Supporting Information:

Dehydrogenative coupling promoted by copper catalysts: a way to optimise and upgrade bio-alcohols

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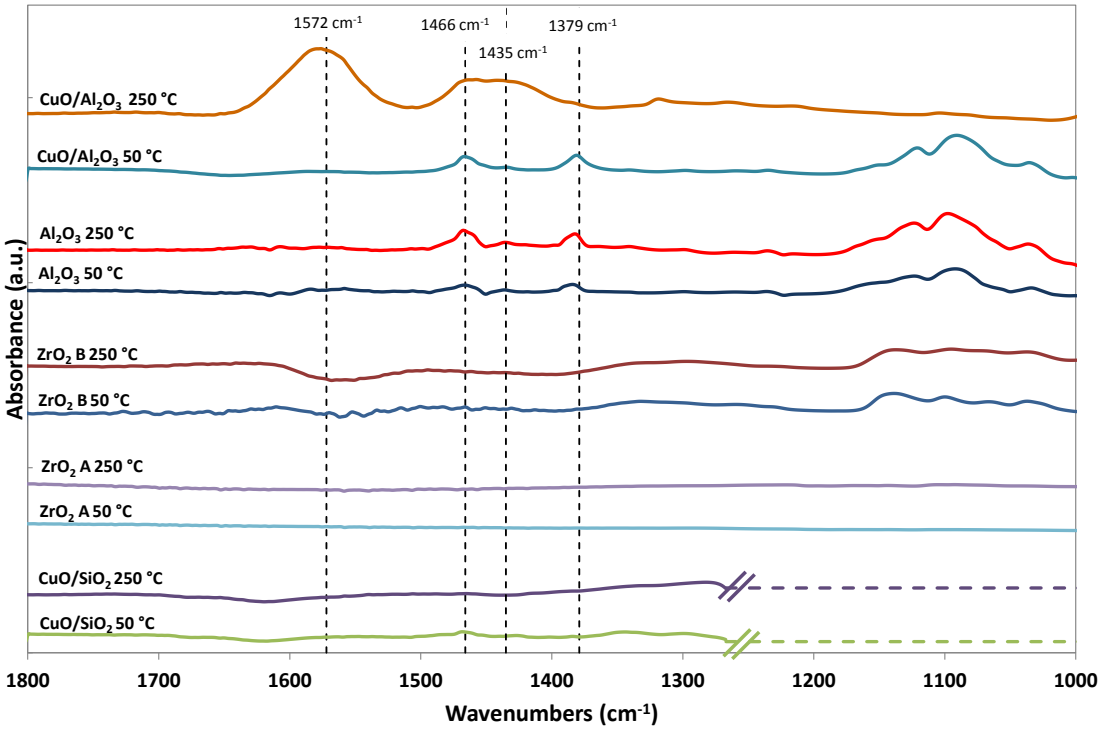
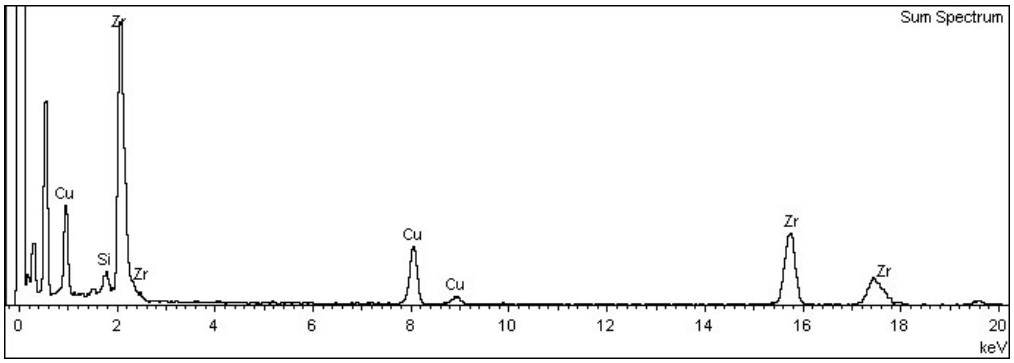


