SUPPORTING INFORMATION

Structure-reactivity relations in Cu/ZrO_2 catalysed glycerol dehydration to acetol in continuous flow

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Reactor operation

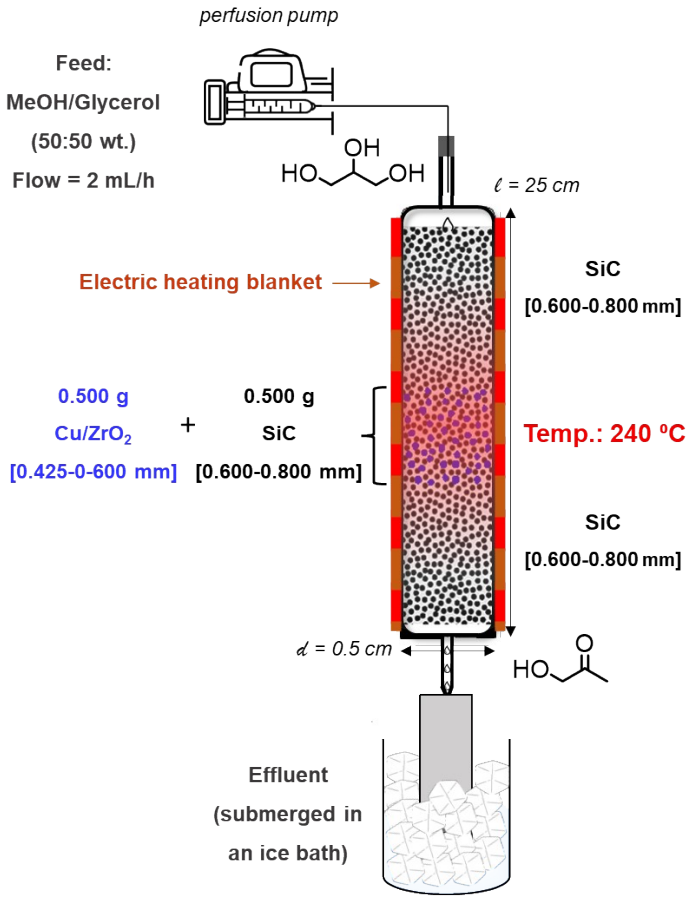

Figure S1. Schematic of continuous flow reactor for the selective dehydration of glycerol into acetol.

Diagnostic tests (**Figure S2a-b**) were selected according to reference 1 to assess internal and external diffusional limitations. The following conditions were thus selected to ensure that experiments were free from such limitations: feed (F) = 2 mL/h, WHSV [(glycerol mass·h^{-1}/catalyst mass)] = 1.99 h^{-1}, and particle size (D_p) = 0.425-0.600 mm.

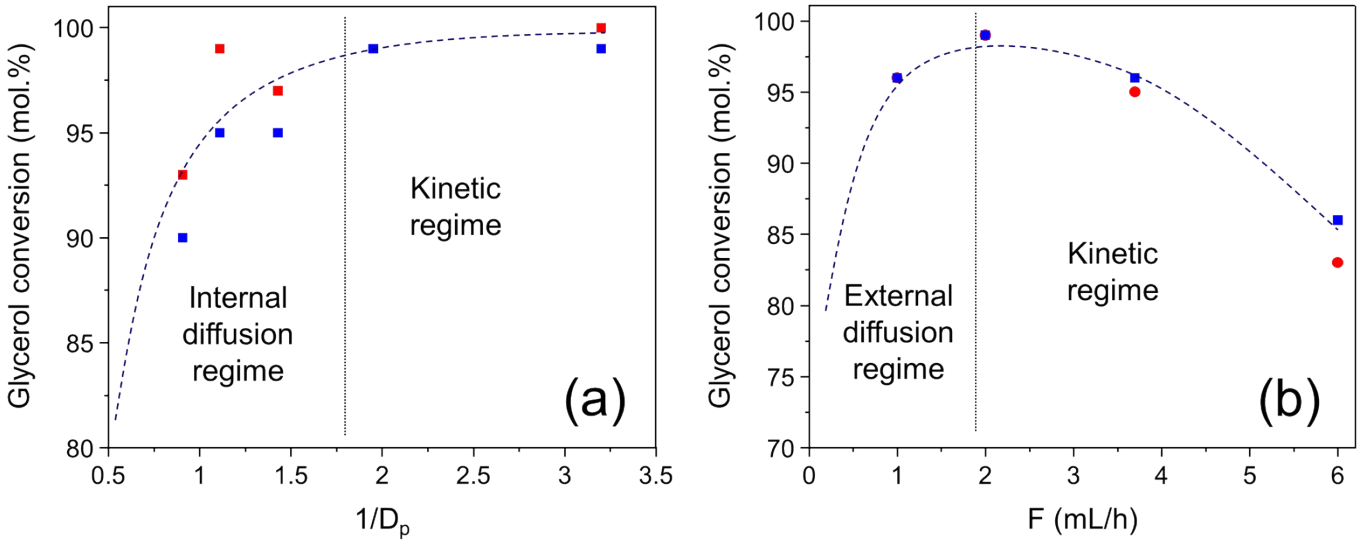

Figure S2. (a) Internal diffusion test: feed = methanol:glycerol (50:50 wt%), F = 2 ml/h, 0.5 g of Cu/*m*-ZrO_2, 240 °C. (b) External diffusion test: feed = methanol:glycerol (50:50 wt%), Cu/*m*-ZrO_2, 240 °C, D_p = 0.425-0.600 mm. In both tests, data are reported for time-on-stream = 1-2 h (**blue**) or 2-3 h (**red**).

