Supplementary Material (ESI) for Green Chemistry

Catalytic Supercritical Fluid Extractions: Selective hydroformylation of olefin-mixtures using $scCO_2$ solubility for differentiation

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Supplementary Informations

1. Material and methods.

Chemicals

Gas: Argon 4.8 (Westfalen AG) carbon dioxide 4.5 (Praxair), synthesis gas (Praxair) were used as received

1-Octene (Aldrich ≥ 98 %) and 1-Octadecene (Aldrich ≥ 95%) were dried, degassed and stored under an argon atmosphere.

$[Rh(acac)(CO)_2]$ (Strem 99 %) and triphenylphosphine trisulfonic acid trisodium salt, TPPTS, (0.6 mol dm^{-3} in water, generous gift from Hoechst) were used as received.

$[HRh(CO)(TPPTS)_3]$, **1**, was prepared according to [1]. Typically, $[Rh(acac)(CO)_2]$ (0.25 g, 1 mmol) was suspended in 5 cm^3 of an aqueous solutions of TPPTS (0.6 mol dm^{-3}, 3 mmol). Syngas was bubbled overnight through the suspension to yield a yellow-brown solution. After addition of water (10 cm^3), addition of absolute ethanol (30 cm^3) led to the precipitation of **1** as a yellow powder. The complex was recovered by filtration, washed with fresh ethanol and dried at room temperature under vacuum (0.005 mbar). 1.73g, 96 % yield. $^{31}P\text{-}\{^1H\}$-NMR: δ_P (400 MHz, D_2O) 43.5 (d, $^1J_{P\text{-}Rh}$ 155.7). ^1H-NMR: δ_H (400 MHz, D_2O) -9.57 (1H, q, $^2J_{P\text{-}H}$ 13.5, *H*-Rh), 7.2 (9H, t, arom), 7.36-7.54 (18H, m, broad, arom), 7.62 (9H, d, arom).

The anion exchange resins Amberlyst 26 OH (Aldrich), Dowex Marathon A2 (Aldrich) and the controlled porous glass Trisopor 50 (Vitra Bio GmbH) and Trisopor 137 (Vitra Bio GmbH) were dried under vacuum (0.03 mbar) at room temperature until constant weight and stored under Argon.

Table S 1 Characteristics of the used supports

	Dowex Marathon A2	Amberlyst 26 OH	Trisopor 50	Trisopor 137
pore size / nm	50	29	50	137
pore volume/cm^3 g^{-1}	1.43	0.20	1.43	0.95
surface area / m^2 g^{-1}	112	30	112	32
particle size / µm	520-620	560-700		

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[1] I. Toth, B. E. Hanson, I. Guo and M. E. Davis, *Catal. Letters*, 1991, **8**, 209

Methods

Gas Chromatography analyses were carried out using a Trace GC ultra (Thermo Elektron) equipped with a flame ionization detector (FID) and fitted with CP-Sil 8CB capillary column for quantitative analysis. The temperature program was: 50 °C (1 min); Δ 12 °C min^{-1} to 80 °C (2.5 min), 80°C (1 min), Δ 25 °C min^{-1} to 150 °C (2.8 min), 150 °C (2 min), Δ 20 °C min^{-1} to 250°C (5 min), 250°C (5 min). The temperature of the injector and the detector were both 300°C. Helium was used as a carrier gas at a constant flow of 3 cm^3 min^{-1}.

^{1}H and ^{31}P NMR spectra were recorded on Bruker DPX 400 NMR spectrometer. ^{1}H NMR spectra were referenced internally to deuterated solvents; which were referenced relative to TMS, $\delta = 0$ ppm, D$_2$O δH = 4.79 ppm. ^{31}P NMRspectra were referenced externally to 85% H3PO4. Coupling constants are given in Hz.

ICP measurements were carried out by the company Currenta Analytik (www.analytik.currenta.de) with a detection limit of 1 ppm for rhodium and 2 ppm for phosphorus.