Figure S1. FT-IR of adsorbed 1-butanol over different catalysts and supports



Element	Atomic %	Wt %
Cu	19.3	11.2
Si	8.1	2.1
Zr	72.6	60.5

PM		PA			Atomic %		wt TOT			wt%			wt%	
SiO_2	60	Si	28.1		Si	8.1	SiO_2	4.9		SiO_2	4.4%	→	Si	2.1
ZrO_2	123	Zr	91.2		Zr	72.6	ZrO_2	89.3		ZrO_2	81.6%	→	Zr	60.5
CuO	79,5	Cu	63.5		Cu	19.3	CuO	15.3		CuO	14.0%	→	Cu	11.2
					TOT	100.0	wt tot	109.5						

Figure S2. EDX spectrum of the CuO/ZrO_2 C grain represented in Figure 3. In the tables are reported the Cu, Zr and Si atomic and weight composition and the calculation from atomic% to wt%.

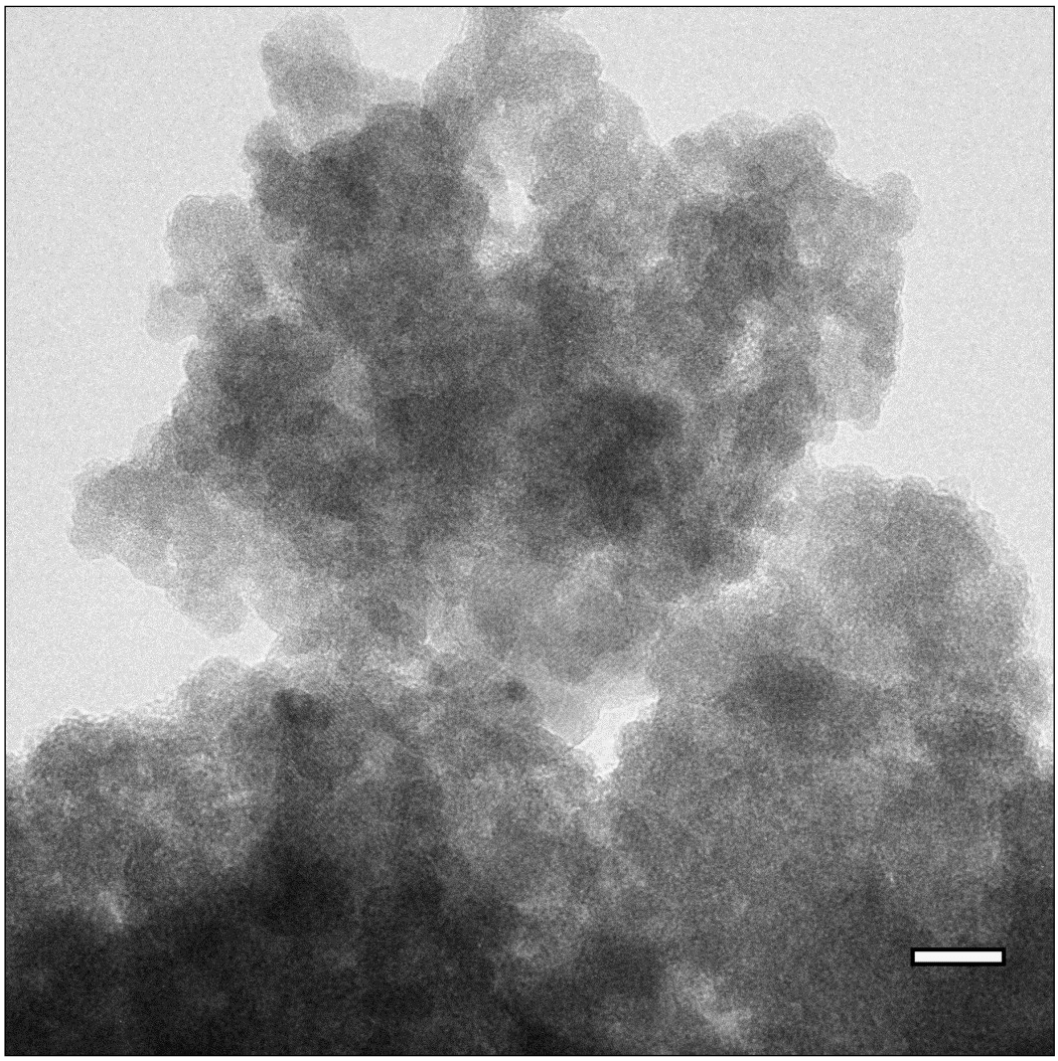


Figure S3. HRTEM micrograph of CuO/ZrO_2 C catalyst.

