edge measurements. Cu₂O (≥ 99.99%, Aldrich) and CuO (99.99%, Aldrich) were used as reference compounds. Electron spin resonance (ESR) spectra were recorded at room temperature on a Bruker A200 spectrometer operating at X-band (~ 9.45 kHz) with 100-kHz field modulation. Before each ESR analysis, each sample was placed in a quartz tube, pretreated from room temperature to 400 °C at a ramp rate of 10 °C min⁻¹ with pure O₂ and were held for 1 h at 400 °C, evacuated for 10 minutes at the same temperature. After sealing the tube, ESR measurements were carried out in the field region from 2250 to 3750 G with a sweep time of 102.4 seconds. g values were determined through comparison of the resonant field with that of the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical at $g = 2.0036$. The Cu²⁺ species supported on γ -Al₂O₃, was also prepared and used as a reference material.^[S3]

Structural analysis

For detailed structural analysis, the fresh and 750 °C-aged forms of the Cu-LTA-16-0.48 catalyst were loaded in a 0.5 mm quartz glass capillary, dehydrated at 350 °C under a vacuum of 10⁻⁵ Torr for 10 h. The capillary was sealed and analyzed at room temperature on the station I11 at the Diamond Light Source (DLS, Didcot, UK) in transmission mode (Debye-Scherrer geometry), using monochromated X-rays ($\lambda = 0.826056$ Å). The synchrotron powder XRD data were obtained with a step size of 0.001° for a scan time of 2 s per step over the 2θ range 0-150°. The detector consists of 5 MAC arms made of 9 Si crystals each, giving a total of 45 crystals.

A model for the LTA structure was obtained from the IZA database^[S4] and used as a starting point for the Rietveld refinement of the structures of the fresh and aged forms of Cu-LTA-16-0.48 using the GSAS suite of programs and EXPGUI graphical interface.^[S5-S7] Both forms were modelled as a pure-silica framework. In fact, substitution of tetrahedral Al atoms for Si based on their Si/Al ratio (16), together with an adjustment of the fractional occupancy had

very little impact on the overall refinement of the patterns and also led to little change to the atomic positions, bond length, and bond angles. The framework Si-O and O-O distances were soft constrained to 1.624 Å ($\sigma = 0.01$ Å) and 2.65 Å ($\sigma = 0.01$ Å), respectively. Total contents of extraframework cations were soft restrained based on chemical compositions of samples determined elemental analyses. The peak shape was modelled using the pseudo-Voigt profile function. The isotropic atomic displacement parameters of the framework atoms have been constrained in groups for the tetrahedral Si and O atoms, respectively. The positions of extraframework cations were derived from Fourier difference maps. The convergence was achieved by refining simultaneously all profile parameters, scale factor, lattice constants, 2θ zero-point, atomic positional and thermal displacement parameters, and occupancy factors for the framework atoms and water O atoms. The data collection and crystallographic parameters are summarized in Table S1.

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- [S1] D. Jo, T. Ryu, G. T. Park, P. S. Kim, C. H. Kim, I. Nam, S. B. Hong, *ACS Catal.* **2016**, *6*, 2443–2447.
- [S2] M. Itakura, I. Goto, A. Takahashi, T. Fujitani, Y. Ide, M. Sadakane, T. Sano, *Microporous Mesoporous Mater.* **2011**, *144*, 91–96.
- [S3] Y. J. Kim, J. K. Lee, K. M. Min, S. B. Hong, I. Nam, B. K. Cho, *J. Catal.* **2014**, *311*, 447–457.
- [S4] International Zeolite Association, Structure Commission, <http://www.iza-structure.org>.
- [S5] H. Rietveld, *J. Appl. Crystallogr.* **1969**, *2*, 65–71.
- [S6] A. C. Larson, R. B. Von Dreele, *General Structure Analysis System (GSAS)*. Report No. LAUR 86-748 (Los Alamos National Laboratory, 2004).
- [S7] B. H. Toby, *J. Appl. Crystallogr.* **2001**, *34*, 210–213.

