Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Continuous Flow Aerobic Alcohol Oxidation Using Heterogeneous Ru^0 Catalyst

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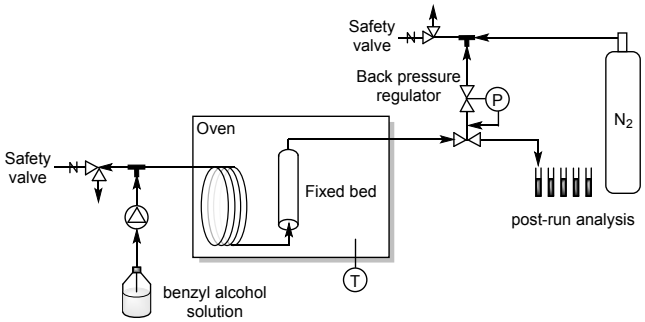
1. Experimental set-up for acceptor free dehydrogenation of benzylic alcohols



Scheme S1. General schematic of the G/L fixed bed reactor used for the acceptor-free dehydrogenation of alcohols

2. Possible elementary steps during the regeneration of Ru^0 from ruthenium hydride

Scheme S2 depicts the series of steps that could lead to the formation of H_2O_2 and/or H_2O using catalysts in liquid solvents. These elementary steps have been described in literature during the direct synthesis of H_2O_2 and H_2O using Pd catalyst.[1,2]

$$O_2 + ** \rightleftharpoons O_2**$$

$$H* \rightleftharpoons H^+ + e^- + *$$

$$2H* \longrightarrow H_2 + 2*$$

$$O_2** + H^+ + e^- \rightleftharpoons OOH**$$

$$OOH** + H^+ + e^- \longrightarrow H_2O_2**$$

$$H_2O_2** \rightleftharpoons H_2O_2 + **$$

$$O_2** \longrightarrow 2O*$$

$$OOH** \longrightarrow OH* + O*$$

$$O* + H* \longrightarrow OH* + *$$

$$OH* + H* \longrightarrow H_2O* + *$$

$$H_2O* \rightleftharpoons H_2O + *$$

$$H_2O_2** \longrightarrow 2OH*$$

Scheme S 2 Plausible series of elementary steps for hydrogen peroxide and/or water formation during the regeneration of Ru^0 from ruthenium hydride. A * denotes an empty site, X* represents an adsorbate bound to a single metal atom, X** signifies an intermediate adsorbed in an η^2 configuration. All reversible arrows represent a quasi-equilibrate step and each of the steps has its own rate constants. Scheme adapted from D. W. Flaherty *et al.*[3].

3. Composition of the liquid phase as the function of the temperature

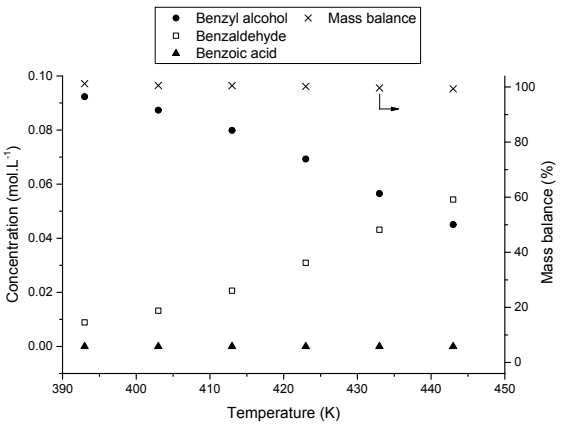


Figure 1. Composition of the liquid phase as the function of the temperature. [Benzyl alcohol]°=0.1 mol.L^{-1} in tert-amyl alcohol, Q_{O2}=49 NmL.min^{-1}, liquid flow rate=4 mL.min^{-1}, P=9 bar, T=393 to 433K. Reactor dimensions: lenght 136 mm and diameter 4.65 mm filled with 1.05 g of Ru^0/γ-Al_2O_3 at 1 wt% of Ru.

