Identification of the catalytically active component of Cu-Zr-O catalyst for the hydrogenation of levulinic acid to γ-valerolactone

Supplementary information

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Table S1. Lattice parameters and mixing energies for DFT calculations of Cu doping in 3x3x3 ZrO_2 lattice

Doping %	E_{mixing}/eV	E_{mixing}/x /eV	Lattice Parameters (error) Å		
			a	*b*	*c*
0%	0.00	0.00	3.59	3.6	5.27
2%	0.71	0.71	3.59 (0.02)	3.59 (0.02)	5.20 (0.03)
4%	3.29	1.65	3.58 (0.01)	3.61 (0.02)	5.20 (0.02)
6%	5.79	1.93	3.57 (0.02)	3.61 (0.01)	5.19 (0.03)
8%	7.61	1.90	3.58 (0.03)	3.61 (0.03)	5.18 (0.03)

Table S2. Physicochemical properties of catalysts prepared by Dp or Og method

Catalyst	Cu / (Cu + Zr)[a]	BET surface area[b]/m^2 g^{-1}	CuO particle size[c] /nm	Cu particle size[d] /nm	Cu particle amount[e] /µmol g^{-1}
t-ZrO2	0.0	43.4	-	-	-
7.6Cu (Me)	7.6	64.3	-	-	63
10.7Cu (Og)	10.7	62.6	-	7.6	891
2.5wt%Cu/7.6Cu (Me)	11.6	-	-	19.1	671
41.6Cu (Og)	41.6	57.9	8.5	17.1	4130
20wt%Cu/t-ZrO_2	33.3	44.2	9.1	50.2	3831
20wt%Cu/7.6Cu (Me)	36.9	55.9	8.5	46.3	3954

[a] Determined by ICP. The value in bracket represents the bulk composition after the reduction.
[b] Obtained by N_2 adsorption at liq. N_2 temperature. Surface area in bracket is the one of the reduced catalysts.
[c] Obtained by XRD of the oxidized catalysts and estimated from scherrer equation.
[d] Obtained by XRD of the reduced catalysts and estimated from scherrer equation.
[e] Estimated by TPR signal area.