2. Supported catalysts preparation

All the supported catalysts were prepared by wet impregnation. The dried support was suspended in an aqueous solution of **1** through which syngas was bubbled overnight at room temperature. After the bubbling, the solid showed a yellow coloration while the aqueous phase had completely decolorized. After filtration and drying under vacuum (0.005 mbar) the supported catalyst were obtained as yellow free flowing solids.

Typical procedure for ***1*** *on Amberlyst 26 OH:*

Dried Amberlyst (0.777 g, 4.2 mEq of NR$_4$ group g^{-1}) was suspended in an aqueous solution (10 cm^3) of **1** (70 mg, 0.038 mmol). Syngas was bubbled through the suspension for 15 h. After the bubbling, the support beads had turned yellow while the aqueous phase was colorless. The loaded Amberlyst beads were collected by filtration and dried under vacuum (0.005 mbar) at room temperature. The free flowing yellow beads were stored under argon until used. The catalyst loading corresponds to 10% of the support capacity based on the SO$_3$ groups of complex **1**.

3. Catalyst testing for single olefin hydroformylation in repetitive batch mode.

The hydroformylation reactions were performed as described in the experimental part of the communication. After collection of the crude product and venting, the autoclave was heated up to 80°C and pressurized with syngas (20 bar). Fresh olefin was introduced at the bottom of the autoclave through a valve connected to a, HPLC pump. The magnetic stirrer was switched on and the autoclave pressurized with CO$_2$. This procedure was repeated several times to assess the catalyst stability. For all the repetitive batch experiments, the catalyst stayed at all time in the reactor, care was taken to exclude air admission within the autoclave.

*[HRh(CO)(TPPTS)$_3$], **1**, supported onto controlled porous glass (Trisopor 50 and 137).*

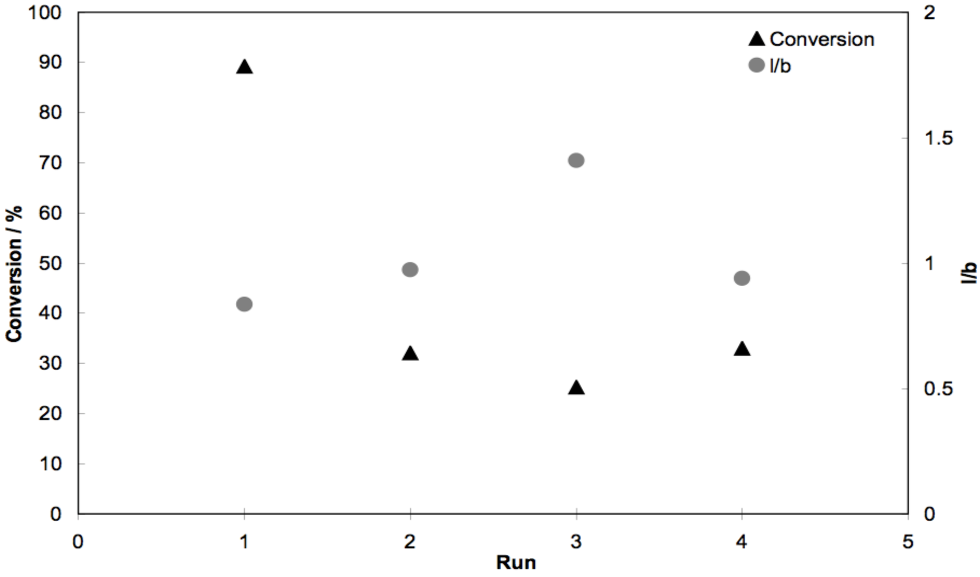

Figure S 1 Repetitive batch experiments for the hydroformylation of 1-octene with complex 1 supported onto Trisopor 50 (80°C, pCO_2 = 100 bar, CO/H_2 = 20 bar, 2.35 mmol 1-octene; S/C = 500, 3h)