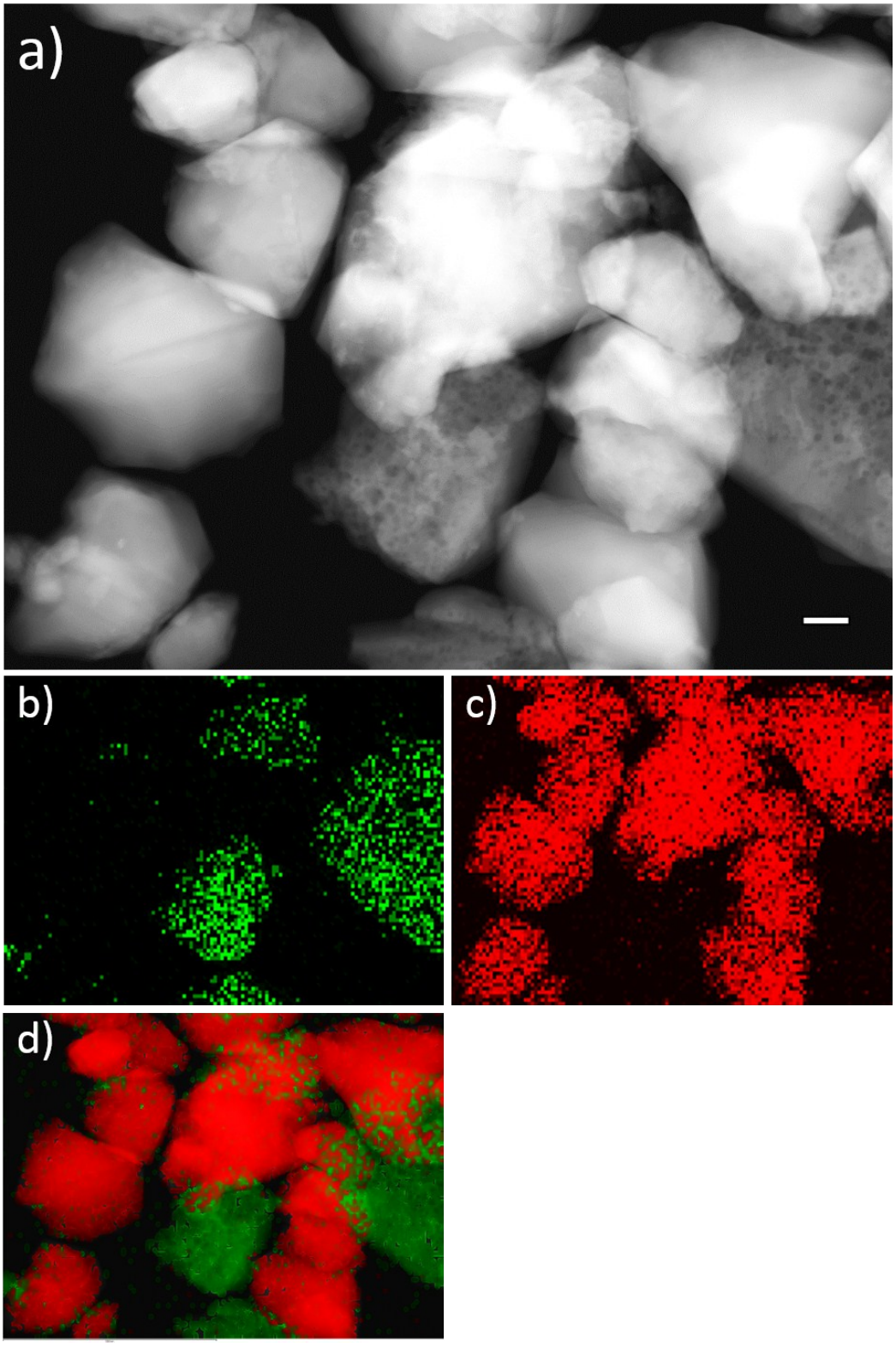


Figure S4. STEM measurements of CuO/ZrO_2 A: a) HAADF image of a catalyst grain (the length of the bar corresponds to 50 nm); b-d) STEM-EDX mapping of the catalyst showing the copper dispersion present in the catalyst: b) copper map (green), c) zirconium map (red), d) overlay of copper (green) and zirconium (red) maps.