4. Thermodynamic approach used for O_2 solubility prediction

Oxygen solubility in *tert*-amyl alcohol and solvent vaporization have been estimated numerically with PROSIMPLUS® software[4] using G-L equilibrium flash calculations at constant temperature and pressure for a binary mixture of oxygen and tert-amyl alcohol. Calculations were done with the UNIFAC model in the different process conditions (T, P, inlet molar ratio). Typical results (Figure S 1) are given below for a pressure of 9 bar with a temperature varying between 393K and 443K and for a molar ratio alcohol/O_2 of 21.3 (which corresponds to a 49 NmL/min of O_2 and 5 mL/min of $_{tert}$-amyl alcohol).

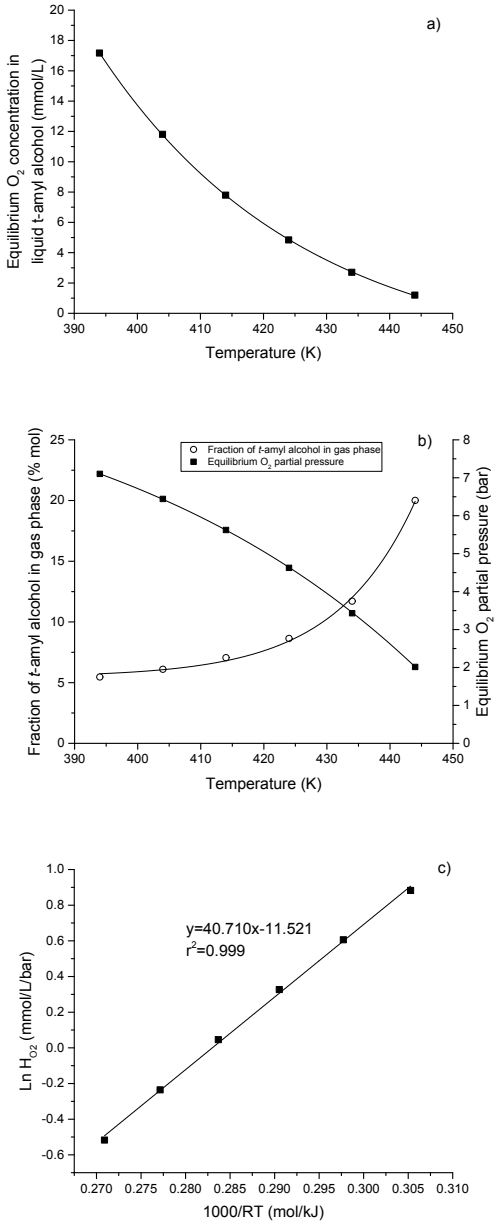


Figure S 2. Typical examples of G-L equilibrium calculations in the binary system O_2 / $_{tert}$-amyl alcohol (P_{tot} = 9 bar – $F_{alcohol}$ / F_{O2} = 21.28): (a) Effect of temperature on O_2 solubility; (b) Effect of temperature on O_2 partial pressure and solvent vaporization; (c) corresponding Henry's law.

5. Appreciation of possible mass transfer resistances

The different mass transfer limitations have been evaluated using common chemical engineering approaches regarding the limiting reagent O_2. The physical properties of the gas, liquid and solid phases used in the following calculations are summarized in Table S 1. When necessary (If temperature and/or pressure have an impact), the range of value corresponding to our experimental domain is given.

Table S 1. Considered physical properties of the different phases used in the mass transfer resistance estimations (393K<T<433K and 6bar<P<9bar)

Solid Catalyst/bed				Liquid Phase				Gas phase	
d_p (mm)	e_{cata} (µm)	ε (-)	D_{eff} (10^{-10} m²/s)	ρ_L (kg/m³)	μ_L (mPa.s)	σ_L (N/m)	$D_{m,L}$ (10^{-9} m²/s)	ρ_G (kg/m³)	μ_G (10^{-6} Pa.s)
1.58	100	0.52	2.2 – 2.5	815	0.10 – 0.32	0.021 (at 298K)	1.3 – 1.5	5.3 – 8.8	25.5 – 27.4

a. G-L external mass transfer

G-L mass transfer coefficients, $k_L a_{GL}$, for the different reaction conditions have been evaluated using the correlation established by Zhang et al.[5] (Eq. 1) for 3-phase milli-packed bed reactors. Depending on the experimental conditions, it varies between 0.5 s^{-1} and 36 s^{-1}.