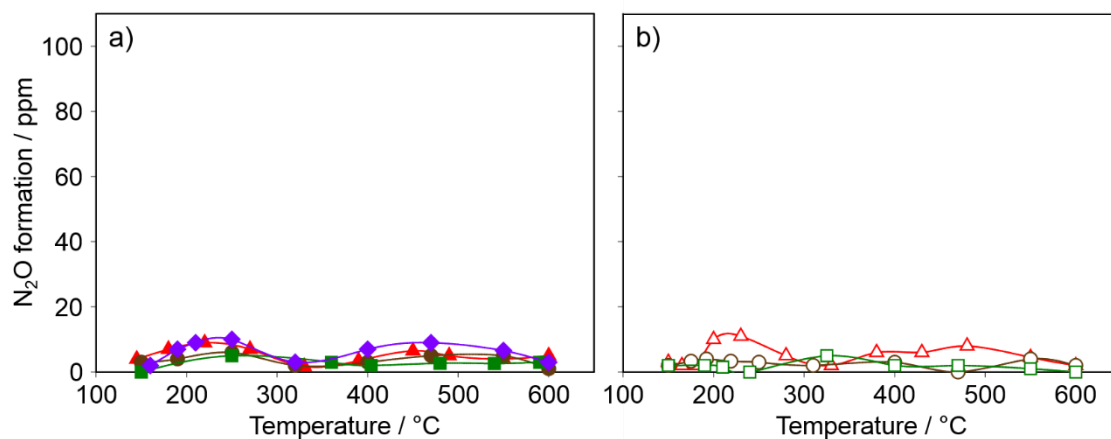


Figure S1. N_2O formation as a function of temperature in NH_3 -SCR reaction over fresh a) Cu-LTA and b) Cu-SSZ-13 catalysts with the same Si/Al ratio (16) but different Cu/Al ratios: Cu-LTA-16-0.14 (■), Cu-LTA-16-0.32 (●), Cu-LTA-16-0.48 (▲), Cu-LTA-16-0.65 (◆), Cu-SSZ-13-16-0.15 (□), Cu-SSZ-13-16-0.34 (○), and Cu-SSZ-13-16-0.49 (△). The feed contains 500 ppm NH_3 , 500 ppm NO, 5% O_2 , 10% H_2O balanced with N_2 at $100,000 \text{ h}^{-1}$ gas hourly space velocity. The last two values of the catalyst identification correspond to the Si/Al and Cu/Al ratios of the catalysts, respectively. We also found no noticeable differences in the N_2O formation over aged (example, at $750 \text{ }^\circ\text{C}$ for 24 h) Cu-LTA and Cu-SSZ-13 catalysts with similar Cu/Al ratios.

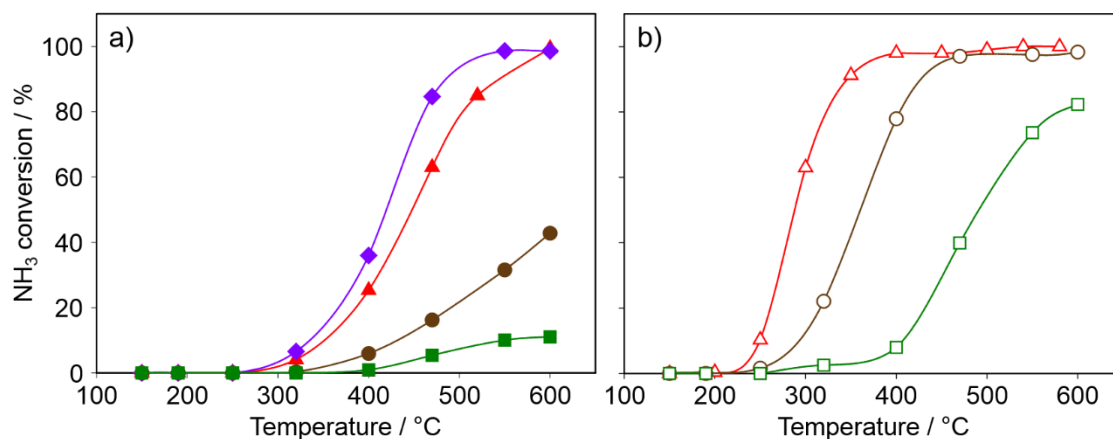


Figure S2. NH₃ conversion as a function of temperature in NH₃ oxidation reaction over fresh a) Cu-LTA and b) Cu-SSZ-13 catalysts with the same Si/Al ratio (16) but different Cu/Al ratios: Cu-LTA-16-0.14 (■), Cu-LTA-16-0.32 (●), Cu-LTA-16-0.48 (▲), Cu-LTA-16-0.65 (◆), Cu-SSZ-13-16-0.15 (□), Cu-SSZ-13-16-0.34 (○), and Cu-SSZ-13-16-0.49 (△). The feed contains 500 ppm NH₃, 5% O₂, 10% H₂O balanced with N₂ at 100,000 h⁻¹ gas hourly space velocity.