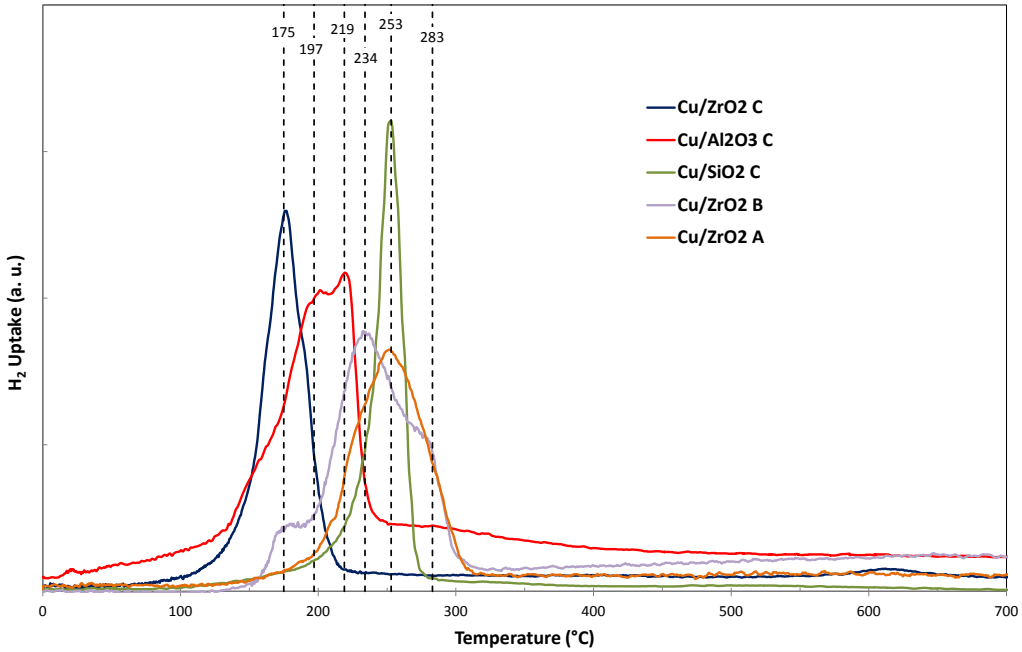


Figure S5.TPR analysis of CuO/ZrO_2 C, CuO/ZrO_2B, CuO/ZrO_2 A, CuO/Al_2O_3 and CuO/SiO_2