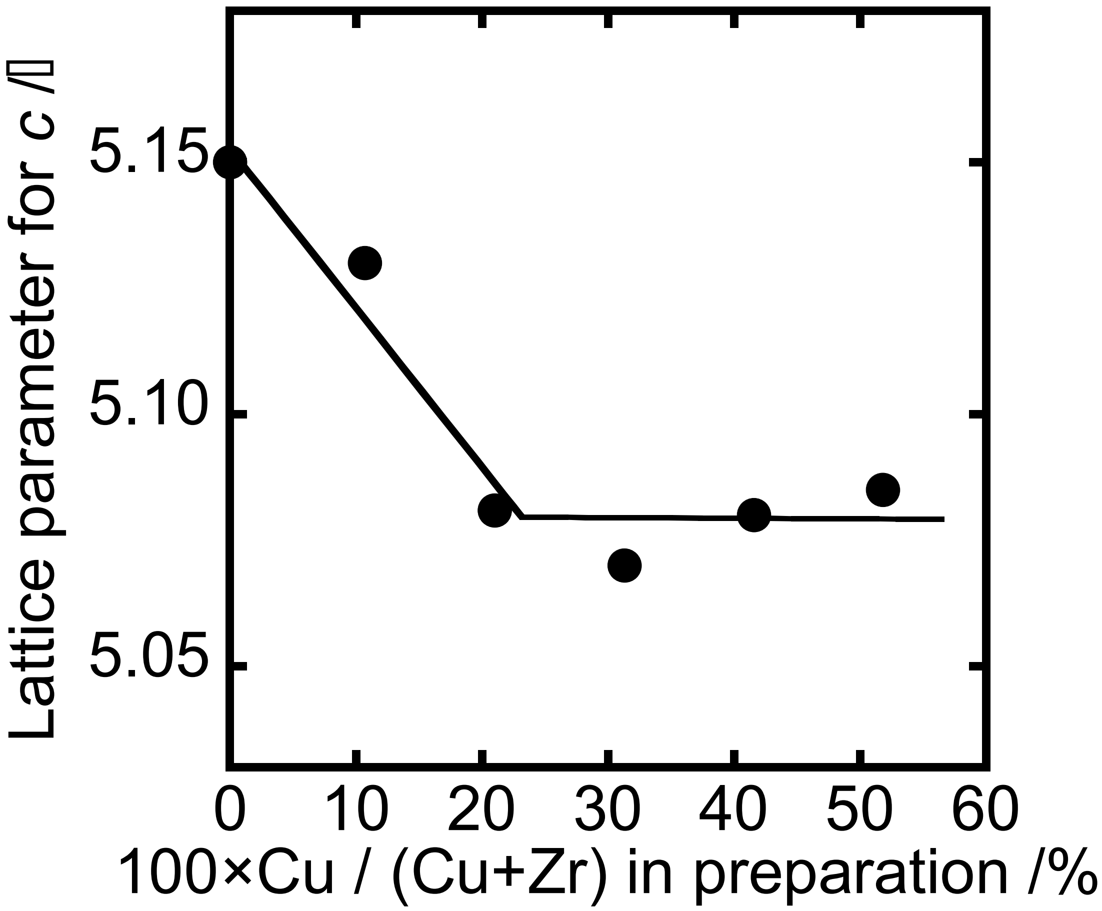

Figure S1. Narrowed region of PXRD patterns of calcined and reduced catalysts (for Figure 2)

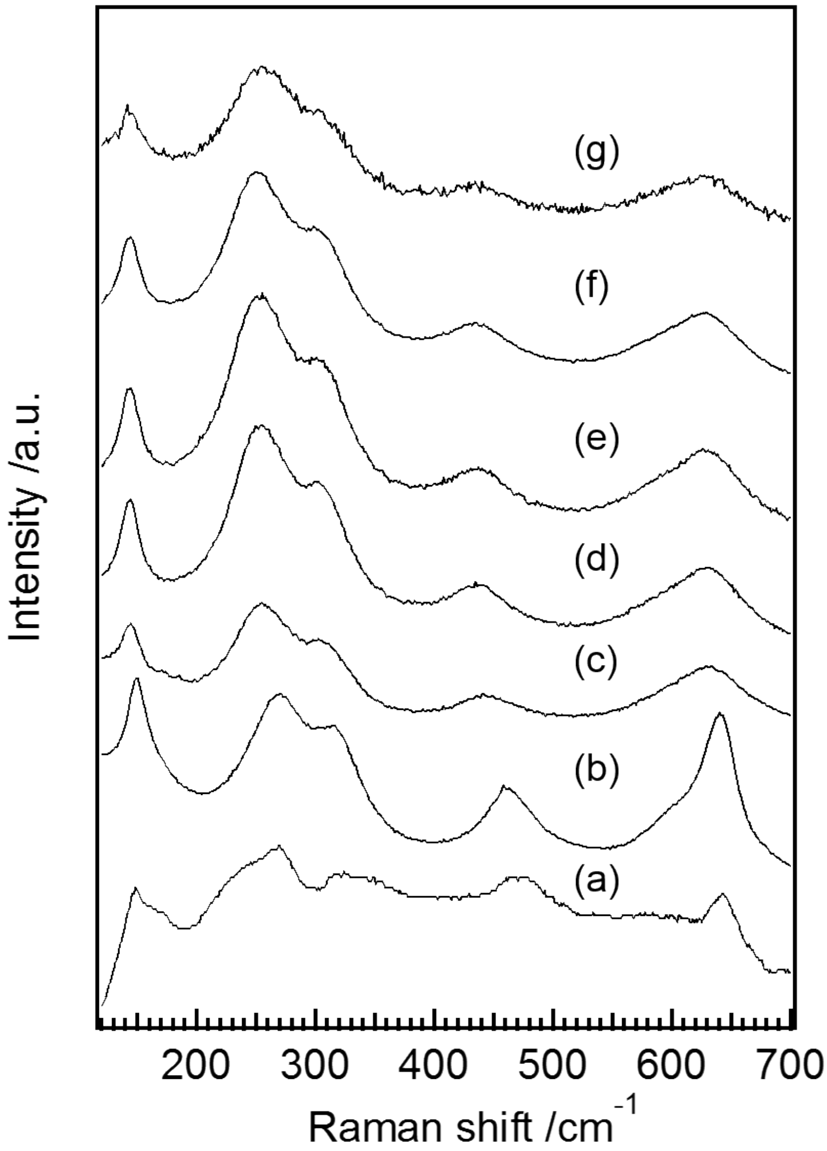

Figure S2. Raman spectra of (a) t-ZrO_2, (b) 7.6Cu (Me), (c) 10.7Cu (Og), (d) 21.0Cu (Og), (e) 31.3Cu (Og), (f) 41.6Cu (Og), and (g) 51.8Cu (Og).