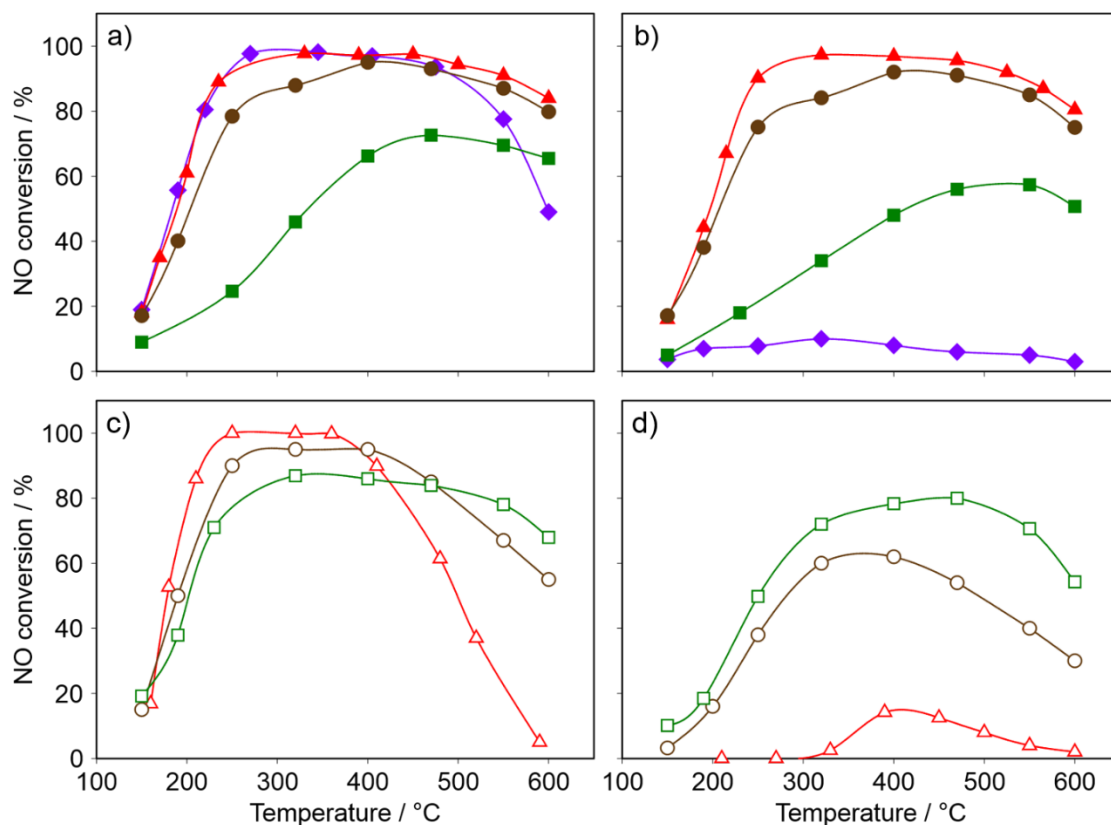


Figure S3. NO conversion as a function of temperature in NH₃-SCR reaction over the a) 750 °C- and b) 850 °C-aged forms of (top) Cu-LTA and (bottom) Cu-SSZ-13 catalysts with the same Si/Al ratio (16) but different Cu/Al ratios: Cu-LTA-16-0.14 (■), Cu-LTA-16-0.32 (●), Cu-LTA-16-0.48 (▲), Cu-LTA-16-0.65 (◆), Cu-SSZ-13-16-0.15 (□), Cu-SSZ-13-16-0.34 (○), and Cu-SSZ-13-16-0.49 (△). Hydrothermal aging was performed under flowing air containing 10% H₂O at 750 and 850 °C for 24 h. The feed composition is the same as that in Figure S1.