$$\frac{k_L a_{GL} d_p^2}{D_{O_2}^L} = 3.41 \times 10^{-5} X_G^{0.08} Re_L^{3.1} We_L^{-1.33} \quad \text{(Eq. 1)}$$

Considering the catalyst totally wetted by the liquid phase and the reactor as isothermal, a classical steady state mass balance on O_2 (the limiting reagent) at the different interfaces in a thin layer of the fixed bed (Eq. 2) helps us defining a dimensionless number, $"f_{ex}^{GL}"$ (Eq. 3), analogous the fraction of external mass transfer resistance, $"f_{ex}"$ (Eq. 4), for monofluid/solid cases.

$$k_L a_{GL}\left(C_{O_2}^* - C_{O_2}^L\right) = k_S a_{LS}\left(C_{O_2}^L - C_{O_2,su}^S\right) = (1-\varepsilon)\bar{r}_p \quad \text{(Eq. 2)}$$

$$f_{ex}^{GL} = \frac{\bar{r}_p(1-\varepsilon)}{k_L a_{GL} C_{O_2}^*} \quad \text{(Eq. 3)}$$

$$f_{ex} = \frac{\bar{r}_p(1-\varepsilon)}{k_S a_{LS} C_{O_2}^L} = \frac{\bar{r}_p L}{k_S C_{O_2}^L} \quad \text{(Eq. 4)}$$

This number compares the apparent rate of reaction on the solid catalyst, $(1-\varepsilon)\bar{r}_p$, with the highest rate of G-L mass transfer, $k_L a C_{O_2}^*$. It has been evaluated at the entrance of the fixed bed where reactant concentrations and where reaction rates are the highest. In all the tested conditions, the f_{ex}^{GL} fractions are always lower than 0.5%, indicating that the G-L mass transfer is efficient and not limiting for this kinetic determination.

b. L-S external mass transfer

Similarly to the G-L interface, the L-S mass transfer coefficients and fractions of L-S external resistances ("f_{ex}") have been evaluated for all the reaction conditions at the fixed bed entrance. Here using the correlation of Lakota and Levec[6] (Eq. 5) developed for multiphase packed beds in low interaction regime under trickling conditions, assuming totally wetted solid catalyst particles again.

$$Sh = \frac{k_S d_p}{D_{m,L}} = 0.487 \frac{1-\varepsilon}{\varepsilon} \left(Re_L \frac{\varepsilon}{(1-\varepsilon)(\varepsilon_L - \varepsilon_{Lc})} \right)^{0.495} Sc_L^{0.333} \qquad \text{(Eq. 5)}$$

The f_{ex} values obtained here are always lower than 0.1%, indicating low and negligible external resistances at the L-S interface.

c. Internal mass transfer

To evaluate the relative impact of internal mass transfer resistance, the classical Weisz criterion[3], "φ'" (Eq. 6), has been used and estimated in all the experiments at the reactor entrance.

$$\varphi' = \frac{\bar{r}_p L^2}{D_{eff} C_{O_2}^L} \qquad \text{(Eq. 6)}$$

It is noticeable that the catalyst used in all this study is an egg-shell catalyst with a homogeneously impregnated layer of approximately 300 µm as estimated by optical microscopy (*Figure S 2*, digital microscope Keyence VHX 6000). Thus, this characteristic length is logically used here.

