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

Electronic Supplementary Information

Counting bubbles: precision process control of gas-liquid reactions in flow with an optical inline sensor

Nikolay Cherkasov[a,b,*], Antonio José Expósito[a,b], Yang Bai[a], Evgeny V. Rebrov[a,b,c,*]

[a] School of Engineering, University of Warwick, Coventry CV4 7AL, UK

[b] Stoli Catalysts Ltd, Coventry, CV3 4DS, UK

[c] Department of Biotechnology and Chemistry, Tver State Technical University, 170026, Nab. A. Nikitina 22, Russia,

Corresponding authors: n. cherkasov@warwick.ac.uk, e.rebrov@warwick.ac.uk

S1. Calculation of the product selectivity and conversion

The liquid samples collected during the experiments were analysed with the offline gas chromatograph. The conversion and selectivity to semi-hydrogenated product were calculated using equations 1 and 2

$$X = 1 - \frac{C_{substrate}}{C^0_{substrate}}, \tag{1}$$

$$S = \frac{C_{product}}{C^0_{substrate} - C_{substrate}}, \tag{2}$$

where $C_{substrate}$ and $C^o_{substrate}$ are the substrate concentrations in the outlet and initial streams; $C_{product}$ is the product concentration. The control system used a proportional-integral algorithm to adjust the substrate and proportional H_2 flow rates to maintain the readings of the optical sensor at 95±1%.

S2. Experimental details in validation of the liquid sensor

The system used for the optical sensor calibration and validation experiments (Fig. S1) contained an HPLC pump (Knauer P4.1S) for isopropanol and a mass-flow controller Bronkhorst for N_2 (0.03-3.00 mL min^{-1}; All gas flow rates in the work are related to normal temperature and pressure). Gas and liquid flows were combined in a standard IDEX T mixer flowing into fluorinated ethylene propylene (FEP) tubing 0.5 mm internal diameter (ID), 0.5 m long. Taylor flow with constant bubble sizes was observed after the T mixer. Gas and liquid flow rate were independently verified with the standard volumetric and gravimetric methods.[1] The optical sensor (Optek OCB350L125Z) was placed 4 cm before the tube exit to ensure that the bubble pressure is close to atmospheric. In a separate set of experiments, a semi-prep inline IDEX A-410 filter was inserted after the T mixer to introduce non-uniformity into the flow.

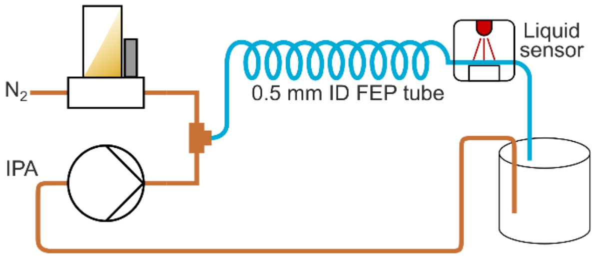

Fig. S1 *Scheme of the system used for validation of the optical sensor readings*

The known liquid fraction (LF) was calculated with equation 3, where Q_{liq} is the liquid flow rate and Q_{gas} is the gas flow rate at normal temperature and pressure from the mass flow controller.

$$LF = {Q_{liq}}\Big/{\left(Q_{liq} + Q_{gas} \cdot k\right)}. \qquad (3)$$

Coefficient *k* accounts for solvent evaporation and the difference between the observed and the normal conditions. Equation 4 shows the calculation of *k*, where T_{NTP} and P_{NTP} are normal temperature and pressure, T_m and P_m are temperature and atmospheric pressure during the measurements, P_{vap} is the saturated vapour pressure of isopropanol at T_m.[1]

$$k = \frac{P_{NTP}}{P_m - P_{vap}} \frac{T_m}{T_{NTP}}. \qquad (4)$$

S3. Long-term stability of the Pd/ZnO catalyst at constant flow rates

Fig S2 shows deactivation of the 5 wt% Pd/ZnO tube in solvent-free hydrogenation of 2-methyl-3-butyn-2-ol under constant flow rates described in detail in reference.[2]

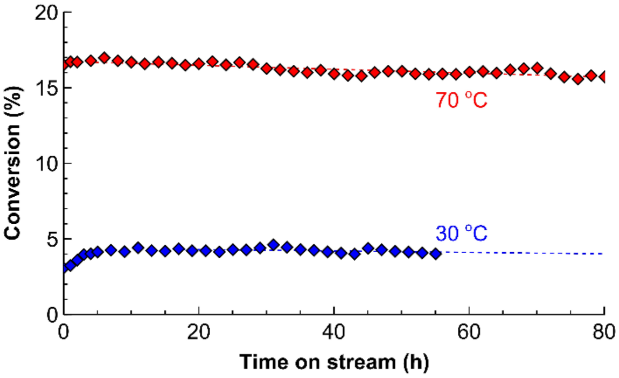

Fig. S2 *Deactivation of the Pd/ZnO catalyst coated inside a 0.86 m tube reactor at 30 °C and 70 °C at constant flow rates of 100 μL min^{-1} solvent-free MBY and 10 mL min^{-1} (STP) H$_2$ at 1 bar. The figure is taken from ref.*[2]

References:

1 W. C. Baker and J. F. Pouchot, *J. Air Pollut. Control Assoc.*, 1983, **33**, 156–162.

2 N. Cherkasov, Y. Bai and E. Rebrov, *Catalysts*, 2017, **7**, 1–16.