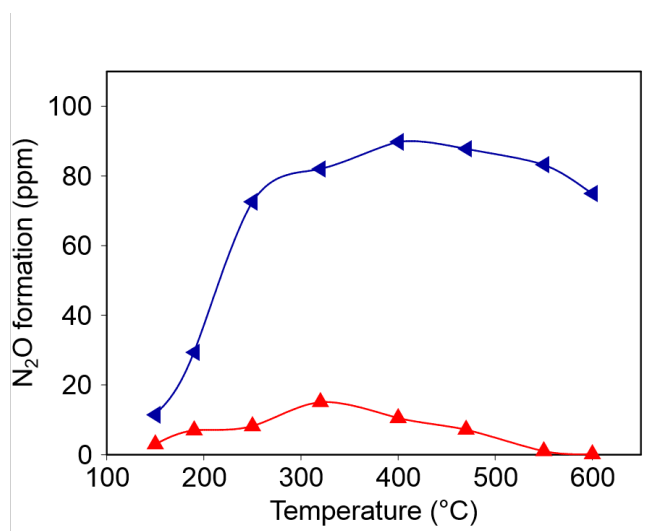


Figure S4. NO conversion as a function of temperature in NH₃-SCR reaction over Cu-LTA-16-0.48 (▲) and Cu-LTA-23-0.50 (◄) after hydrothermal aging under flowing air containing 10% H₂O at 900 °C for 24 h. The feed composition is the same as that in Figure S1.