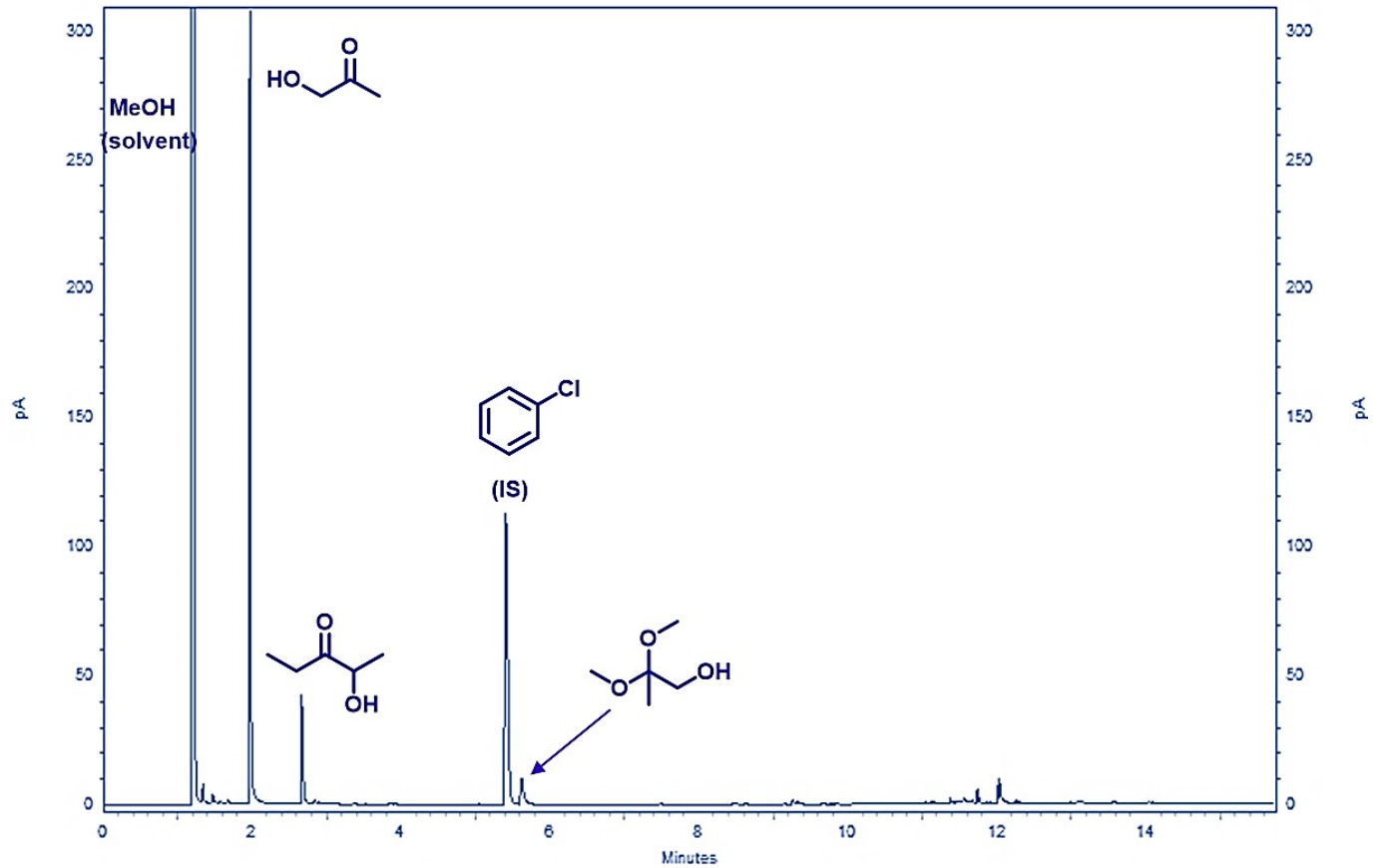

Figure S3. Gas chromatogram from Agilent Technologies 7890A GC, equipped with FID and HP-5 MS capillary column (30m x 250µm x 0.25µm) after 7-8 h time-on-stream. Reaction conditions: feed = methanol:glycerol (50:50 wt%), F = 2 ml/h, 0.500 g Cu/*m*-ZrO_2, 240 °C.

