Supporting Information

Rate enhancement by Cu in Ni_xCu_{1-x}/ZrO_2 bimetallic catalysts for hydrodeoxygenation of stearic acid

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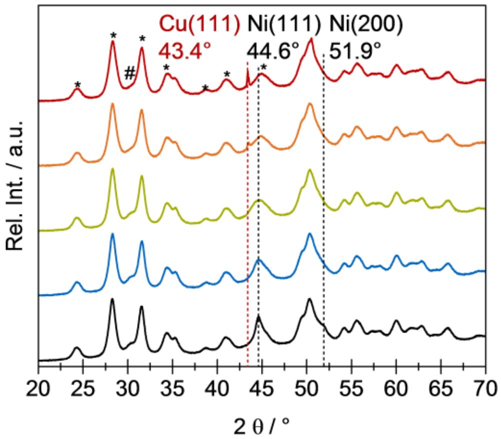


Fig. S1 XRD patterns of Ni_xCu_{1-x}/ZrO_2 (x = 1, 0.79, 0.59, 0.29, 0) in the 2θ range of 20–70°. Monoclinic ZrO_2 (*), tetragonal ZrO_2 (#).

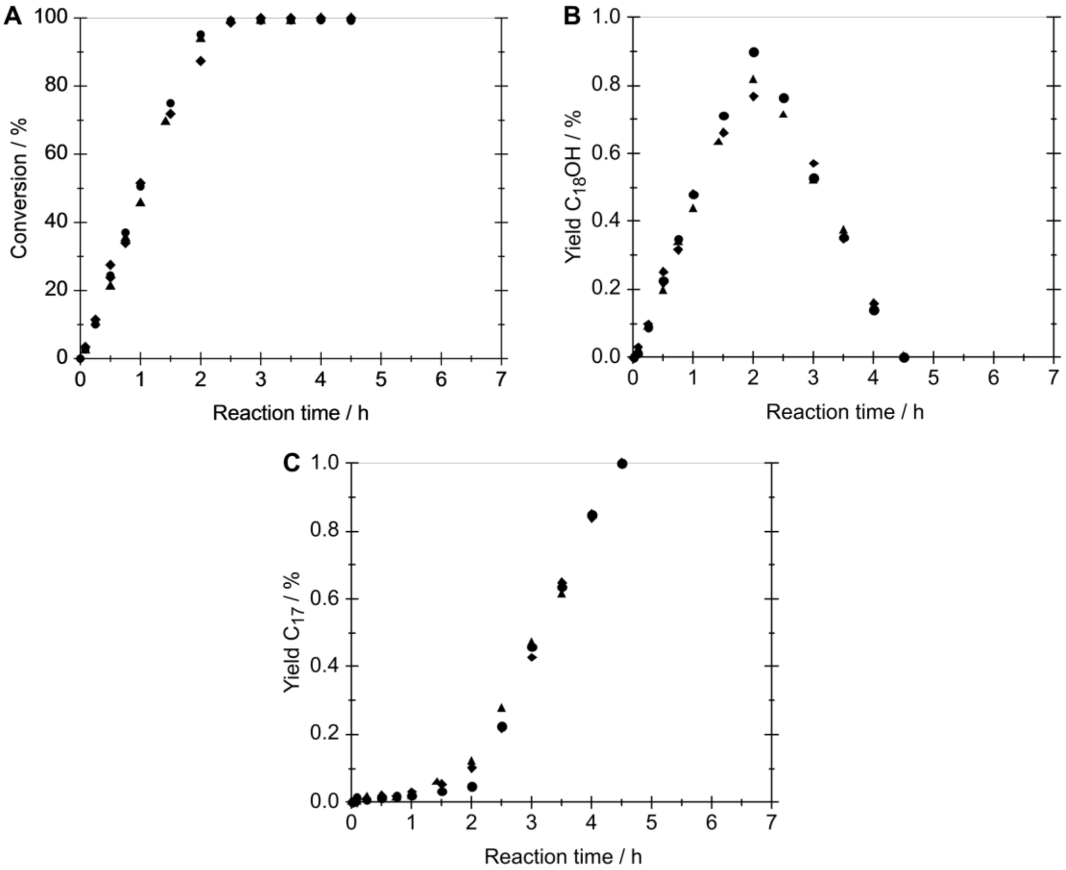


Fig. S2 Recycling experiments (**S2A**/Conversion vs reaction time; **S2B**/Yield of $C_{18}OH$ vs reaction time; **S2C**/Yield C_{17} vs reaction time). (● 1st, ♦ 2nd, ■ 3rd cycle) Reaction conditions: stearic acid (0.212 g), $Ni_{0.59}Cu_{0.41}/ZrO_2$ (0.085 g), *n*-dodecane (100 mL), 260 °C, $p(H_2)$ = 40 bar, stirring at 600 rpm. At 25°C stearic acid (0.212 g) was added for a new experiment. The reaction volume was balanced with *n*-dodecane to 100 mL