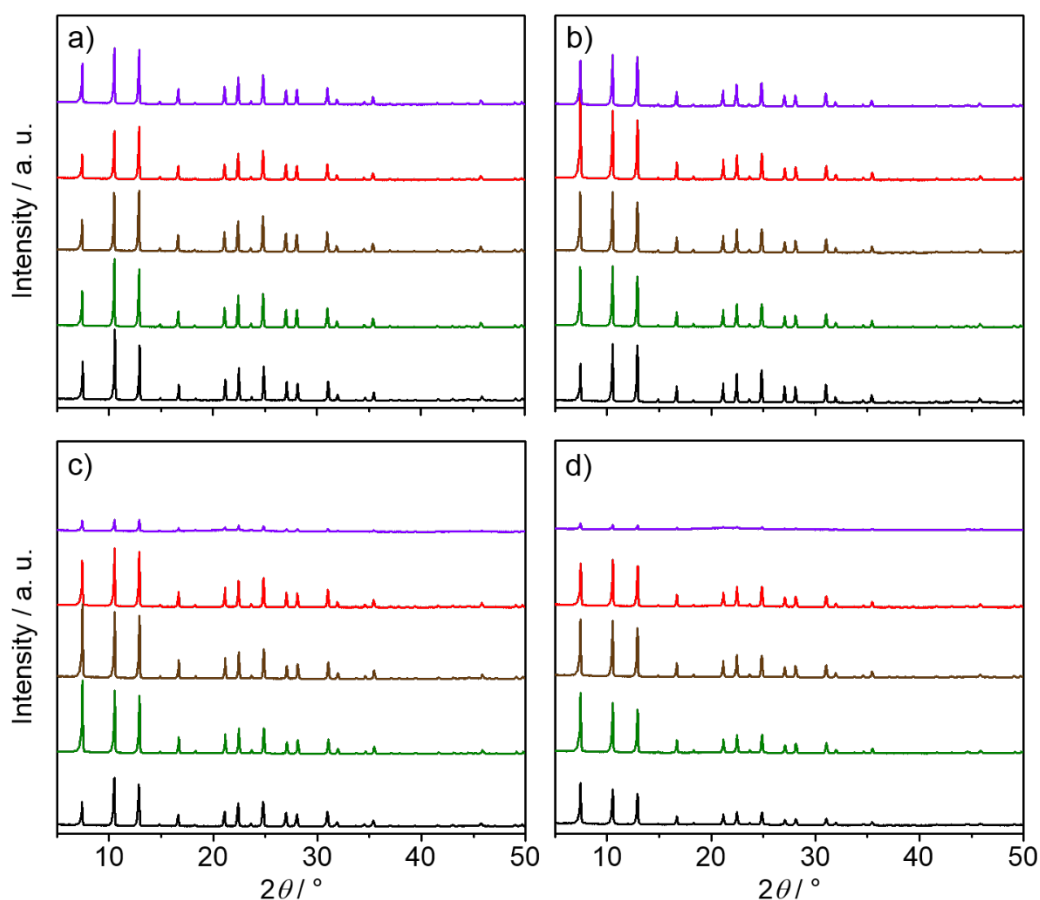


Figure S5. Powder XRD patterns of a) fresh, b) 750 °C-, c) 850 °C-, and d) 900 °C-aged Cu-LTA catalysts with the same Si/Al ratio (16) but different Cu/Al ratios: (from bottom to top) Cu-LTA-16-0 (black), Cu-LTA-16-0.14 (green), Cu-LTA-16-0.32 (brown), Cu-LTA-16-0.48 (red), and Cu-LTA-16-0.65 (violet). Hydrothermal aging was conducted under flowing air containing 10% H₂O at 750 and 850 °C for 24 h and at 900 °C for 12 h.

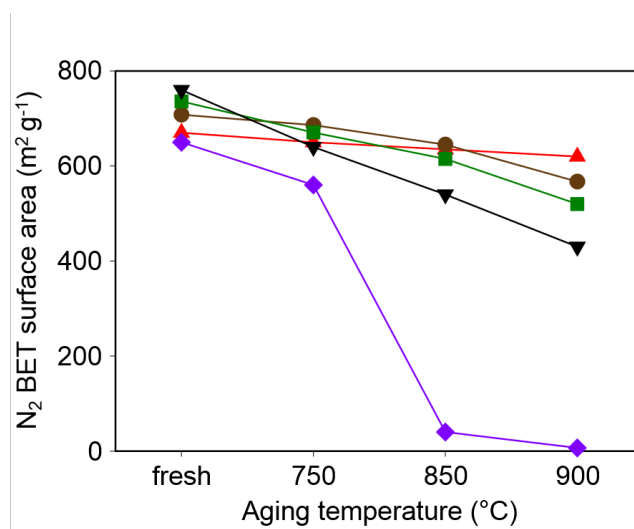


Figure S6. N₂ BET surface area as a function of hydrothermal aging temperature for Cu-LTA-16-0 (▼), Cu-LTA-16-0.14 (■), Cu-LTA-16-0.32 (●), Cu-LTA-16-0.48 (▲), and Cu-LTA-16-0.65 (◆). The hydrothermal aging conditions are the same as those in Figure S5.

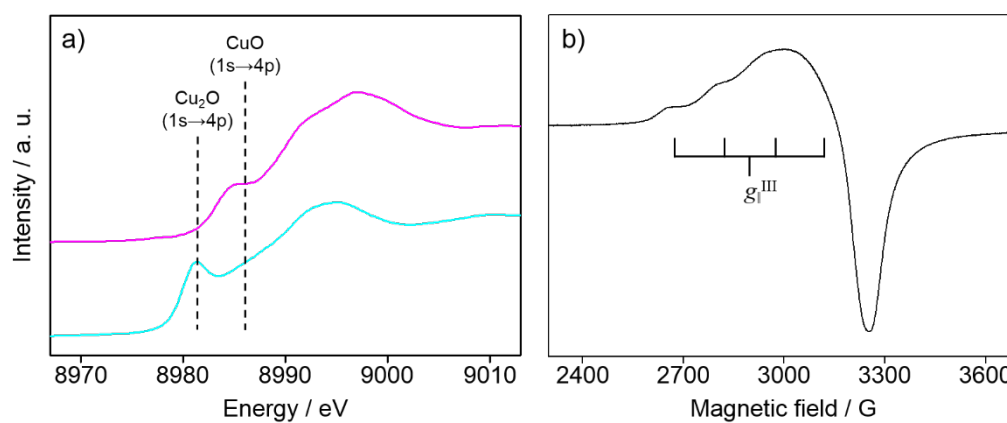


Figure S7. a) Cu K-edge XANES spectra of CuO (magenta) and Cu₂O (cyan) used as reference compounds and b) ESR spectrum at room temperature of Cu²⁺ species supported on γ -Al₂O₃ used as a reference material.