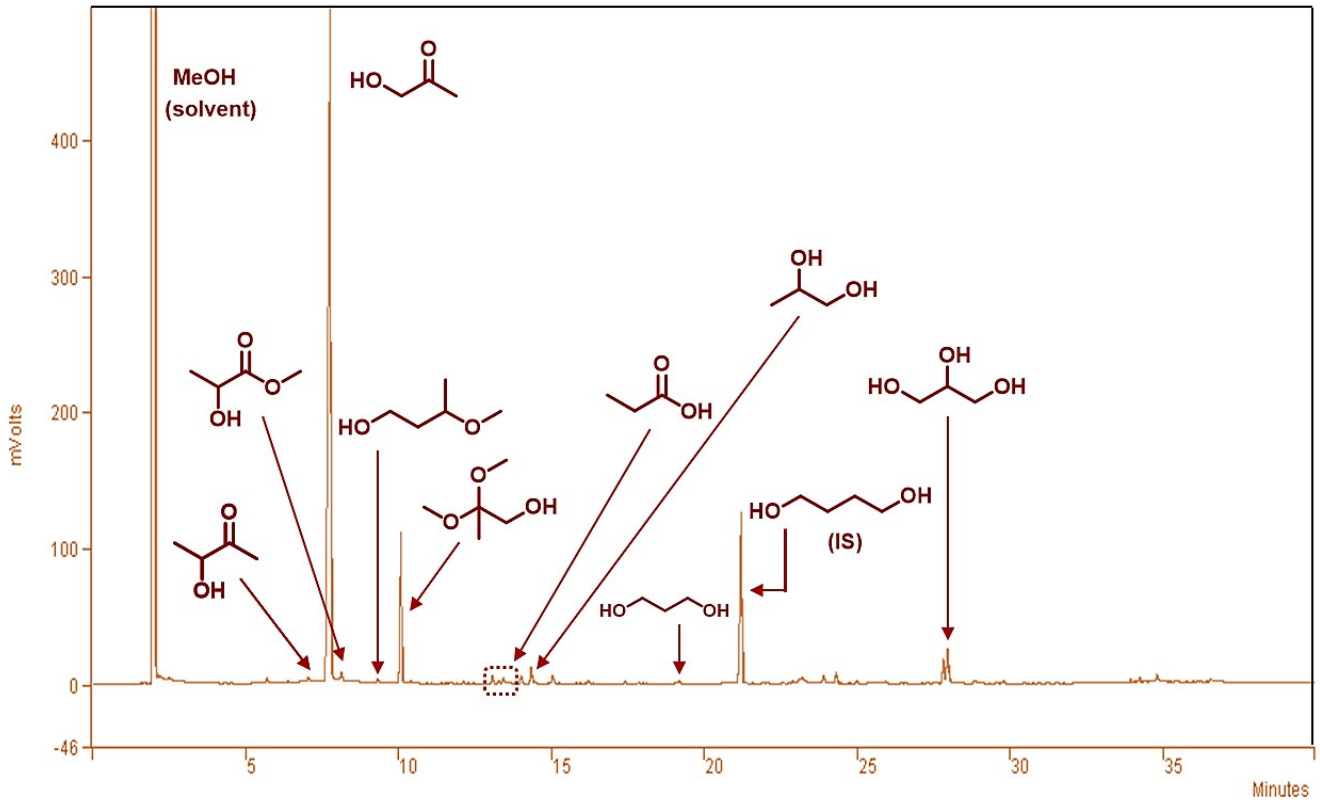

Figure S4. Gas chromatogram from Varian CP-3800 GC, equipped with FID detector and CARBOWAX Column (15 m x 3.2 mm) after 7-8 h time-on-stream. Reaction conditions: feed = methanol:glycerol (50:50 wt%), F = 2 ml/h, 0.500 g Cu/*m*-ZrO_2, 240 °C.

Catalyst characterisation

Table S1. Textural properties of ZrO_2 supports from N_2 physisorption.

ZrO_2 phase	Commercial supplier	Code	BET area (m^2/g) [a]	Pore volume (cm^3/g) [a]	Average pore diameter [b] (nm)
Monoclinic	Chempur	*m*-ZrO_2	102	0.28	8.0
Tetragonal	Chempur	*t*-ZrO_2	138	0.20	3.8

[a]BET method. [b]BJH method applied to desorption isotherm.

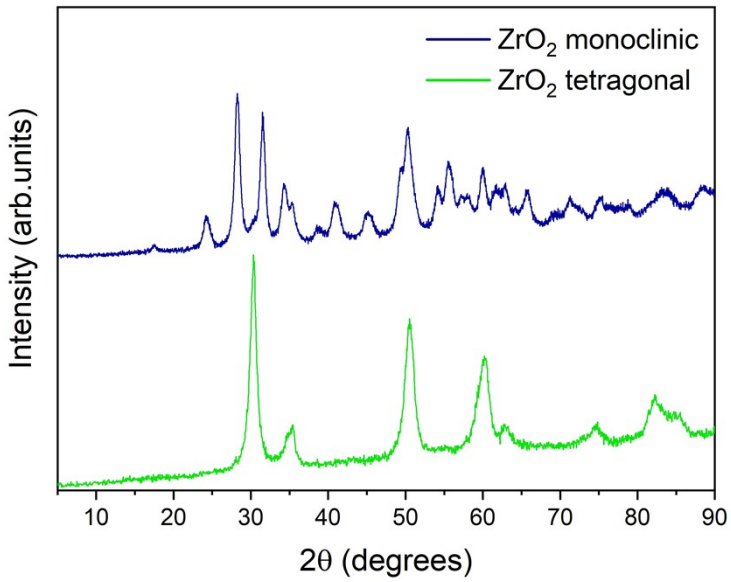

Figure S5. Powder X-ray diffraction patterns of commercial ZrO_2 supports.