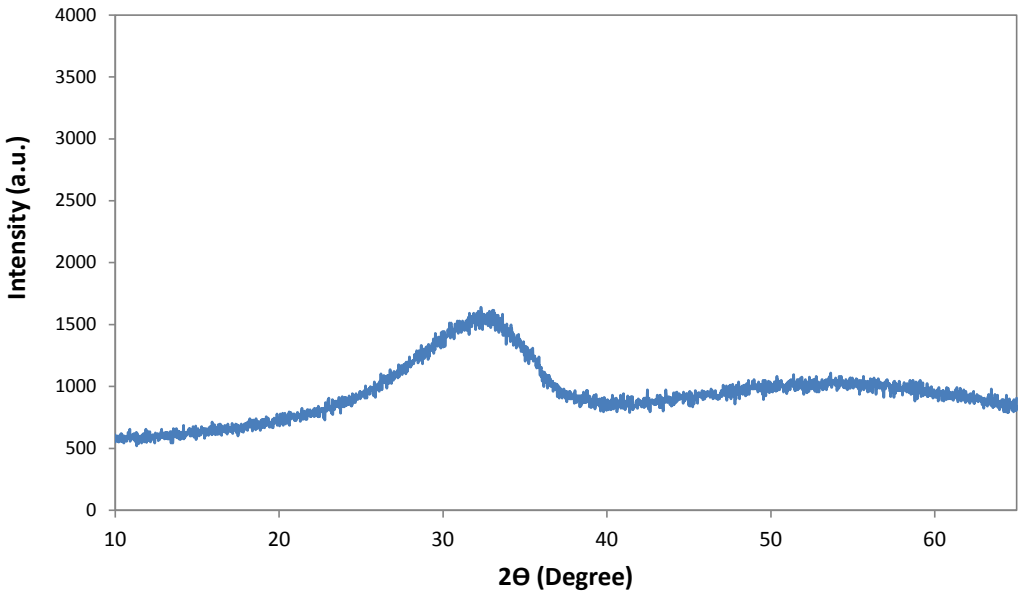


Figure S6. XRD of CuO/ZrO_2 C

Figure S5 shows the XRD pattern for the CuO/ZrO_2 C catalyst. No reflections for the CuO were detected, indicating the high dispersion of the copper phase, while the broad peak is typical of amorphous materials (in the present case the ZrO_2 C phase).

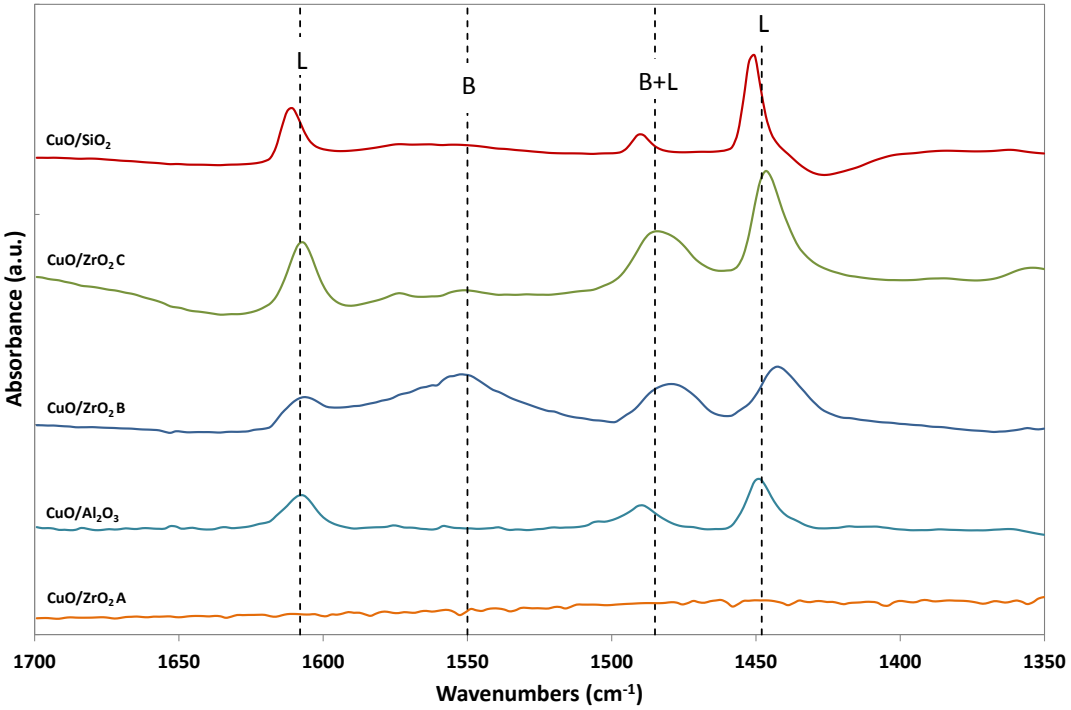


Figure S7. FT-IR of pyridine over different catalysts after degassing at 150 °C

The FT-IR spectrum of pyridine after degassing at 150 °C (Figure S6) shows three main bands at 1446, 1607 and 1485 cm^{-1}, that are in agreement with the presence of Lewis acid sites. For zirconia-based materials the band at 1446 cm^{-1} lies at relative low wavenumbers, very close to the one usually assigned to physisorbed or hydrogen bonded pyridine, but its resistance to outgassing up to 250 °C (together with the bands at 1607 and 1485 cm^{-1}) indicate unambiguously a Lewis acid-base interaction with pyridine. In the case of CuO/ZrO_2 C (very weak) and B a broad band at around 1450 cm^{-1} is typical of the presence of Brønsted acid sites.