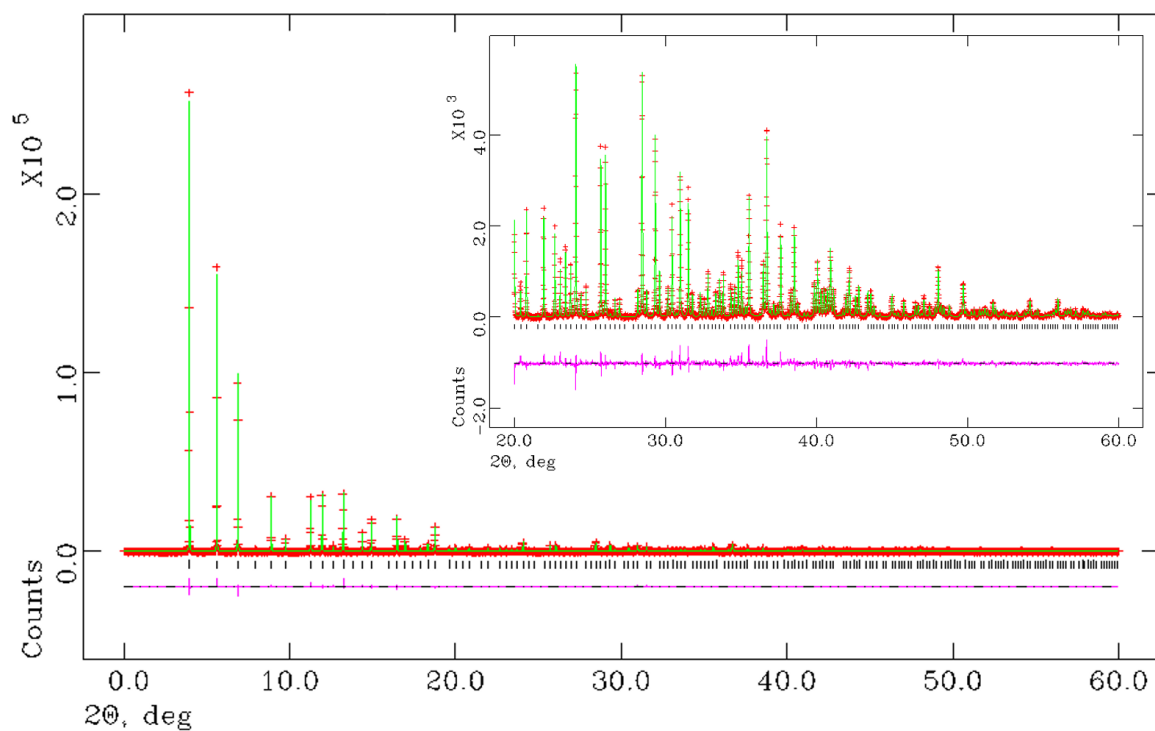


Figure S8. Rietveld plot for the fresh, dehydrated Cu-LTA-16-0.48 catalyst: observed data (crosses), calculated fit (solid line) and difference plot (lower trace). The tick marks represent the positions of allowed reflections.