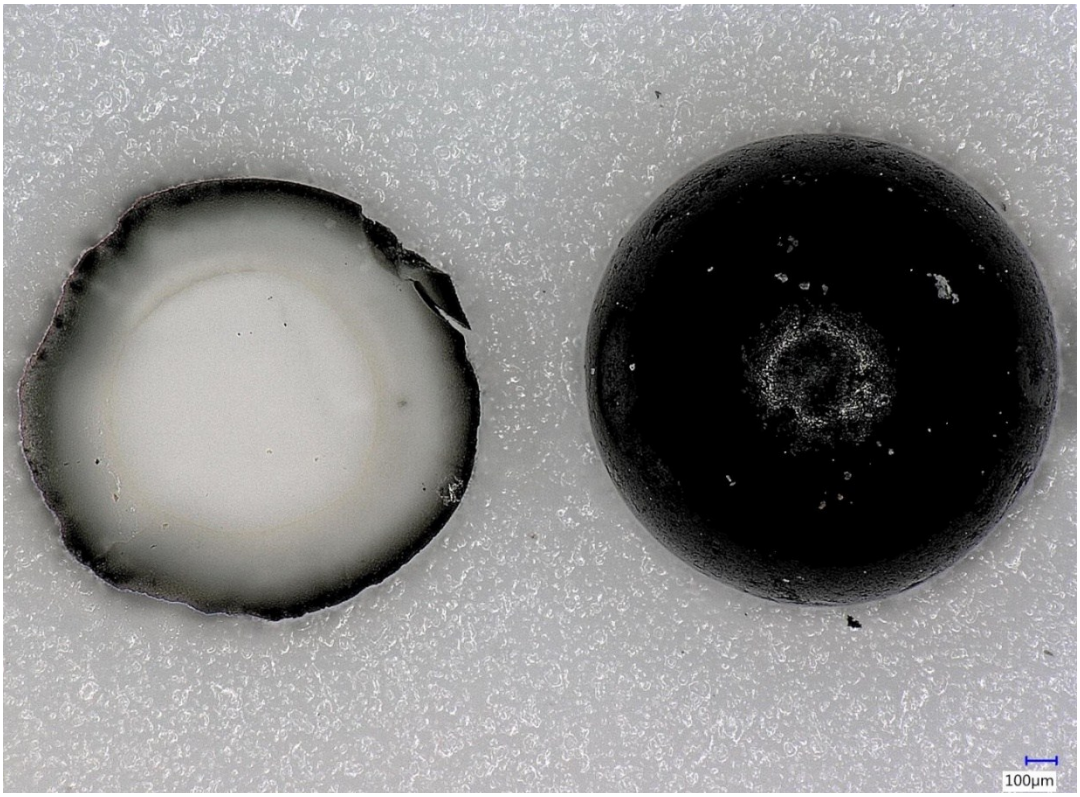


Figure S 3. View of Ru^0/Al_2O_3 catalyst particles showing the egg-shell typical structure on a crushed particle (left) and an intact spherical particle (right)

To estimate the effective diffusivity given in Table S 1, classical order of magnitude of liquid diffusivity ($D_{m,L\ O2}$ = $10^{-9}m^2/s$ at ambient temperature and pressure), internal porosity (β_p = 50%) and tortuosity (τ=3) have been used. Knudsen diffusivity has been neglected (liquid phase wetting the catalyst) and the effect of temperature on $D_{m,L\ O2}$ has been taken into account. All the Weisz criterions fall always under a value of 0.06 (<< 1), indicating no appreciable internal mass transfer limitation.

Overall, a work under chemical regime in this reactor has been determined for all the tested conditions, allowing a correct and direct determination of intrinsic kinetic parameters.

