

Combined 1,4-Butanediol Lactonization and Transfer Hydrogenation/Hydrogenolysis of Furfural-Derivatives under Continuous Flow Conditions

Supporting Information

Table S1. Screening of different supports. Performance of Cu catalysts with different supports at a residence time of 0.25 min (activation T : 250 °C, (25 mL min⁻¹ H₂ flow, 45 min), c_{BDO} : 0.2 mol L⁻¹, C_{furfural} : 0.2 mol L⁻¹, p : 16 bar, T : 220 °C).

Supports	Conversion BDO / %	Yield GBL / %	Conversion furfural / %	Yield FA / %
Cu/AlO _x	29	28	53	52
Cu/SiO ₂	47	32	37	23
Cu/Fe ₂ O ₃	2	<1	4	3

Table S2. Screening of different Cu loadings. Performance of Cu/AlO_x catalysts with different Cu loadings determined by ICP-OES at a residence time of 0.25 min (activation T : 250 °C, (25 mL min⁻¹ H₂ flow, 45 min), c_{BDO} : 0.2 mol L⁻¹, C_{furfural} : 0.2 mol L⁻¹, p : 16 bar, T : 220 °C).

Cu loading (w%)	Conversion BDO / %	Yield GBL / %	Conversion furfural / %	Yield FA / %
39	29	28	53	52
22	24	22	46	44
17	14	13	28	27

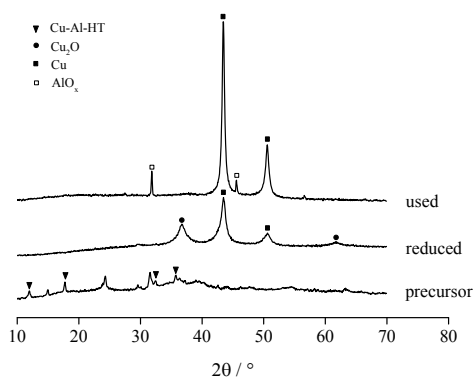


Figure S1. XRD pattern of Cu-Al-HT as prepared, the reduced catalyst ($25 \text{ mL min}^{-1} \text{ H}_2$, 45 min, 200°C) and the catalyst exposed to reaction solution (c_{BDO} : 0.2 mol L^{-1} , c_{furfural} : 0.2 mol L^{-1} , p : 16 bar, T : 220°C) for 6 hours.

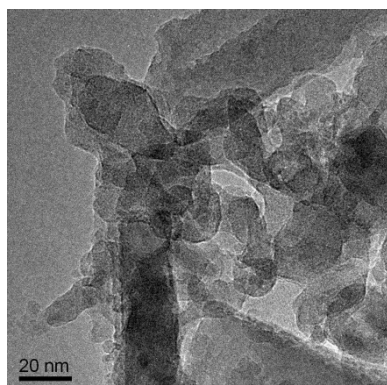


Figure S2. TEM image of untreated Cu-Al-HT.

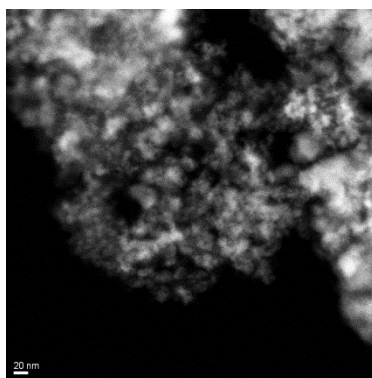


Figure S3. STEM image of Cu-Al-HT after reduction at 200°C .

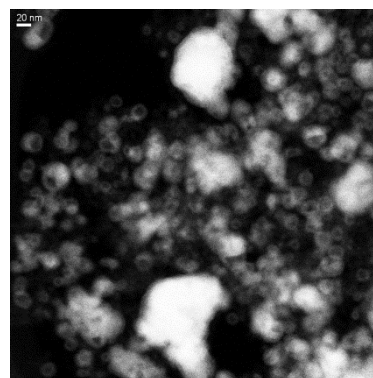


Figure S4. STEM image of Cu-Al-HT, reduced at 200°C , after reaction (6 h).

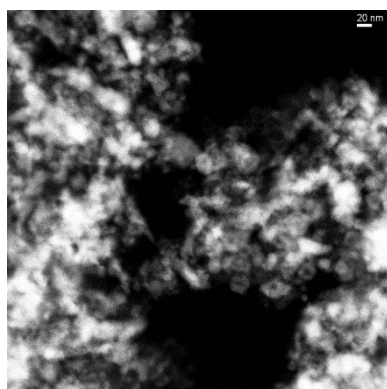


Figure S5. STEM-image of Cu-Al-HT after reduction at 250°C .