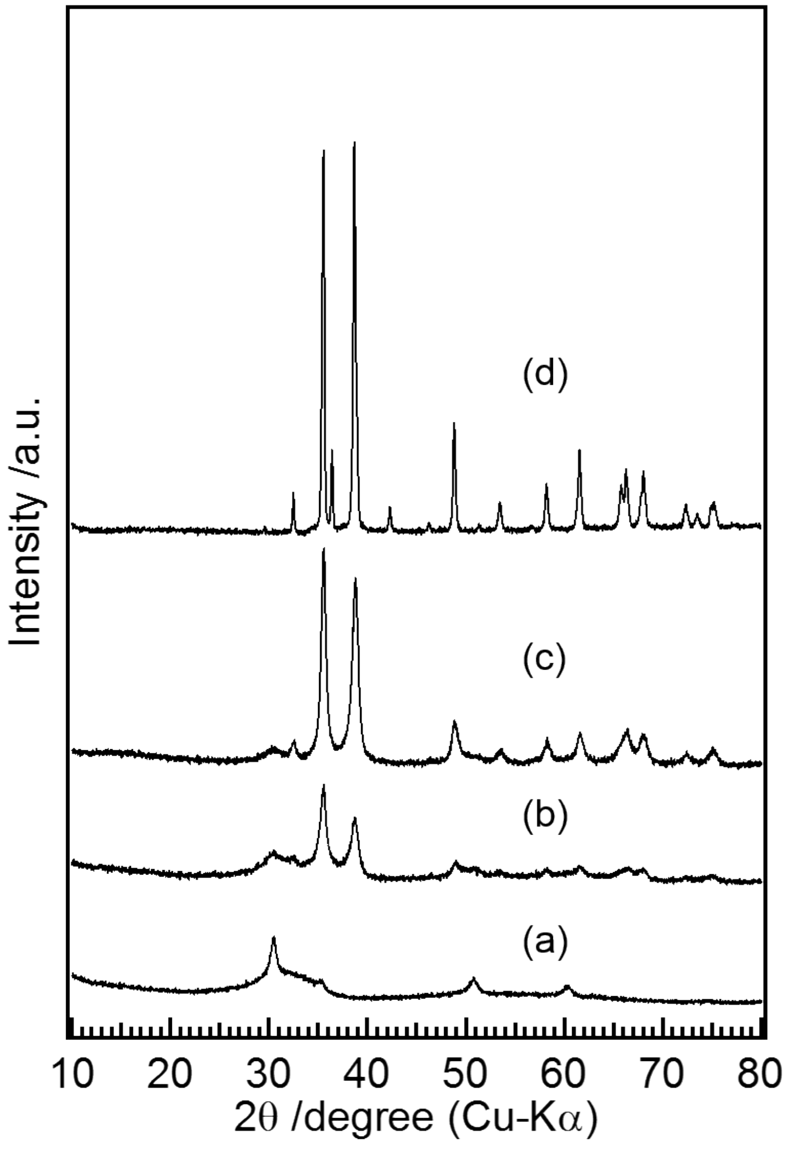

Figure S3. XRD patterns of (a) 14.8Cu (Me), (b) 71.7Cu (Og), (c) 91.7Cu (Og), (d) 100 Cu (Og).