Table S2. Textural properties of copper phase.[a]

Catalyst	Cu dispersion / %	Surface area Cu metal / $m^2.g^{-1}$	Mean particle diameter / nm
Cu/*t*-ZrO_2	40.2	261	2.6
Cu/*m*-ZrO_2	38.3	248	2.7

[a]N_2O reactive chemisorption.

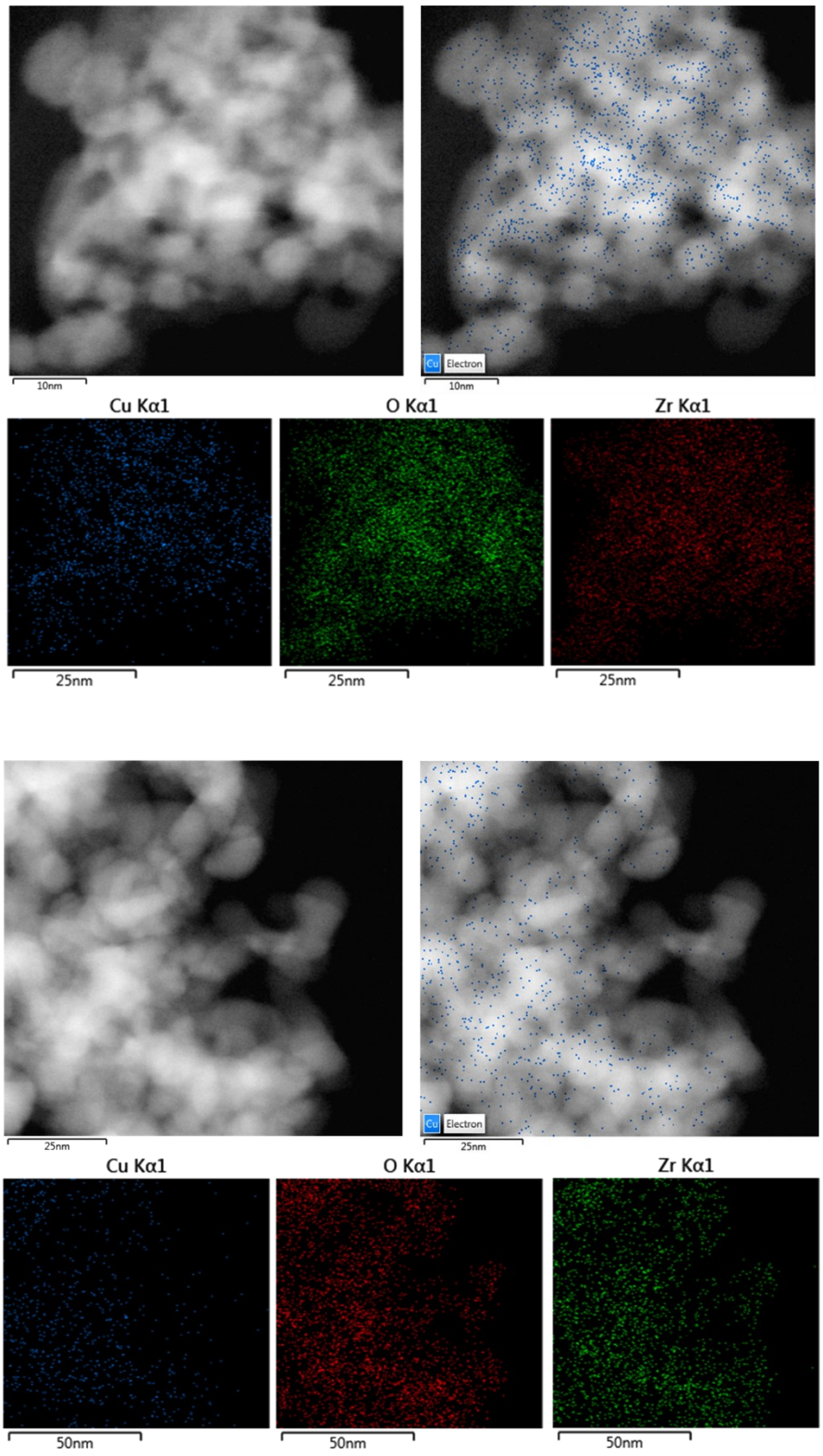

Figure S6. Elemental maps of (top) Cu/*t*-ZrO_2 and (bottom) Cu/*m*-ZrO_2 determined by EDS.