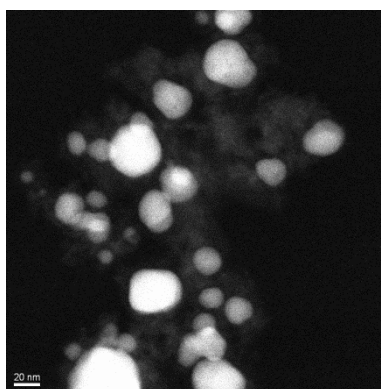


Figure S6. STEM-image of Cu-Al-HT, reduced at 250°C , after reaction (6 h).

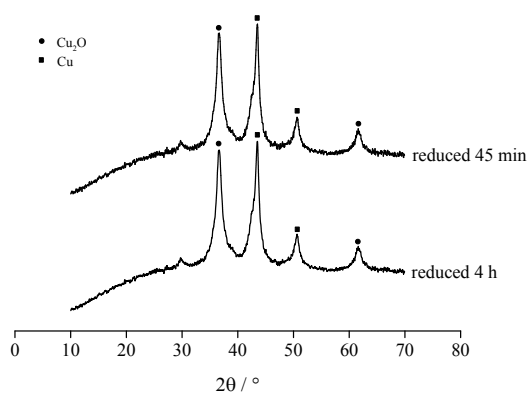


Figure S7. XRD-measurements of reduced Cu-Al-hydrotalcite ($25 \text{ mL min}^{-1} \text{ H}_2$, 45 min or 4 h, 250°C).

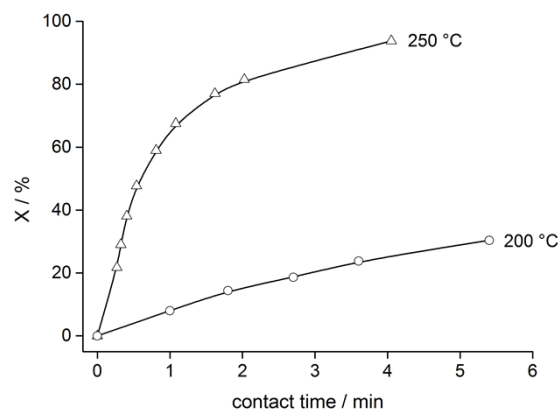


Figure S8. Conversion of BDO vs. residence time at different activation temperatures (activation T : 200 or 250 °C (25 mL min⁻¹ H₂ flow, 45 min), c_{BDO} : 0.2 mol L⁻¹, c_{furfural} : 0.2 mol L⁻¹, p : 16 bar, T : 220 °C).

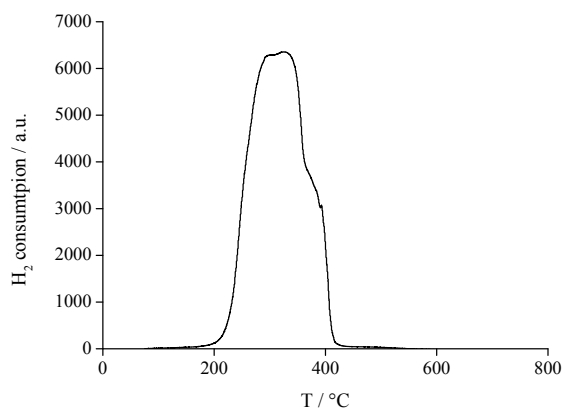


Figure S9. H₂-TPR profile of Cu-Al-hydrotalcite.

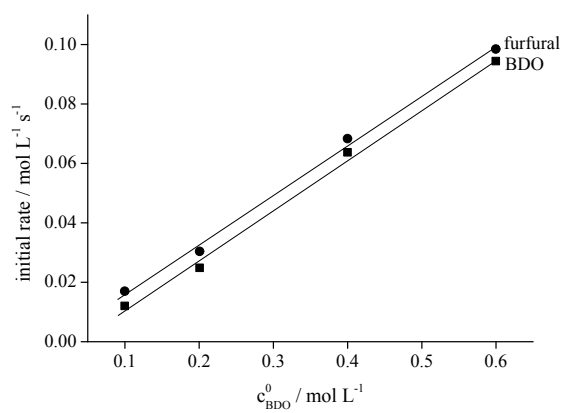


Figure S10. Initial rate vs. BDO concentration (activation T : 250 °C (25 mL min⁻¹ H₂ flow, 45 min), c_{BDO} : 0.1, 0.2, 0.4 and 0.6 mol L⁻¹, c_{furfural} : 0.2 mol L⁻¹, p : 16 bar, T : 230 °C).