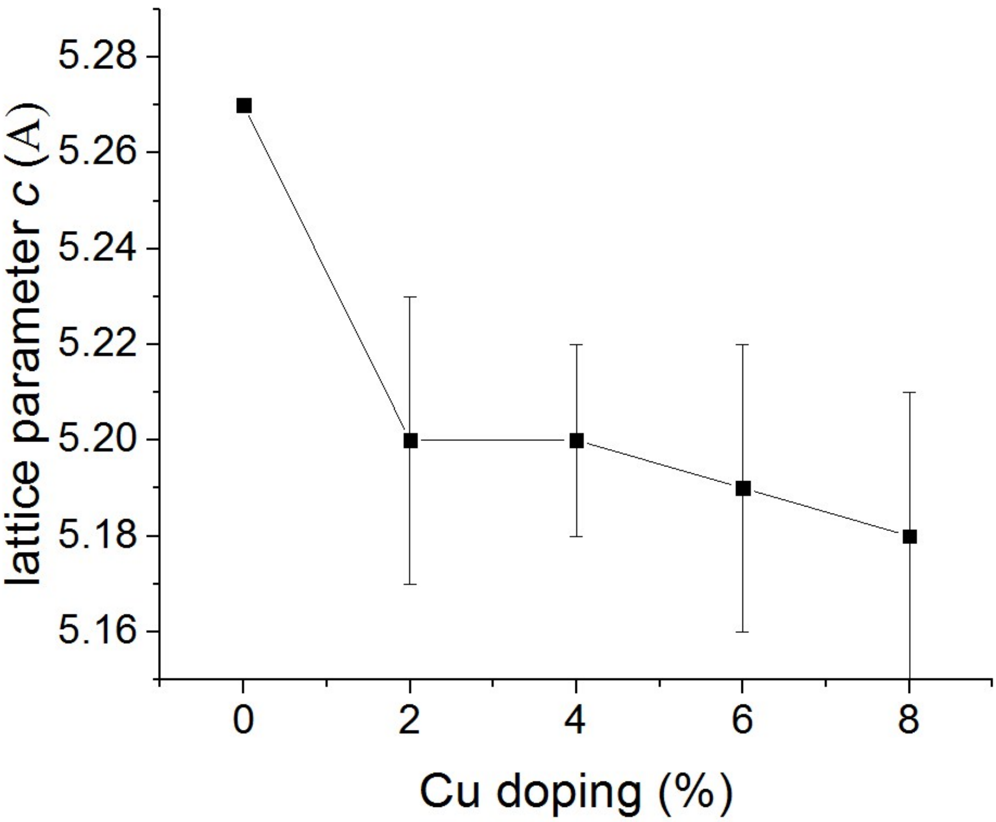

Figure S4. Lattice parameters *c* as a function of Cu doping into the ZrO_2 lattice.

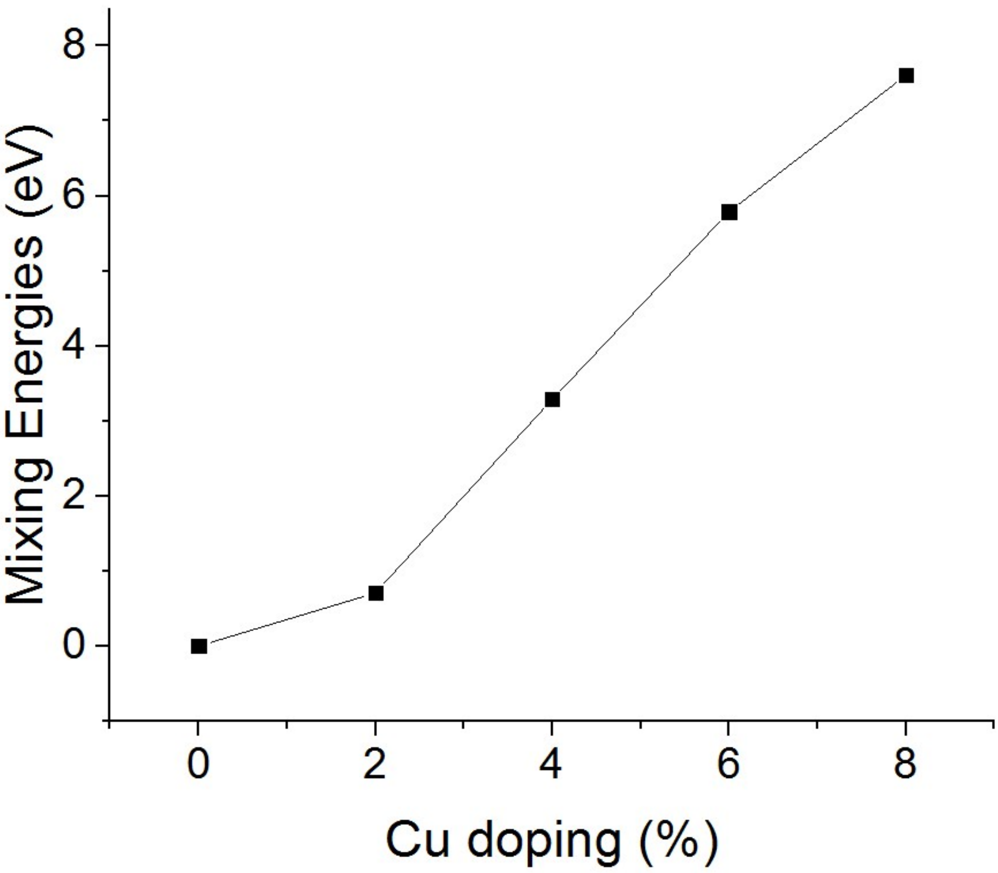

Figure S5. Mixing energy as a function of Cu doping into the ZrO_2 lattice.