6. Determination of adsorption enthalpies through a liquid inverse chromatographic method

The adsorption enthalpies of benzyl alcohol and benzaldehyde (diluted on *tert*-amyl alcohol) on the Ru/Al_2O_3 catalyst were determined using an inverse liquid chromatographic method using pulse injection of each single solute at different temperatures. Precise and constant liquid flowrate of 1.8 mL/min of *tert*-amyl alcohol is applied to the packed catalyst bed with a Shimadzu HPLC pump LC20AD under a pressure of 9 bar and at different temperatures in the range 313-412K. Reproducible pulse injections of a 0.2 mol/L solution of each solute are obtained using a 0.54 mL loop mounted on a switching 6-way valve (Rheodyne 7725i). The resulting transient outlet concentration is recorded on-line at a frequency of 0.5 Hz with a calibrated UV-Vis spectrometer UV5bio from Mettler-Toledo equipped with a quartz cell QS from Hellma Analytics having an internal volume of 80 µL. Mean retention times, t_R are extracted from these measurements through a classical RTD approach with an Excel program. The residence time without adsorption, t_{R0}, has been determined independently with a pulse injection of heptane followed by sampling at the outlet of the reactor each 60s and GC off-line analysis. A value of $t_{R,0}$ of 293s has been determined and is necessary to calculate reduced retention times, t'_R, and the corresponding capacity factors, k', of the solutes in given conditions according to equations Eq. 7 and Eq. 8 respectively.

$$t_R^{'} = t_R - t_{R,0} \qquad \text{(Eq. 7)}$$

$$k^{'} = \frac{t_R^{'}}{t_{R,0}} \qquad \text{(Eq. 8)}$$

Given that that the capacity factor is directly linked to the adsorption equilibrium constant (Eq. 9) and knowing the Van't Hoff thermodynamic relationship (Eq. 10), it is easy to determine the adsorption enthalpy for each solute (Eq. 11):

$$k^{'} = K\frac{V_S}{V_M} \qquad \text{(Eq. 9)}$$

$$\frac{d\left(lnk^{'}\right)}{dT} = \frac{d(lnK)}{dT} = \frac{\Delta H}{RT^2} \qquad \text{(Eq. 10)}$$

$$\Delta H = -R\frac{d\left(lnk^{'}\right)}{d(1/T)} \qquad \text{(Eq. 11)}$$

K is defined as the ratio of solute concentrations in the stationary phase and in the mobile phase. V_S and V_M are the volumes of stationary and mobile phases respectively.

The results for both solutes are given in Table S 2 and in Figure S 3.

Table S 2. Experimental enthalpies of adsorption for benzyl alcohol and benzaldehyde on the Ru^0/Al_2O_3 catalyst of this study.

Species	Benzyl alcohol (A)	Benzaldehyde (B)
Adsorption enthalpies (ΔH_{ads}, kJ/mol)	-22.0	-18.6

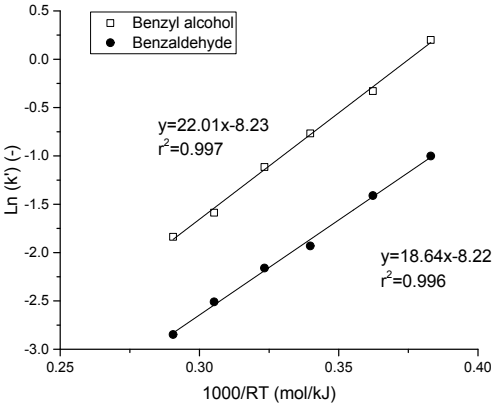


Figure S 4. Graphical determination of adsorption enthalpies of benzyl alcohol and benzaldehyde

7. References

1. M. Selinsek, B. J. Deschner, D. E. Doronkin, T. L. Sheppard, J.-D. Grunwaldt and R. Dittmeyer, *ACS Catal.*, 2018, **8**, 2546-2557.
2. D. W. Flaherty, *ACS Catal.*, 2018, **8**, 1520-1527.
3. N. M. Wilson and D. W. Flaherty, *J. Am. Chem. Soc.*, 2016, **138**, 574-586.
4. Prosim - software and services in process simulation, http://www.prosim.net/, (accessed 18-09-2018).
5. J. S. Zhang, A. R. Teixeira and K. F. Jensen, *AlChE J.*, 2018, **64**, 564-570.
6. A. Lakota and J. Levec, *AlChE J.*, 1990, **36**, 1444-1448.