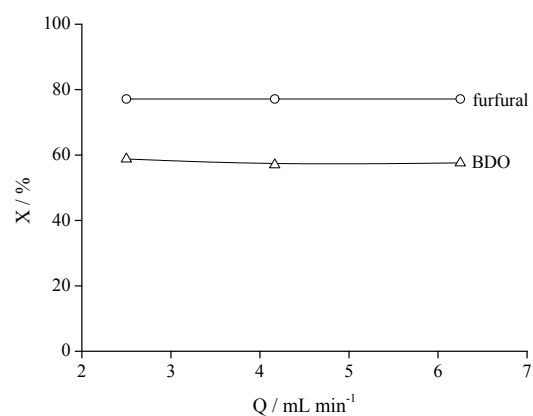


Figure S11. Conversion of BDO and furfural for different column lengths (6 cm, 10 cm and 15 cm) adjusting the flow rate to keep the residence time at 0.45 min (activation T : 250 °C (25 mL min⁻¹ H₂ flow, 45 min), c_{BDO} : 0.2 mol L⁻¹, c_{furfural} : 0.2 mol L⁻¹, p : 16 bar, T : 220 °C).

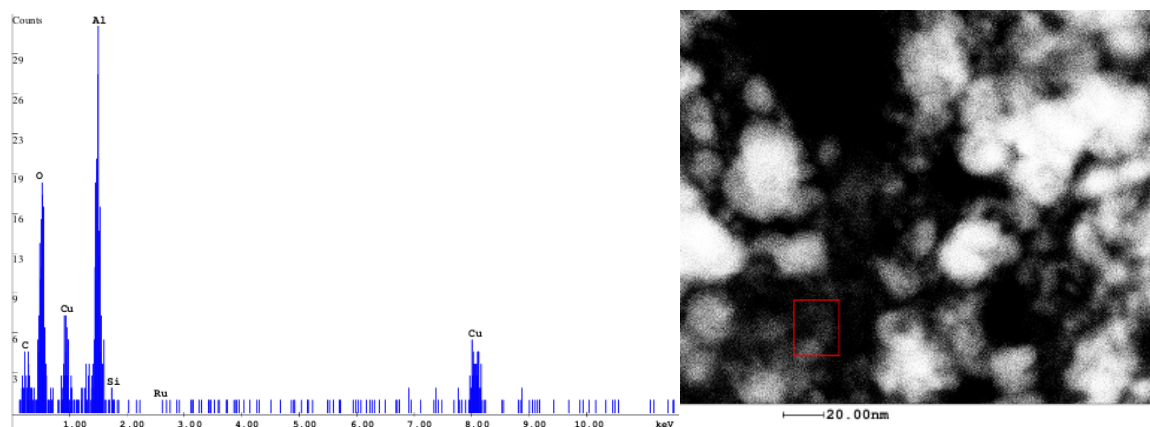


Figure S12. EXDS analysis of Cu-Al-HT after reduction at 240°C.

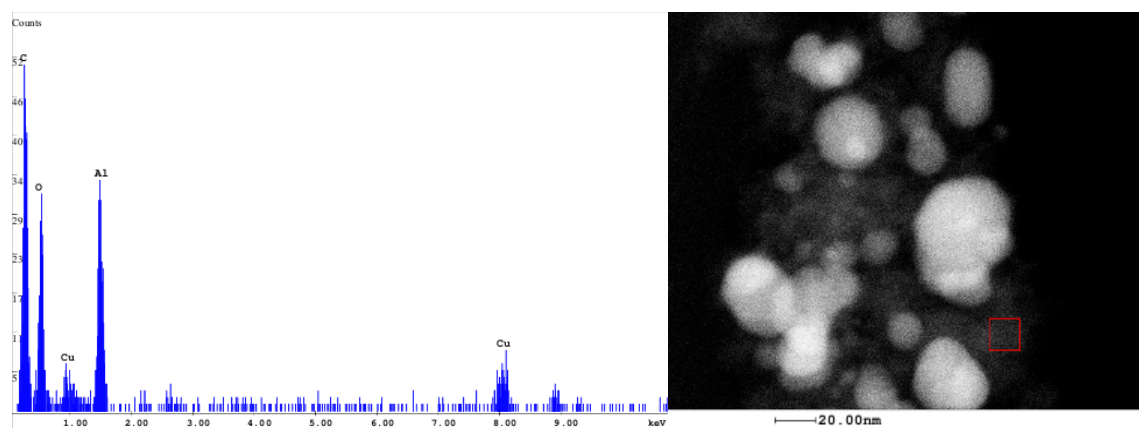


Figure S13. EXDS analysis of Cu-Al-HT (reduced at 240°C) after reaction.