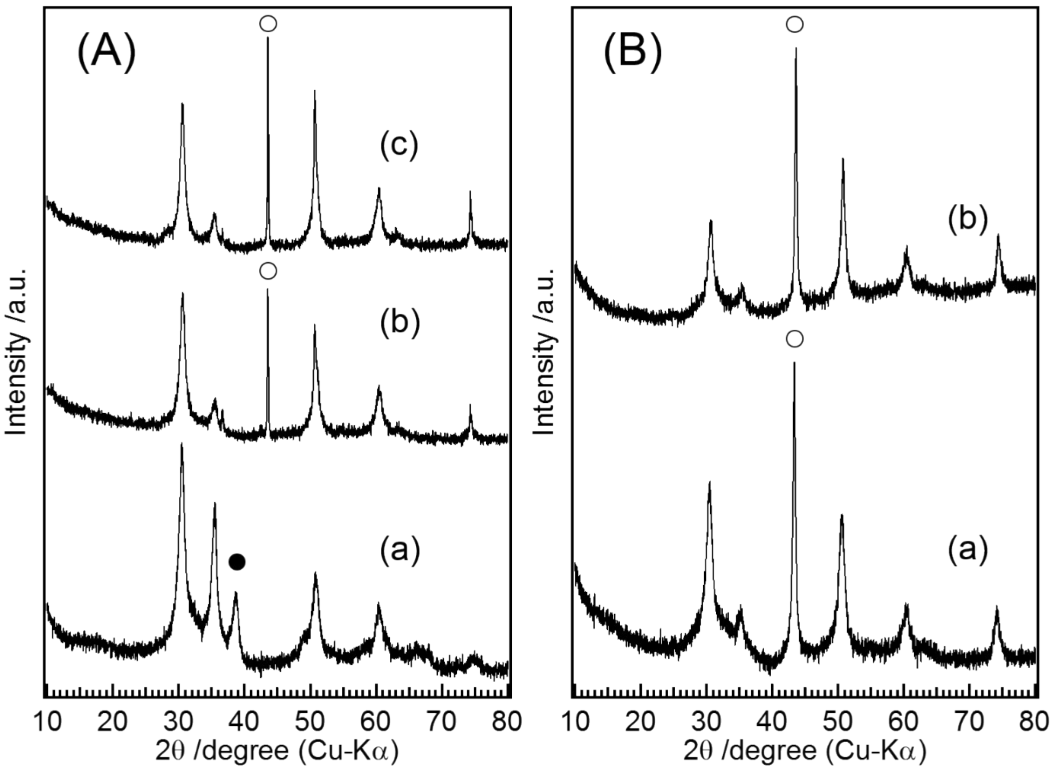

Figure S6. XRD patterns of 51.8Cu (Og) catalyst before (A) and after (B) the reduction. (a) before the reaction, (b) after the reaction for 30 min, (c) after the reaction for 4 h. ●CuO. ○Cu metal.