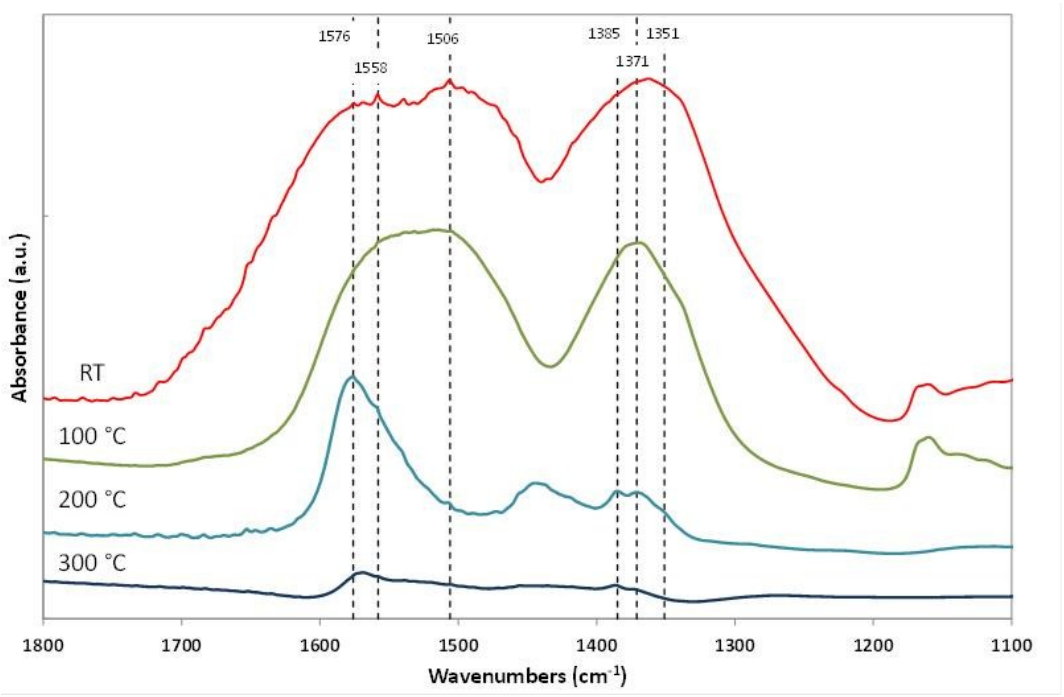


Figure S8. FT-IR of adsorbed CO_2 over CuO/ZrO_2 C

After CO_2 adsorption at RT we obtain a very broad spectrum (Figure S7). After degassing at increasing temperature, three maxima at 1558, 1506 and 1371 cm^{-1} are detectable that could be due to bicarbonates and carbonates species mainly formed on basic hydroxyl group [69] while two peaks at 1576 and 1351cm^{-1}, with a spectral gap of 225 $cm^{-1}$are diagnostic for bidentate carbonate species on coordinatively unsaturated acid-base pair centers. The bands at 1385 and 1371 cm^{-1}, together to the one at 1576 cm^{-1}, are also indicative for the presence of coordinatively unsaturated O^{2-} centres characterized by high basicity [69, 70]. Therefore the CO_2 adsorption revealed the presence of superficial strongly basic centres and acid-base pairs.

For comparison the spectrum of ZrO_2 C is reported. After evacuation in ultra-high vacuum at 350 °C for one night the material already shows bands due to high-resistant species arising from the contact with atmospheric CO_2 (Figure S8). After CO_2 adsorption and desorption at increasing temperature spectra do not change significantly.