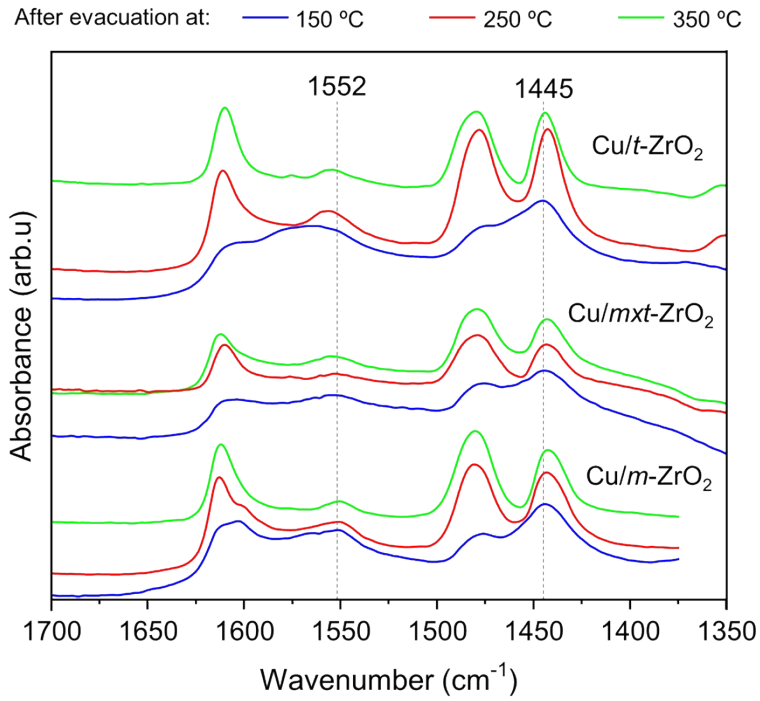

Figure S7. FTIR spectra of chemisorbed pyridine on Cu/ZrO_2. Band assignment: Brønsted acid sites, 1547-1540 cm^{-1}; Lewis acid sites, 1452-1445 cm^{-1}.[2,3]

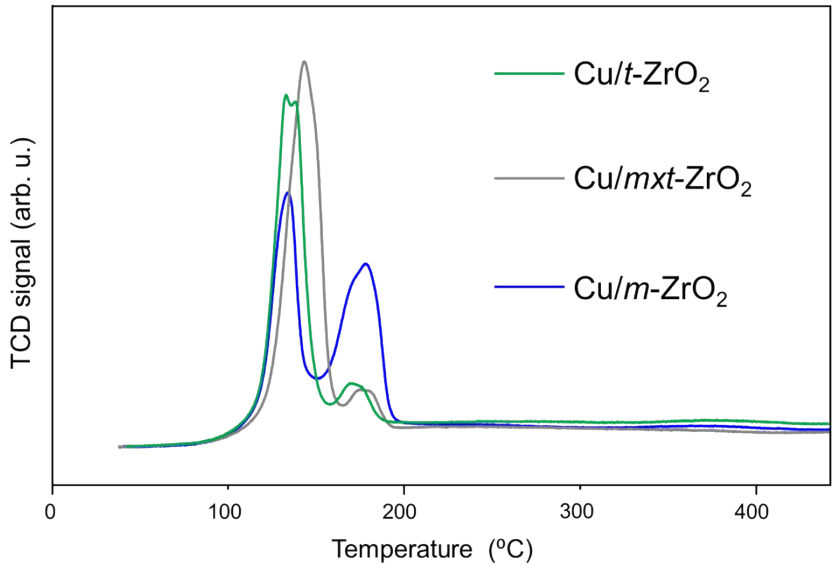

Figure S8. H_2 temperature-programmed reduction (TPR) profiles for Cu/ZrO_2. Conditions: 50 mL/min H_2 (10 vol% in Ar), ramp rate 10 °C/min.

