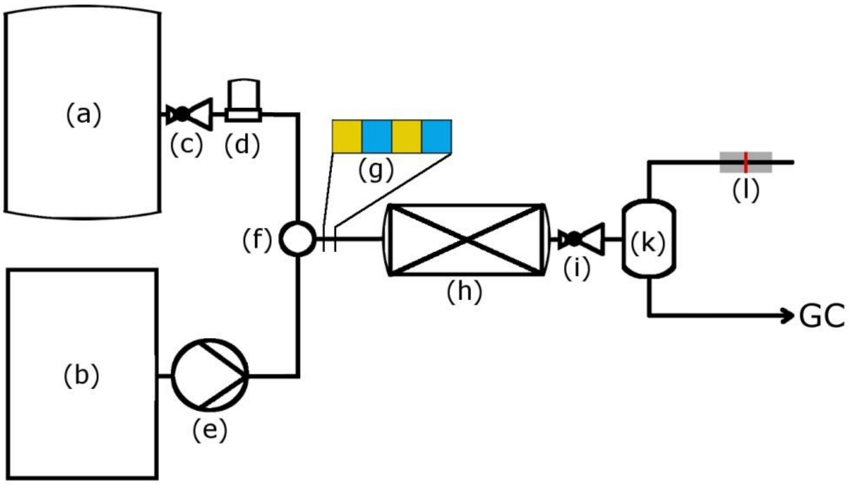
Supporting Information

The following reactor set-up was used to perform the continuous flow experiments:



Scheme 1 Experimental set-up: (a) O_2 reservoir, (b) liquid reservoir, (c) pressure reduction valve, (d) mass flow controller, (e) HPLC pump, (g) segmented flow, (h) fixed-bed reactor, (i) back-pressure regulator, (k) phase-seperator and (l) gas-flow passing through transmission IR cell.

Transmission IR spectra of the gas phase for a reaction performed at 55 °C (Fig. 1), indicating that at this temperature only traces of N_2O are formed (*viz.*, the catalyst is stable).

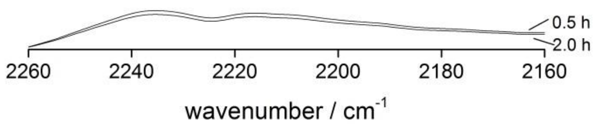


Fig. 1 Gas phase transmission IR spectra from an oxidation reaction of benzyl alcohol performed at 55 °C, contact time 0.5 min. for 0.5 and 2 h time-on-stream: ν_3 vibrational mode of N_2O around 2220 cm^{-1}. (solvent: DCE, $[BzOH]_0$ = 500 mM, $[HNO_3]$ = 5 mol%, 5 bar O_2)

EPR spectra of the catalyst before and after the reaction performed at 55 °C (Fig. 2) indicate that the decomposition of the catalyst is neglectable at that temperature.

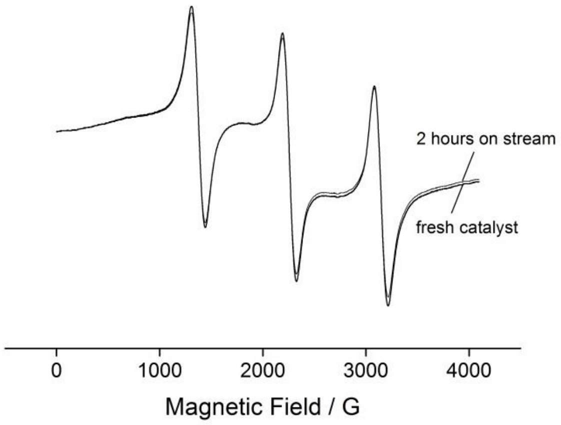


Fig. 2 EPR spectra of the initial catalyst and of the used catalyst 2 hours time-on-stream at 55 °C. (solvent: DCE, $[BzOH]_0$ = 500 mM, $[HNO_3]$ = 5 mol%, 5 bar O_2)

As mentioned in the paper, a slug flow could be observed visually (Fig. 3).