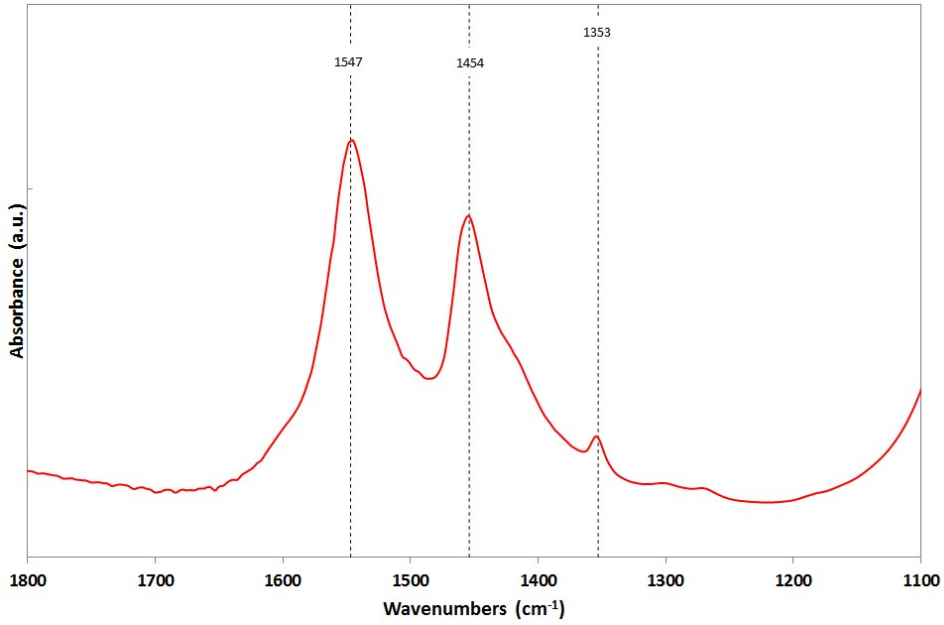


Figure S9. FT-IR of adsorbed CO_2 overZrO_2 C

Experimental details

All the experiments were performed in duplicate and in triplicate for the best results obtained (that is for experiments 4 and 5 in Table 1 and for the experiments 1 and 6 in Table 2.

Quantitative analysis

Conversion of butanol and **yield** of butylbutanoate were evaluated by GC analysis by using hexadecane as internal standard according to the following formulas:

$$Conv\ \% = \left(\frac{Mol\ butanol\ i - mol\ butanol\ f}{mol\ butanol\ i}\right) \times 100$$

$$Mol\ Butanol\ f = \left[\left(\frac{A\ butanol}{A\ std} - b\right)/a\right] \times Mol\ std$$

$$Y\ \% = \left[\frac{Mol\ butylbutanoate\ f}{Mol\ butanol/2} \times 100\right]$$

$$Mol\ Butylbutanoate = \left[\left(\frac{A\ butylbutanoate}{A\ std} - b\right)/a\right] \times Mol\ st$$

with *a* and *b* drawn by the calibration curve.

The **amount of hydrogen** produced has been calculated as follows:

Starting mol of butanol = 0,17 mol
Autoclave dead volume = 100 mL
H_2 pressure produced during reaction = 15 atm

$$mol\ H_2\ produced = \frac{15\ atm \times 0{,}1\ L}{0{,}082\left(\frac{atm\ L}{mol\ K}\right) 298\ K} = 0{,}061\ mol$$

$$Theoretical\ mol\ of\ H_2\ at\ 40\%\ conv = 0{,}17\ mol \times 0{,}40 = 0{,}068\ mol$$