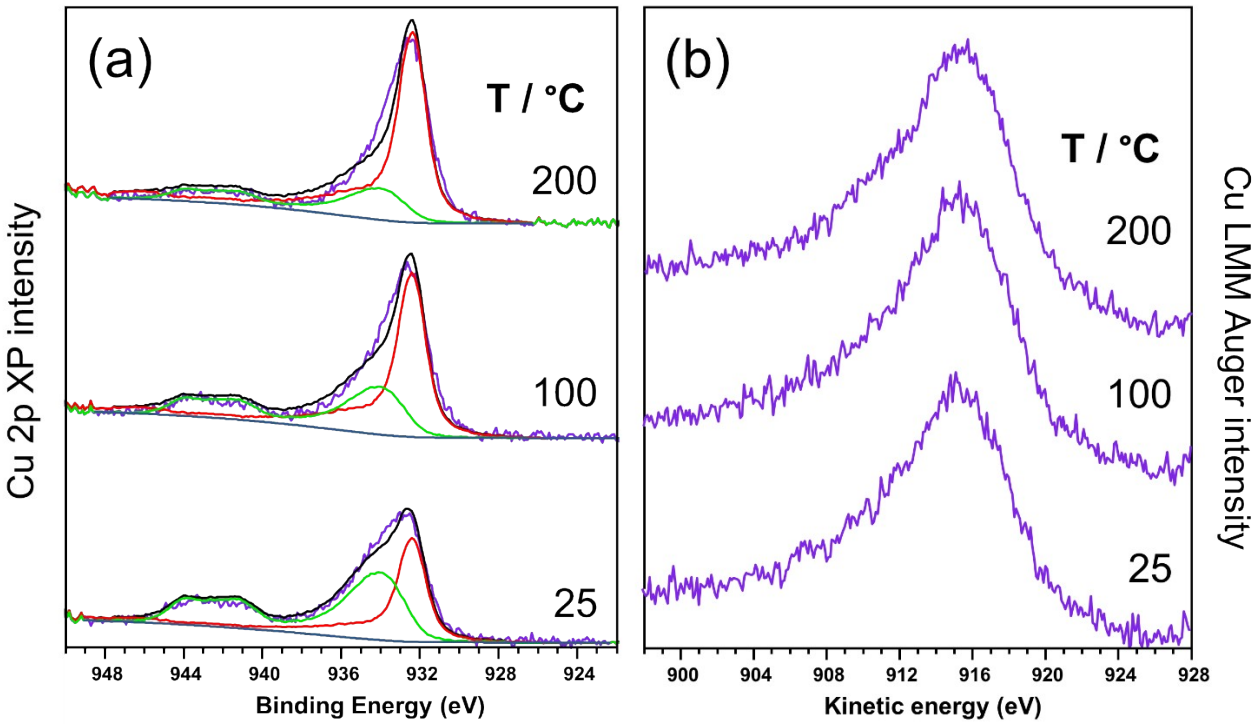

Figure S9. (a) Cu $2p_{3/2}$ XP and (b) Cu LMM Auger spectra of Cu/*t*-ZrO_2 wet-impregnated with a MeOH:Glycerol (50:50 wt) mixture as a function of in-situ annealing temperature.

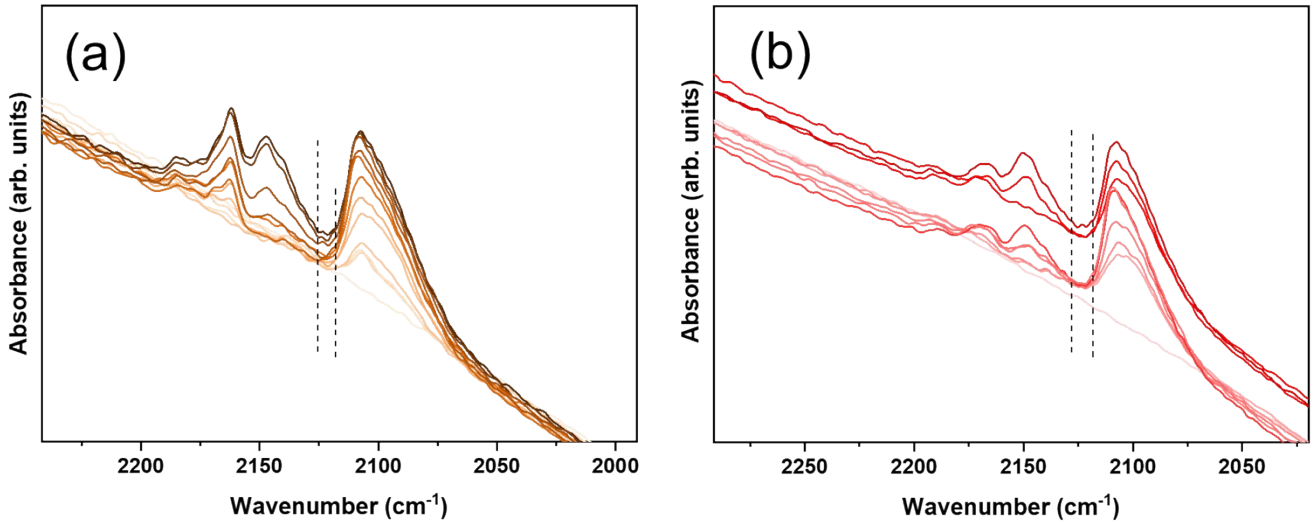

Figure S10. FTIR of chemisorbed CO at different coverages following N_2O titration as described in *Section 2.3.4*, to determine the stoichiometry of the Cu^0 oxidation by N_2O (section in between dashed lines corresponding to Cu_2O–CO).