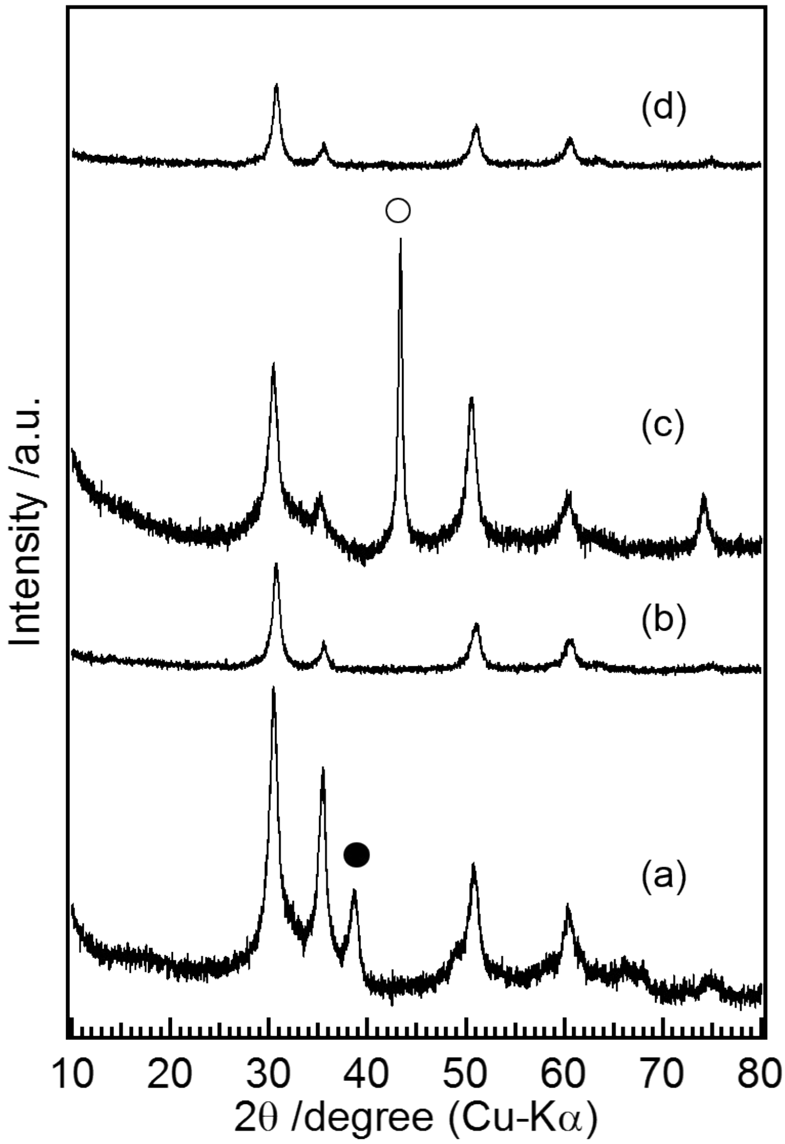

Figure S7. XRD patterns of (a) 51.8Cu (Og), (b) 51.8Cu (Og)-AR (Og), (c) 51.8Cu (Og)-HR, (d) 51.8Cu (Og)-AR-HR. ●CuO. ○Cu metal.