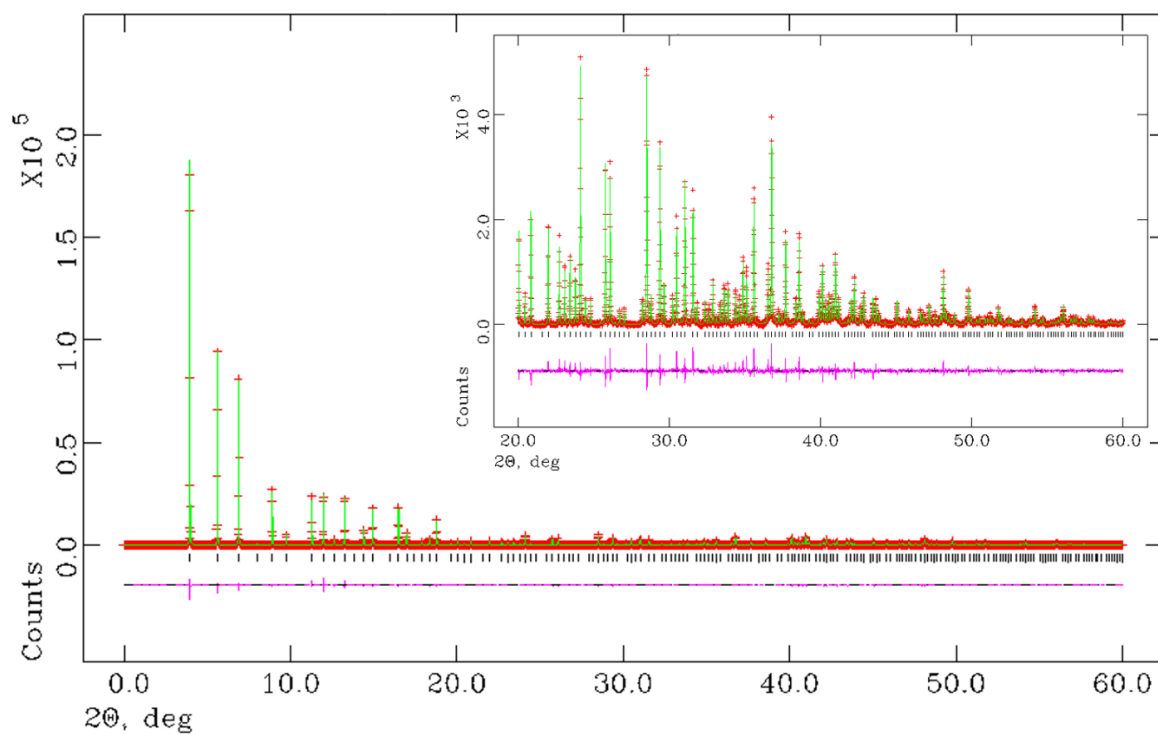


Figure S9. Rietveld plot for the 750 °C-aged, dehydrated Cu-LTA-16-0.48 catalyst: observed data (crosses), calculated fit (solid line) and difference plot (lower trace). The tick marks represent the positions of allowed reflections.

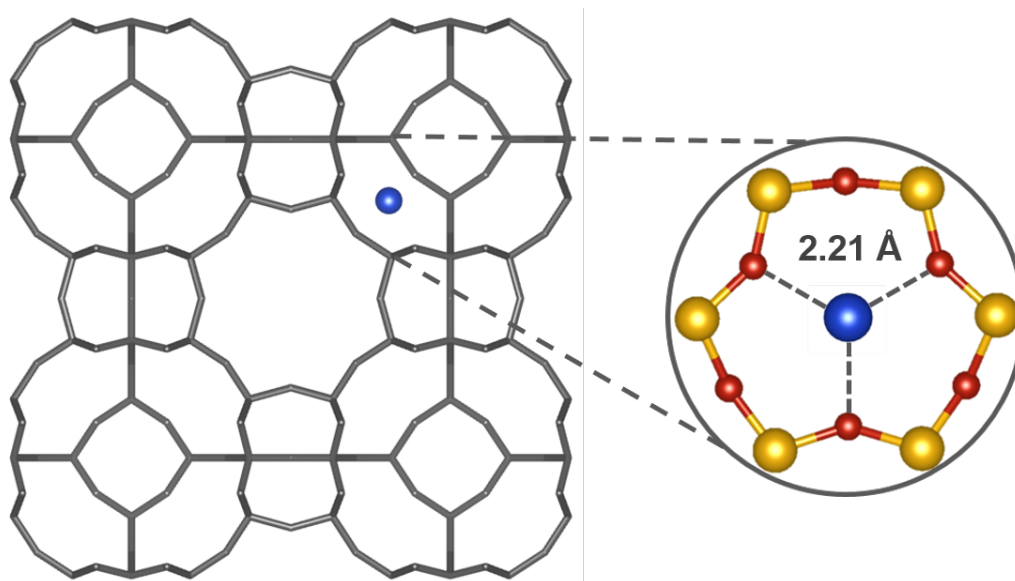


Figure S10. Structure of the 750 °C-aged, dehydrated Cu-LTA-16-0.48 catalyst with one distinct Cu²⁺ site. A Cu²⁺ cation located at the center of single 6-rings are shown at the right. Color code: yellow, Si; red, O; blue, Cu.