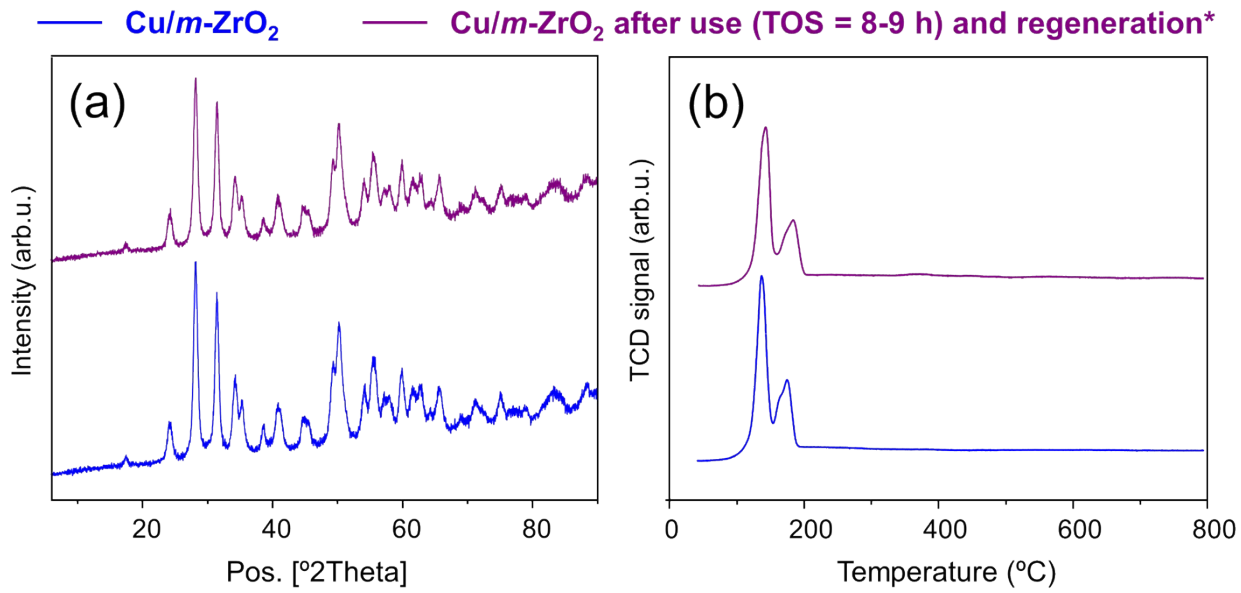

Figure S11. (a) Powder XRD patterns, and (b) H_2 TPR profiles for as-prepared (blue) and post-reaction and regenerated (purple) Cu/*m*-ZrO_2. *Regeneration involved washing with 40 mL of MeOH (2 mL/h) in the same reactor at the reaction temperature, then calcination at 550 °C for 4 h under flowing air (3 ºC/min, 50 mL/min).

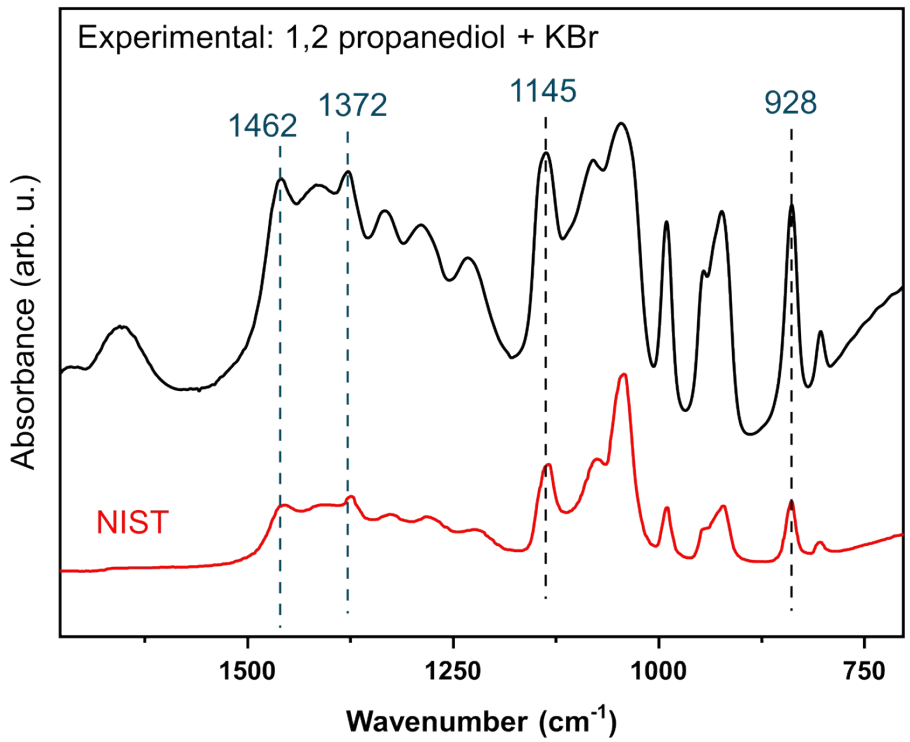

Figure S12. Experimental versus reference FTIR spectra of 1,2-propanediol.