prior. Assuming that 0 % *n*-heptadecane was produced within the first 5 min of reaction time, this amount was subtracted in runs 2 and 3 from each sample.

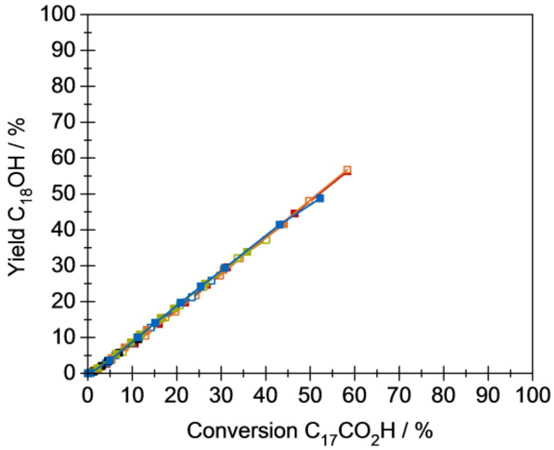


Fig. S3 Yield of 1-octadecanol as function of stearic acid conversion over Ni_xCu_{1-x}/ZrO_2 (x = 1, 0.79, 0.59, 0.29, 0) and respective physical mixtures (empty symbols) Reaction conditions: Stearic acid (0.5 g), Stearic acid (0.5 g), (x) Ni/ZrO_2 and (1-x) Cu/ZrO_2 catalyst (x = 1, 0.79, 0.59, 0.29, 0; sum 0.05 g), *n*-dodecane (100 mL), 260 °C, $p(H_2)$ = 40 bar, 600 rpm.

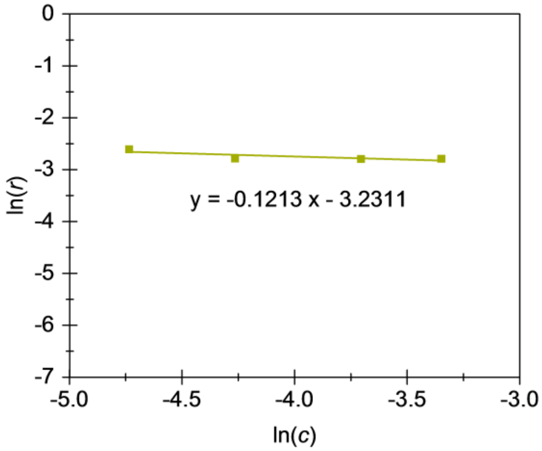


Fig. S4 Determination of reaction order of stearic acid for $Ni_{0.59}Cu_{0.41}/ZrO_2$. Reaction conditions: Stearic acid (1.0 – 0.250 g), $Ni_{0.59}Cu_{0.41}/ZrO_2$ catalyst (0.05 g), *n*-dodecane (100 mL), T = 260, °C, $p(H_2)$ = 40 bar, stirring at 600 rpm.