Table S1. Data collection and crystallographic data for the fresh and 750 °C-aged forms of Cu-LTA-16-0.48 catalysts in dehydrated state.

Material	Fresh, dehydrated Cu-LTA-16-0.48	750 °C-aged, dehydrated Cu-LTA-16-0.48
Refined structure	[Cu _{0.69}][Si ₂₄ O ₄₈]	[Cu _{0.69}][Si ₂₄ O ₄₈]
Symmetry		cubic
Space group		<i>Pm</i> $\bar{3}$ <i>m</i>
<i>a</i> (Å)	11.865921(11)	11.852731(11)
<i>b</i> (Å)	11.865921	11.852731
<i>c</i> (Å)	11.865921	11.852731
α (°)		90
β (°)		90
γ (°)		90
Unit cell volume (Å ³)	1670.723(5)	1665.157(4)
Diffractometer		I11 at DLS
Geometry		Debye-Scherrer
Wavelength (Å)		0.826056
2 θ scan range (°)		2.0-60.0
No. of contributing reflections	370	370
No. of refined parameters	57	57
No. of geometric restraints	17	17
<i>R</i> _{wp} (%)	5.00	5.57
<i>R</i> _p (%)	3.66	4.19
<i>R</i> _{F²} (%)	2.82	2.78
χ^2	3.42	2.81

Table S2. Atomic coordinates and thermal parameters for the fresh, dehydrated Cu-LTA-16-0.48 catalyst.

Atom	x	y	z	Occupancy	$U_{\text{iso}} \times 100$ (\AA^2)
Si1	0	0.18412(3)	0.36965(3)	1	1.087(8)
O1	0	0.21994(8)	0.5	1	1.967(18)
O2	0.11098(4)	0.11098(4)	0.34177(5)	1	1.967(18)
O3	0	0.29653(5)	0.29653(5)	1	1.967(18)
Cu1	0.19278(17)	0.19278(17)	0.19278(17)	0.0866(5)	3.94(15)

Table S3. Selected bond lengths and angles for the fresh, dehydrated Cu-LTA-16-0.48 catalyst.

Bond length (Å)		Bond angle (°)	
Si1-O1	1.6042(4)	O1-Si1-O2	109.92(3)
Si1-O2	1.6115(3)	O1-Si1-O3	107.67(5)
Si1-O3	1.5912(4)	O2-Si1-O2	109.62(5)
Si-O (Avg.)	1.6023	O2-Si1-O3	109.85(3)
Cu1-O2	2.2382(7)	O-Si-O (Avg.)	109.27
		Si1-O1-Si1	149.26(8)
		Si1-O2-Si1	146.93(6)
		Si1-O3-Si1	156.08(7)
		Si-O-Si (Avg.)	150.76

Table S4. Atomic coordinates and thermal parameters for the 750 °C-aged, dehydrated Cu-LTA-16-0.48 catalyst.

Atom	x	y	z	Occupancy	$U_{\text{iso}} \times 100$ (Å ²)
Si1	0	0.18331(3)	0.36959(3)	1	1.153(9)
O1	0	0.2190(3)	0.5	1	2.047(18)
O2	0.11155(3)	0.11155(3)	0.33969(5)	1	2.047(18)
O3	0	0.29512(5)	0.29512(5)	1	2.047(18)
Cu1	0.19161(14)	0.19161(14)	0.19161(14)	0.0865(4)	0.34(10)

Table S5. Selected bond lengths and angles for the 750 °C-aged, dehydrated Cu-LTA-16-0.48 catalyst.

Bond length (Å)		Bond angle (°)	
Si1-O1	1.6008(4)	O1-Si1-O2	110.46(3)
Si1-O2	1.6116(3)	O1-Si1-O3	108.59(5)
Si1-O3	1.5923(4)	O2-Si1-O2	110.25(5)
Si-O (Avg.)	1.6016	O2-Si1-O3	108.51(3)
Cu1-O2	2.2094(6)	O-Si-O (Avg.)	109.45
		Si1-O1-Si1	149.87(8)
		Si1-O2-Si1	144.85(5)
		Si1-O3-Si1	157.32(7)
		Si-O-Si (Avg.)	150.68