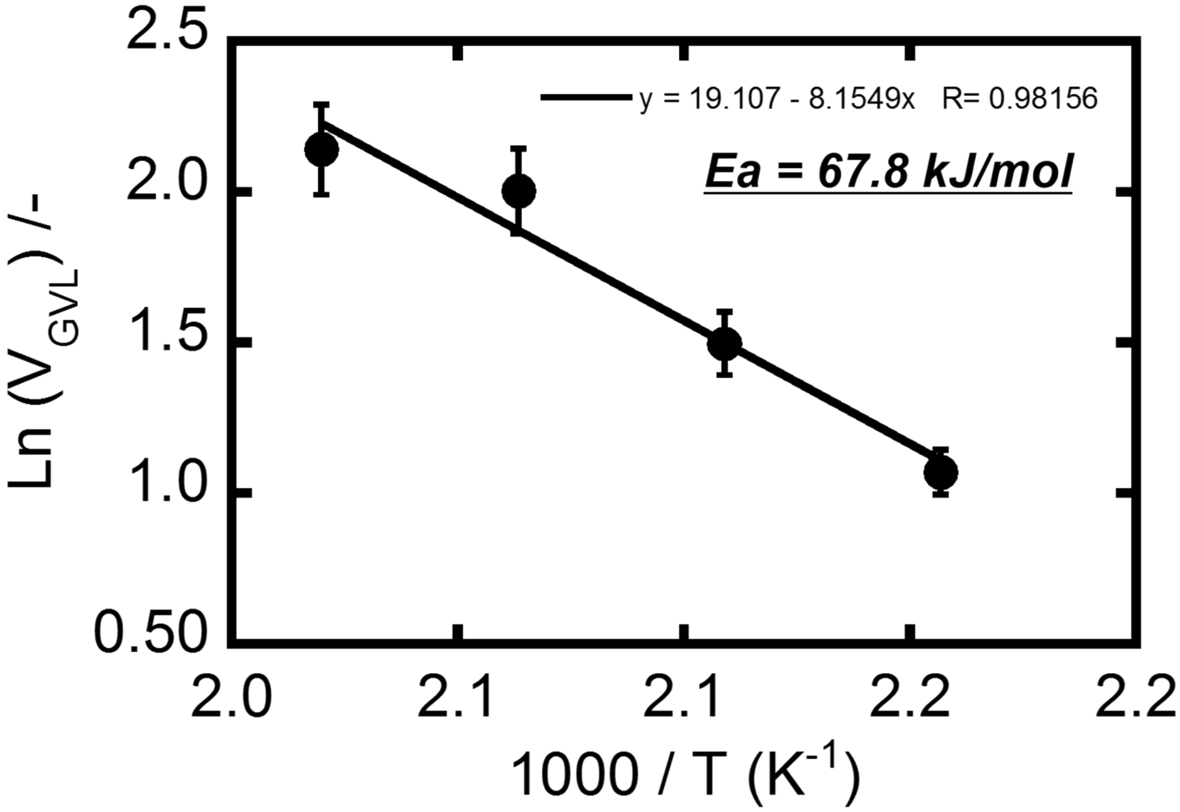

Figure S8. Arrenius plot of the reaction. Catalyst amount was changed from 0.010 g to 0.025 g in order to set the LA conversion below 10%. *Reaction conditions:* 180 °C to 210 °C, 30 min, 35 barg H_2.

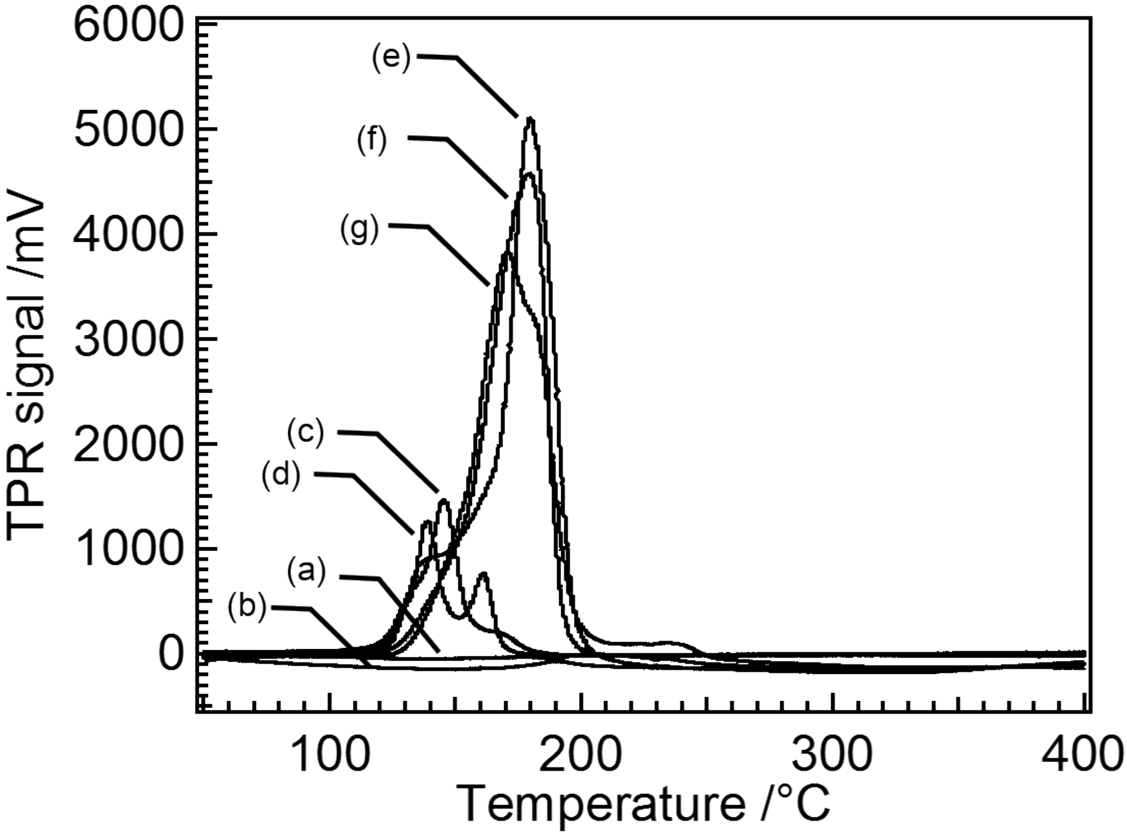

Figure S9. TPR spectra of (a) t-ZrO_2, (b) 7.6Cu (Me), (c) 10.7Cu (Og), (d) 2.5Cu/ 7.6Cu (Me), (e) 41.6Cu (Og), (f) 20Cu/t-ZrO_2, and (g) 20Cu/7.6Cu (Me).