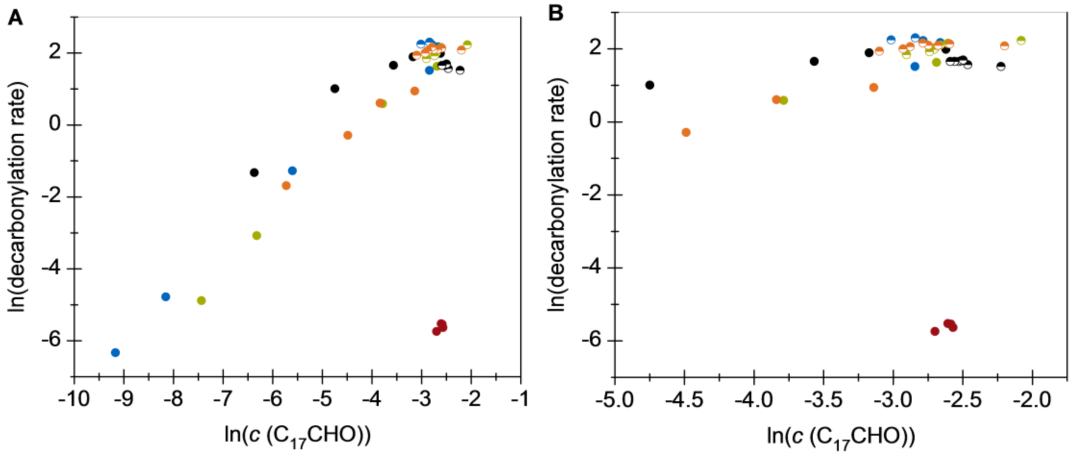


Fig. S5 Determination of reaction order of 1-octadecanal for Ni_xCu_{1-x}/ZrO_2 (x = 1, 0.79, 0.59, 0.29); **A** full concentration range first order regime – 10 < ln(c($C_{17}CHO$)) < – 5 and zero order regime ln(c($C_{17}CHO$)) > – 4; **B** zero order regime. Reaction conditions: Stearic acid (0.5 g), Ni_xCu_{1-x}/ZrO_2 catalyst (x = 1, 0.79, 0.59, 0.29, 0; 0.2 g (full symbols, 0.05g half symbols), *n*-dodecane (100 mL), T = 260 °C, $p(H_2)$ = 40 bar, stirring at 600 rpm.

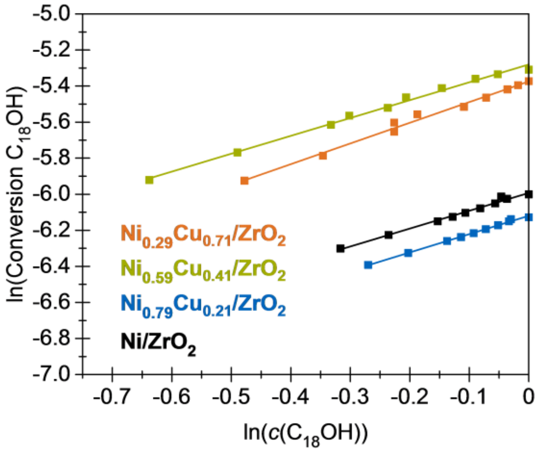


Fig. S6 Determination of reaction order of 1-octadecanol conversion for Ni_xCu_{1-x}/ZrO_2 (x = 1, 0.79, 0.59, 0.29) Reaction conditions: 1-octadecanol (0.5 g), Ni_xCu_{1-x}/ZrO_2 catalyst (x = 1, 0.79, 0.59, 0.29; 0.05 g), *n*-dodecane (100 mL), T = 260 °C, $p(H_2)$ = 40 bar, stirring at 600 rpm.