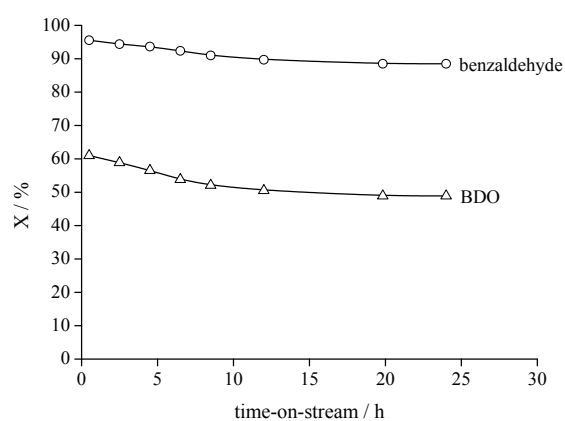


Figure S14. Conversion vs. time-on-stream of a BDO-benzaldehyde mixture. (activation T : 250 °C (25 mL min⁻¹ H₂ flow, 45 min), c_{BDO} : 0.2 mol L⁻¹, $c_{\text{benzaldehyde}}$: 0.2 mol L⁻¹, Q : 0.8 mL min⁻¹, p : 16 bar, T : 220 °C).

Calculation of liquid hold up and residence times

The liquid hold up was calculated according to the correlation of Larachi *et al.* (V. V. Ranade, R. Chaudhari and P. R. Gunjal, *Trickle Bed Reactors, Reactor Engineering & Applications*, Elsevier B.V., Oxford, 2011), in this example for the hydrogenolysis of HMF:

$$\log(1 - \beta) = \frac{-1.22 \cdot We_L^{0.15}}{Re_L^{0.2} \cdot X_G^{0.15}} \Rightarrow \beta = 1 - 10^{\frac{-1.22 \cdot We_L^{0.15}}{Re_L^{0.2} \cdot X_G^{0.15}}} \quad (1)$$

β : liquid saturation ($\frac{\text{liquid volume}}{\text{void volume}}$)

$$We_L = \frac{U_L^2 \cdot d_p \cdot \rho_L}{\sigma_L} \quad (2) \quad \text{Weber number}$$

$$U_L = \frac{Q_L}{\pi \cdot \left(\frac{d_r}{2}\right)^2 \cdot \varepsilon} \quad (3) \quad \text{liquid velocity } \left(\frac{m}{s}\right)$$

d_p : particle size (m)

ρ_L : liquid density ($\frac{kg}{m^3}$)

σ_L : liquid surface tension ($\frac{N}{m}$)

d_r : reactor diameter (m)

Q_L : liquid volumetric flow rate ($\frac{m^3}{s}$)

ε : void fraction

$$Re_L = \frac{\rho_L \cdot U_L \cdot d_r}{\mu_L} \quad (4) \quad \text{Reynolds number}$$

μ_L : liquid dynamic viscosity ($Pa \cdot s$)

$$X_G = \left(\frac{U_L \sqrt{\rho_L}}{U_G \sqrt{\rho_G}} \right)^{-1} \quad (5) \quad \text{modified Lockhart-Martinelli number}$$

$$U_G = \frac{Q_G}{\pi \cdot \left(\frac{d_r}{2}\right)^2 \cdot \varepsilon} \quad (6) \quad \text{gas velocity } \left(\frac{m}{s}\right)$$

$$Q_G = \frac{1}{2} \frac{c_{H_2} \cdot R \cdot T \cdot Q_L}{p} \quad (7) \quad \text{mean gas volumetric flow rate } \left(\frac{m^3}{s}\right)$$

R : universal gas constant ($\frac{J}{mol \cdot K}$)