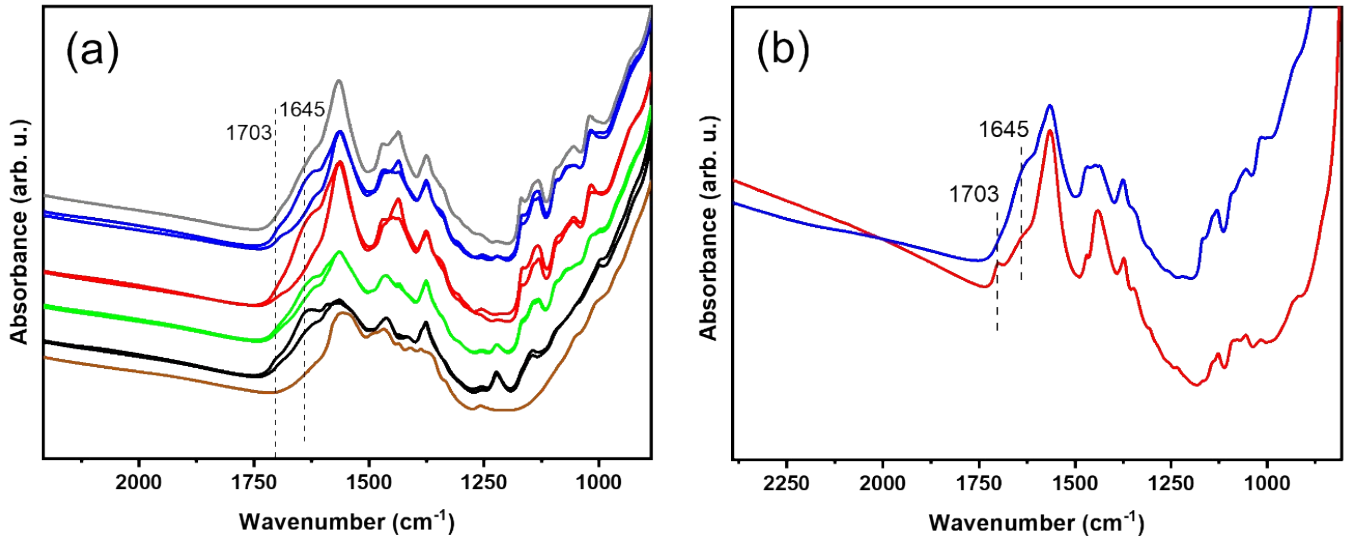

Figure S13. (a) FTIR spectra of *m*-ZrO_2 (**brown**) and adsorbed 1,2-propanediol on *m*-ZrO_2 (**black**). Additional spectra are shown for 1,2-propanediol on *m*-ZrO_2 in-vacuo annealed (10^{-6} mbar) to 25 °C (**green**), 60 °C (**blue**), 120 °C (**red**) or 160 °C (**grey**). In all cases, samples were cooled to room temperature before spectral acquisition. (b) FTIR spectra of adsorbed 1,2-propanediol on *m*-ZrO_2 (**blue**) and Cu/*m*-ZrO_2 (**red**) after in-vacuo annealing at 160 °C and cooling to room temperature.

Table S3. XP and AE spectroscopy data for quasi-in-situ experiments with Cu/*m*-ZrO_2 catalyst to study the influence of water.

Experiment	Cu$2p_{3/2}$ maxima (B.E., eV)	Cu $L_3M_{45}M_{45}$ maxima (K.E., eV)	α[a] (eV)	$Cu^{1+/0}$: Cu^{2+}
Gly/Water + Cu/*m*-ZrO_2 (R.T.)	934.0	915.3	1849.3	16 : 84
Gly/Water + Cu/*m*-ZrO_2 (100 ºC)	932.4	915.3	1847.7	61 : 39
Gly/Water + Cu/*m*-ZrO_2 (200 ºC)	932.5	915.3	1847.8	78 : 22
Gly/MeOH + Cu/*m*-ZrO_2 (R.T.)	934.2	915.5	1849.7	15 : 85
Gly/MeOH + Cu/*m*-ZrO_2 (100 ºC)	932.6	915.4	1848.0	69 : 31
Gly/MeOH + Cu/*m*-ZrO_2 (200 ºC)	932.5	915.4	1847.9	91 : 9

[a]Auger parameter: Cu $2p_{3/2}$ XPS binding energy + Cu $L_3M_{45}M_{45}$ AES kinetic energy.

References

1. C. Perego, S. Peratello, Catal. Today, 52 (2-3) (1999), pp. 133-145.

2. K. Nakajima, J. Hirata, M. Kim, N.K. Gupta, T. Murayama, A. Yoshida, N. Hiyoshi, A. Fukuoka, W. Ueda, ACS Catal. 8 (1) (2018), pp. 283–290.

3. K. Samson, M. Śliwa, R.P. Socha, K. Góra-Marek, D. Mucha, D. Rutkowska-Zbik, J-F. Paul, M. Ruggiero-Mikołajczyk, R. Grabowski, J. Słoczyński, ACS Catal. 10 (4) (2014), pp. 3730–3741.