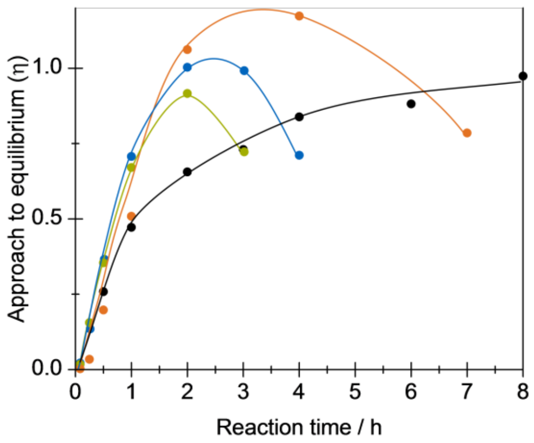


Fig. S7 Approach to equilibrium between 1-octadecanol and 1-octadecanal versus reaction time for Ni_xCu_{1-x}/ZrO_2 (x = 1, 0.79, 0.59, 0.29) Reaction conditions: Stearic acid (0.5 g), Ni_xCu_{1-x}/ZrO_2 catalyst (x = 1, 0.79, 0.59, 0.29; 0.2 g), *n*-dodecane (100 mL), T = 260 °C, $p(H_2)$ = 40 bar, stirring at 600 rpm.

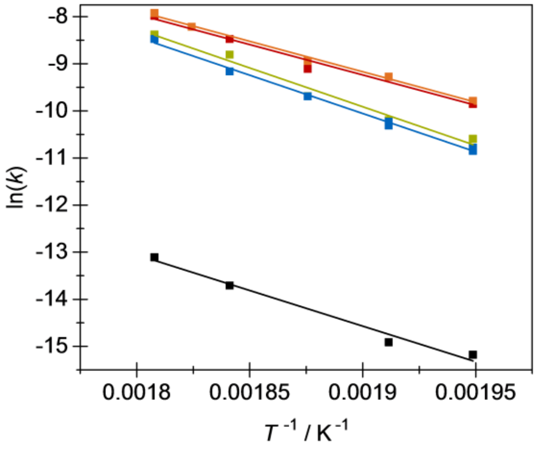


Fig. S8 Arrhenius-plot for the conversion of stearic acid to 1-octadecanol on Ni_xCu_{1-x}/ZrO_2 catalyst (x = 1, 0.79, 0.59, 0.29, 0) Reaction conditions: Stearic acid (0.5 g), Ni_xCu_{1-x}/ZrO_2 catalyst (x = 1, 0.79, 0.59, 0.29, 0; 0.05 g), *n*-dodecane (100 mL), T = 240 — 280 °C, $p(H_2)$ = 40 bar, stirring at 600 rpm.