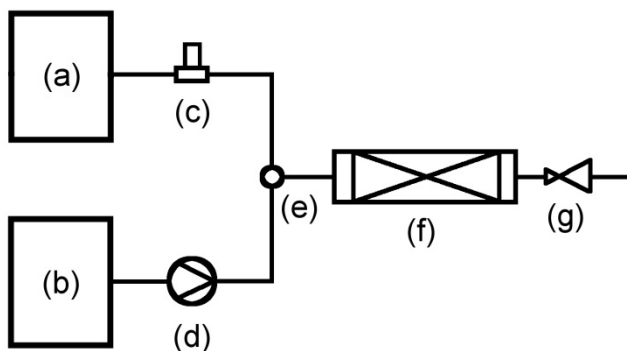
$$c_{H_2} = 2 \cdot c_{GBL} - c_{BHMF} - 3 \cdot c_{DMEF} - 2 \cdot c_{MFA} - L_{H_2} \quad (8) \quad \text{concentration of hydrogen gas } \left(\frac{mol}{m^3}\right)$$

c_{GBL} :	concentration of γ -butyrolactone ($\frac{mol}{m^3}$)	
c_{BHMF} :	concentration of 2,5-bis(hydroxymethyl)furan ($\frac{mol}{m^3}$)	
c_{DMF} :	concentration of 2,5-dimethylfuran ($\frac{mol}{m^3}$)	
c_{MFA} :	concentration of 5-methylfurfuryl alcohol ($\frac{mol}{m^3}$)	
$L_{H_2} = k_H \cdot \rho_L \cdot p_{H_2}$:	solubility of hydrogen ($\frac{mol}{m^3}$)	(9)
p_{H_2} :	partial hydrogen pressure (Pa)	
k_H :	Henry's law constant ($\frac{mol}{kg \cdot Pa}$)	
$\rho_G = \frac{p}{R_s \cdot T}$:	gas density ($\frac{kg}{m^3}$)	(10)
R_s :	specific gas constant ($\frac{J}{kg \cdot K}$)	
T :	reaction temperature (K)	
$\tau = \frac{(\frac{d_r}{2})^2 \cdot \pi \cdot l \cdot \varepsilon \cdot \beta}{Q_L}$:	residence time (s)	
(11)		
l :	reactor length (m)	

T	503	K
R	8.314	$\frac{J}{mol \cdot K}$
R_s	4124	$\frac{J}{kg \cdot K}$
p	$1.6 \cdot 10^6$	Pa
p_{H_2}	$1.6 \cdot 10^6$	Pa
ρ_L	1033	$\frac{kg}{m^3}$
ρ_G	$7.713 \cdot 10^{-1}$	$\frac{kg}{m^3}$
k_H	$7.8 \cdot 10^{-9}$	$\frac{mol}{kg \cdot Pa}$
L_{H_2}	12.9	$\frac{mol}{m^3}$
c_{GBL}	413.5	$\frac{mol}{m^3}$
c_{BHMF}	144.4	$\frac{mol}{m^3}$
c_{DMeF}	23.8	$\frac{mol}{m^3}$
c_{MFA}	27.6	$\frac{mol}{m^3}$
c_{H_2}	543.1	$\frac{mol}{m^3}$
Q_L	$8.3 \cdot 10^{-9}$	$\frac{m^3}{s}$
Q_G	$5.9 \cdot 10^{-9}$	$\frac{m^3}{s}$
U_L	$7.7 \cdot 10^{-4}$	$\frac{m}{s}$
U_G	$5.5 \cdot 10^{-4}$	$\frac{m}{s}$
d_r	$4.6 \cdot 10^{-3}$	m
d_p	$1.5 \cdot 10^{-4}$	m
ε	0.35	-
μ_L	1.178	$Pa \cdot s$
σ_L	33.32	$\frac{N}{m}$
X_G	$1.94 \cdot 10^{-2}$	-
Re_L	$3.11 \cdot 10^{-3}$	-

We_L	$2.77 \cdot 10^{-9}$	-
β	0.57	-
l	$1.5 \cdot 10^{-1}$	m
τ	110.3	s

Table 2. Physical properties and calculated liquid hold up according to equation (1) and residence time according to equation (11) for transfer hydrogenation/hydrogenolysis of HMF (c_{BDO} : 0.6 mol L^{-1} , c_{HMF} : 0.2 mol L^{-1} , p : 16 bar, T : 220 °C).



Scheme S1. Reactor set-up used in this work with (a) H_2 reservoir (gas cylinder: 50 L, 200 bar, purity: 99.995 %) (b) liquid reactant reservoir (Schott flask 1 L), (c) mass-flow controller (Brooks 5850E series), (d) HPLC pump (Jasco PU-980), (e) T-ball-valve (Swagelok 1/8 inch), (f) fixed-bed reactor (Swagelok stainless steel tube 1/4 inch) and (g) back-pressure regulator (Swagelok 0-375 psi). Swagelok tubing (Teflon and stainless steel) and connections (all 1/8 inch) were used for the reactor set-up.