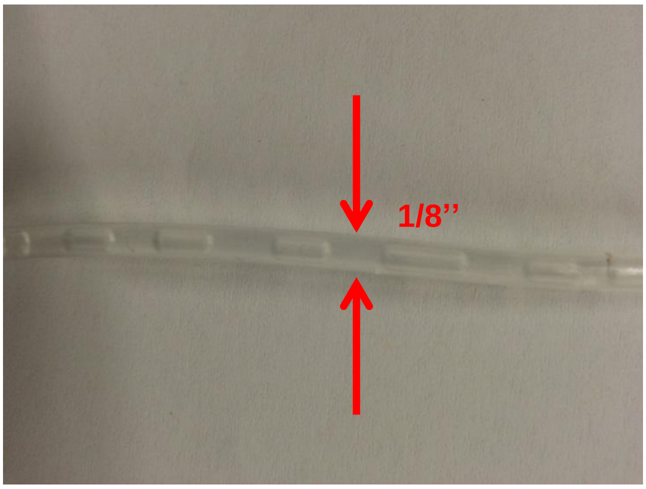


Fig. 3 Slug flow could be observed in the mixing zone before the reactor but also in the fixed bed reactor itself.

For the calculation of the liquid hold up at elevated pressures, the correlation of Larachi *et al* (see *e.g.*, V. V. Ranade, R. Chaudhari and P. R. Gunjal, *Trickle Bed Reactors, Reactor Engineering & Applications*, Elsiever B.V., Oxford, **2011**) was used:

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

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

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

$U_L = \frac{Q_L}{\pi \cdot (\frac{d_r}{2})^2 \cdot \epsilon}$: liquid velocity $(\frac{m}{s})$ (3)

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 $(\frac{m^3}{s})$

$\in$: void fraction

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

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

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

$U_G = \frac{Q_G}{\pi \cdot (\frac{d_r}{2})^2 \cdot \epsilon}$: gas velocity $(\frac{m}{s})$ (6)

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

$$\rho_G = \frac{p}{R_s \cdot T} \quad (7)$$

ρ_G: gas density $(\frac{kg}{m^3})$

R_s specific gas constant (287.058 $\frac{J}{kg \cdot K}$)

T reaction temperature (K)

Physical properties of the system (1,2-dichloroethane)

Q_L	$6.7 \cdot 10^{-9}$ $(0.4\ \frac{mL}{min})$	$\frac{m^3}{s}$
Q_G	$1.7 \cdot 10^{-8}$ $(5\ \frac{mLn}{min}\ at\ 5\ bar)$	$\frac{m^3}{s}$
U_L	$4.8 \cdot 10^{-3}$	$\frac{m}{s}$
U_G	$1.2 \cdot 10^{-2}$	$\frac{m}{s}$
ρ_L	1250	$\frac{kg}{m^3}$
ρ_G	5.3	$\frac{kg}{m^3}$
σ_L	$3.4 \cdot 10^{-2}$	$\frac{N}{m}$
μ_L	$0.65 \cdot 10^{-3}$	$Pa \cdot s$
d_r	$1.65 \cdot 10^{-3}$	m
$\in$	0.65	$-$
d_p	$0.2 \cdot 10^{-3}$	m
T	328	K
We_L	$1.7 \cdot 10^{-4}$	$-$
Re	15.2	$-$
X_G	$1.6 \cdot 10^{-1}$	$-$

According to equation (1) the liquid hold up is:

$$\beta = 1 - 10^{\frac{-1.22 \cdot We_L^{0.15}}{Re_L^{0.2} \cdot X_G^{0.15}}} = 0.44 \qquad (8)$$

The residence time of the system was the calculated in the following way

$$\tau = \frac{V_r \cdot \epsilon \cdot \beta}{Q_l} = \frac{(\frac{d_r}{2})^2 \cdot \pi \cdot l \cdot \epsilon \cdot \beta}{Q_l} \tag{9}$$

In the case of benzyl alcohol oxidation reactions the reactor length was 0.3 m which corresponds to a residence time of:

$$\tau = 28\ s \approx 0.5\ min \tag{10}$$

Since the reaction was performed in transparent teflon tubes, the residence time of the liquid was visually verified for 30 liquid bubbles with a stop watch under the above mentioned operating conditions, resulting in the following 95 % confidence interval:

$$\tau = 29\ \pm 2\ s \tag{11}$$

Since the the correlation of Larachi *et al* is in good agreement with the measured residence time, the correlation was used for all subsequent alcohols and operating conditions.