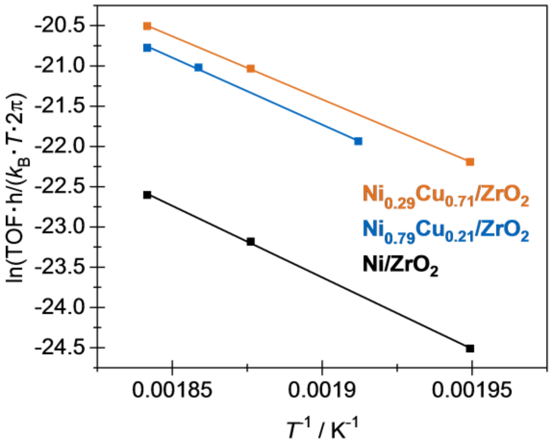


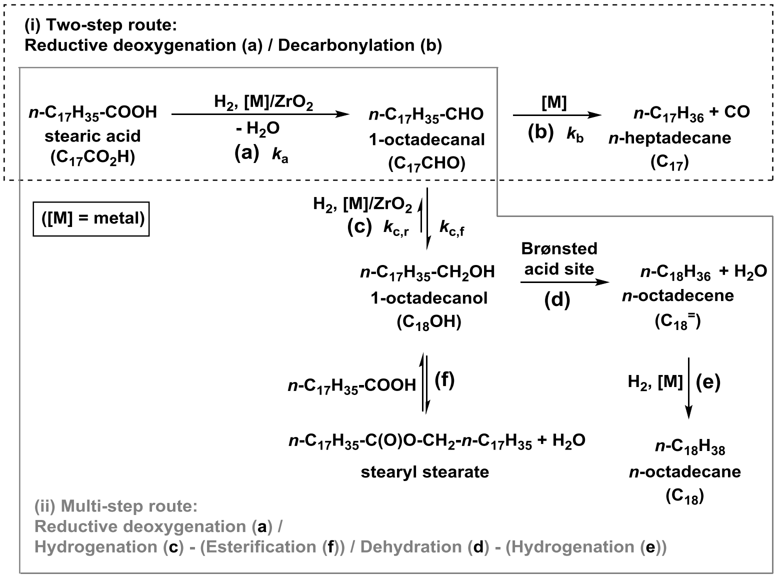
Fig. S9 Determining ΔH and ΔS by using Eyring equation for the decarbonylation of 1-octadecanal over Ni_xCu_{1-x}/ZrO_2 catalyst (x = 1, 0.79, 0.29) Reaction conditions: 1-octadecanol (0.5 g), Ni_xCu_{1-x}/ZrO_2 catalyst (x = 1, 0.79, 0.29; 0.05 g), *n*-dodecane (100 mL), T = 240 – 270°C, $p(H_2)$ = 40 bar, stirring at 600 rpm.

Table S1 Detailed amounts of ZrO_2, $Ni(NO_3)_2$ × $6H_2O$ and $Cu(NO_3)_2$ × xH_2O to synthesize bimetallic Ni_xCu_{1-x}/ZrO_2 via wet impregnation technique.

Catalyst	$m(ZrO_2)$ / g	$m[Ni(NO_3)_2 \times 6H_2O]$ / g	$m[Cu(NO_3)_2 \times xH_2O]$ / g
Ni/ZrO_2	7.0	3.85	–
$Ni_{0.79}Cu_{0.21}/ZrO_2$	7.0	2.89	0.57
$Ni_{0.59}Cu_{0.41}/ZrO_2$	7.0	1.93	1.15
$Ni_{0.29}Cu_{0.71}/ZrO_2$	7.0	0.96	1.72
Cu/ZrO_2	7.0	–	2.30

Kinetic analysis

The kinetic analysis was made based on the below reaction network with the analysis of step (**a**), (**b**) (**c**). (The same scheme in the manuscript is numbered as **Scheme 1**). The reaction rate constant in each step is given as well.



Stearic acid, 1-octadecanal and 1-octadecanol competitively adsorb on catalyst, hence their coverage on catalysts are expressed as:

$$\theta_{\mathrm{Acid}} = \frac{K_{\mathrm{Acid}} c_{\mathrm{Acid}}}{1 + K_{\mathrm{Acid}} c_{\mathrm{Acid}} + K_{\mathrm{Ald}} c_{\mathrm{Ald}} + K_{\mathrm{Alco}} c_{\mathrm{Alco}}} \quad \textbf{(Eqn S1)}$$

$$\theta_{\mathrm{Ald}} = \frac{K_{\mathrm{Ald}} c_{\mathrm{Ald}}}{1 + K_{\mathrm{Acid}} c_{\mathrm{Acid}} + K_{\mathrm{Ald}} c_{\mathrm{Ald}} + K_{\mathrm{Alco}} c_{\mathrm{Alco}}} \quad \textbf{(Eqn S2)}$$

$$\theta_{\mathrm{Alco}} = \frac{K_{\mathrm{Alco}} c_{\mathrm{Alco}}}{1 + K_{\mathrm{Acid}} c_{\mathrm{Acid}} + K_{\mathrm{Ald}} c_{\mathrm{Ald}} + K_{\mathrm{Alco}} c_{\mathrm{Alco}}} \quad \textbf{(Eqn S3)}$$

The θ_{Acid}, θ_{Ald} and θ_{Alco} are the coverages of stearic acid, 1-octadecanal and 1-octadecanol on the catalyst; The K_{Acid}, K_{Ald} and K_{Alco} are their adsorption constants and the c_{Acid}, c_{Ald} and c_{Alco} are the their concentrations.