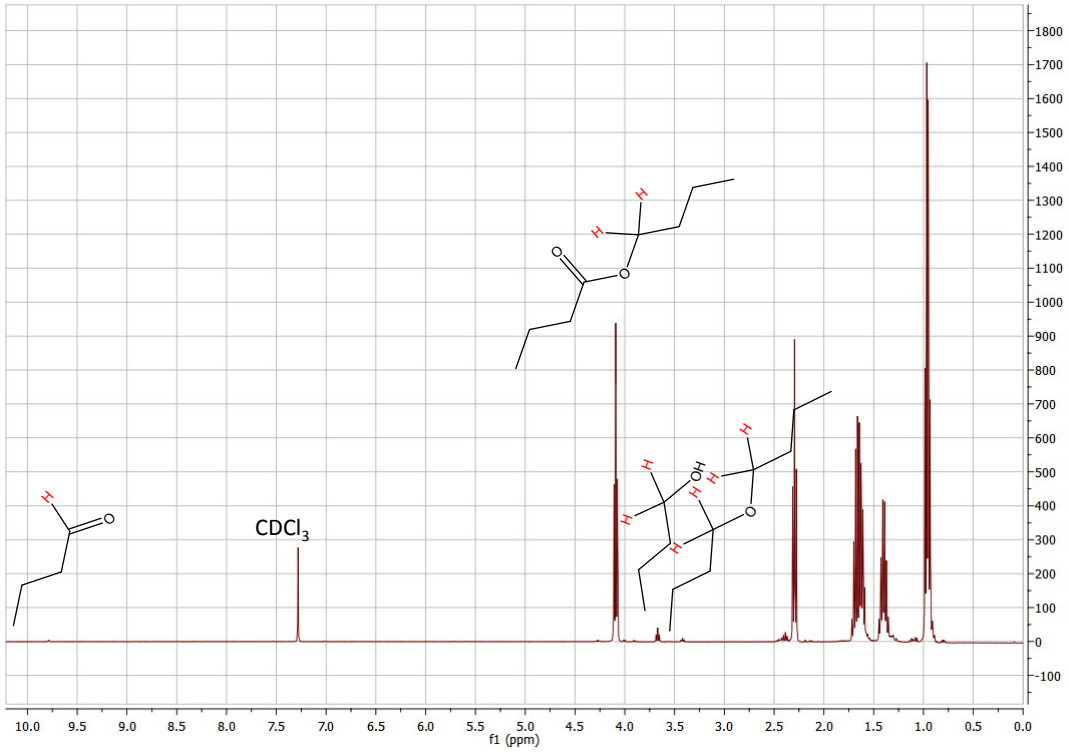


Figure S10.1HNMR analysisof reaction mixture obtained from 1-butanol over CuO/ZrO_2 C after 24 h

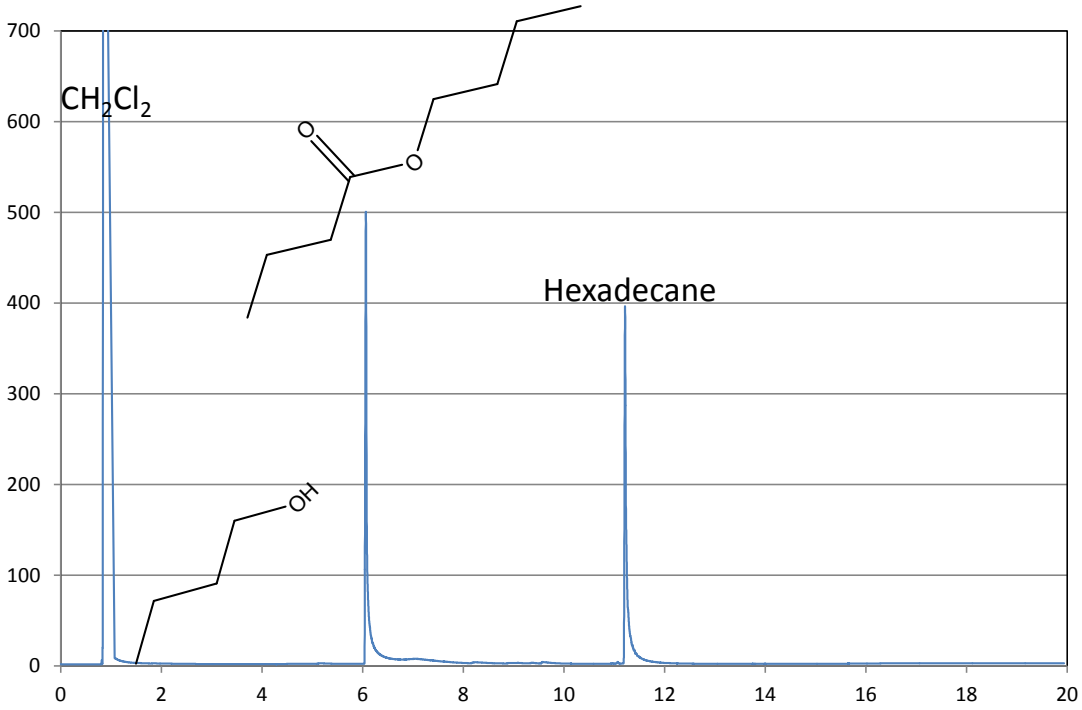


Figure S11. GC-FID analysis of reaction mixture obtained from 1-butanol over CuO/ZrO_2 C after 24 h