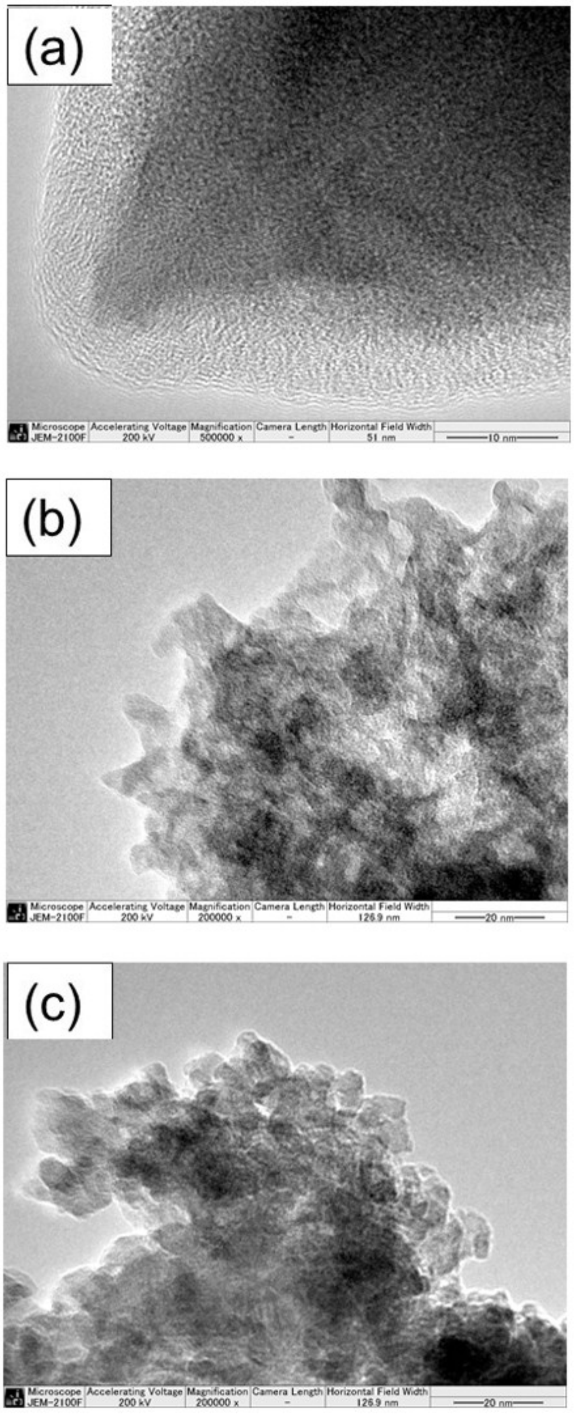

Figure S10. TEM images of (a) 720Cu(Me), (b) 20Cu(Og), (c) 50Cu(Og).

Cu particle and bulk Cu ratios of the catalysts were calculated as follows.

Cu amounts in the entire catalyst is

$$Cu : Zr = x : (100-x) \qquad (1)$$

where x corresponds to the entire Cu ratio estimated by ICP.

y g of catalyst was used for TPR analysis. Cu amount (gram) in y g is

$$(x/100) \times y \text{ (g)} = xy/100 \text{ (g)} \qquad (2)$$

Theoretical Cu amount (mol) is $(xy/100)$ / M_{CuO} (mol), where M_{CuO} corresponds molecular weight of CuO. Therefore, the theoretical entire Cu amount is

$$10^4 \text{ xy} / M_{CuO} \text{ (μmol)} / y \text{ (g)} = 10^4 x / M_{CuO} \text{ (μmol g}^{-1}\text{)} \qquad (3)$$

The ratio of Cu particles (Cu_{sur}) is

$$Cu_{sur} = x \times \{CuO_{TPR} / (10^4 x / M_{CuO})\} = (CuO_{TPR} \times M_{CuO}) / 10^4 \qquad (4)$$

where CuO_{TPR} corresponds to the CuO amount estimated by TPR (μmol g^{-1}).

The ratio of Cu bulk (Cu_{bulk}) is

$$Cu_{bulk} = x - Cu_{sur} \qquad (5)$$