Their reaction rates are given by

$$\frac{\mathrm{d}c_{\mathrm{Acid}}}{\mathrm{d}t} = -k_{\mathrm{a}} n_{\mathrm{cat}} \theta_{\mathrm{Acid}} \quad \textbf{(Eqn S4)}$$

$$\frac{\mathrm{d}c_{\mathrm{Ald}}}{\mathrm{d}t} = k_{\mathrm{a}} n_{\mathrm{cat}} \theta_{\mathrm{Acid}} - k_{\mathrm{b}} n_{\mathrm{cat}} \theta_{\mathrm{Ald}} - k_{\mathrm{c,f}} n_{\mathrm{cat}} \theta_{\mathrm{Ald}} \quad \textbf{(Eqn S5)}$$

$$\frac{\mathrm{d}c_{\mathrm{Alco}}}{\mathrm{d}t} = -k_{\mathrm{c,r}} n_{\mathrm{cat}} \theta_{\mathrm{Alco}} + k_{\mathrm{c,f}} n_{\mathrm{cat}} \theta_{\mathrm{Ald}} \quad \textbf{(Eqn S6)}$$

in which n_{cat} is the number of active site on the catalysts loaded in the reaction. The formation rate of *n*-heptadecane is

$$\frac{\mathrm{d}c_{\mathrm{Hept}}}{\mathrm{d}t} = k_{\mathrm{b}} n_{\mathrm{cat}} \theta_{\mathrm{Ald}} \quad \textbf{(Eqn S7)}$$

k_{a} is quantified by measuring the initial conversion rate of acid, where θ_{Ald}, θ_{Alco} are zero. Reaction order of acid being zero indicates that θ_{Acid} is 1.

$$\frac{\mathrm{d}c_{\mathrm{Acid}}}{\mathrm{d}t} = -k_{\mathrm{a}} n_{\mathrm{cat}} \Rightarrow k_{\mathrm{a}} = -\frac{1}{n_{\mathrm{cat}}} \frac{\mathrm{d}c_{\mathrm{Acid}}}{\mathrm{d}t} \quad \textbf{(Eqn S8)}$$

Strong inhibition of decarbonylation of aldehyde to alkane by the presence of acid indicates the strong adsorption of acid on catalysts. To determine the decarbonylation rate of aldehyde in absence of stearic acid, we performed the experiments to calculate the decarbonylation rate starting with 1-octadecanol. Since the hydrogenation of the 1-octadecanal is enormously higher than the decarbonylation rate, a direct approach for decarbonylation rates using 1-octadecanal fails.

$$\frac{\mathrm{d}c_{\mathrm{Hept}}}{\mathrm{d}t} = \frac{n_{\mathrm{cat}} k_{\mathrm{b}} K_{\mathrm{Ald}} c_{\mathrm{Ald}}}{1 + K_{\mathrm{Ald}} c_{\mathrm{Ald}} + K_{\mathrm{Alco}} c_{\mathrm{Alco}}} \quad \textbf{(Eqn S9)}$$

The reaction order of aldehyde is zero for the formation of 1-heptadecane, indicating a strong adsorption of aldehyde than alcohol. ($K_{\mathrm{Ald}}c_{\mathrm{Ald}} >> K_{\mathrm{Alco}}c_{\mathrm{Alco}}$; $K_{\mathrm{Ald}}c_{\mathrm{Ald}} >> 1$)

$$\frac{\mathrm{d}c_{\mathrm{Hept}}}{\mathrm{d}t} = n_{\mathrm{cat}} k_{\mathrm{b}} \Rightarrow k_{\mathrm{b}} = \frac{1}{n_{\mathrm{cat}}} \frac{\mathrm{d}c_{\mathrm{Hept}}}{\mathrm{d}t} \quad \textbf{(Eqn S10)}$$