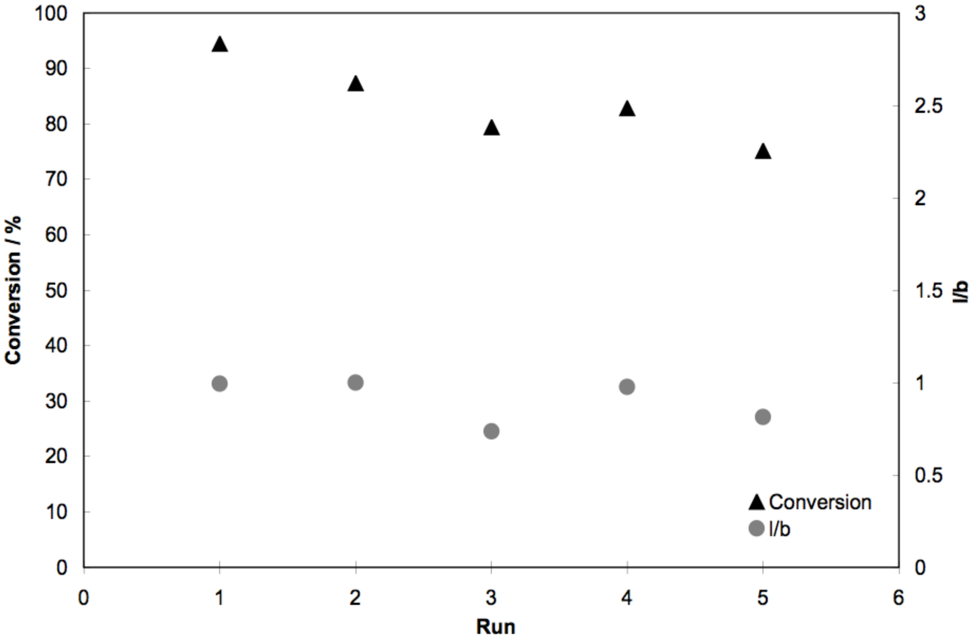

Figure S 2 Repetitive batch experiments for the hydroformylation of 1-octene with complex 1 supported onto Trisopor 137 (80°C, pCO_2 = 100 bar, CO/H_2 = 20 bar, 2.35 mmol 1-octene; S/C = 500, 3h)

*[HRh(CO)(TPPTS)$_3$], **1**, supported onto anion exchange resins (Dowex marathon A2 and Amberlyt 26 OH).*

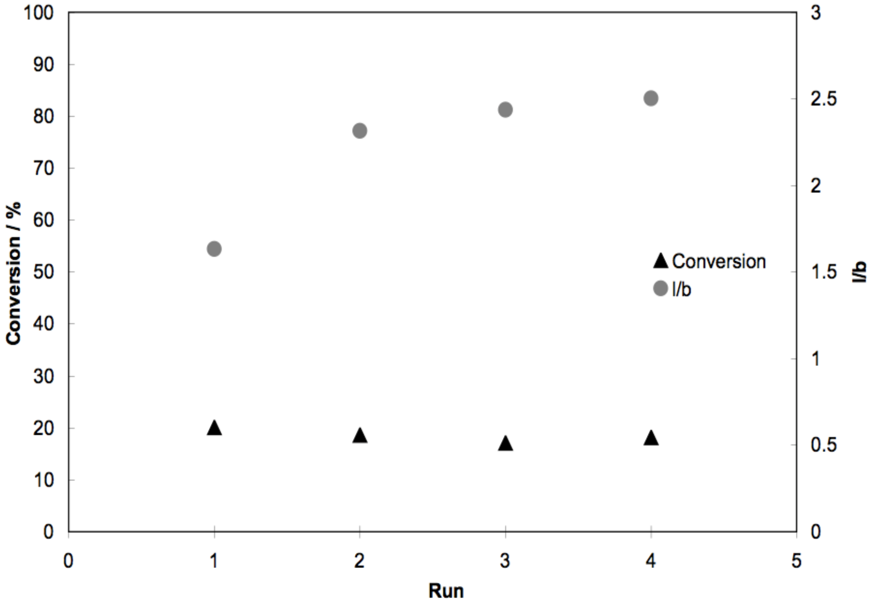

Figure S 3 Repetitive batch experiments for the hydroformylation of 1-octadecene with complex 1 supported onto Dowex marathon A2 (80°C, pCO$_2$ = 100 bar, CO/H$_2$ = 20 bar, 2.19 mmol 1-octene; S/C = 2000, 20h)

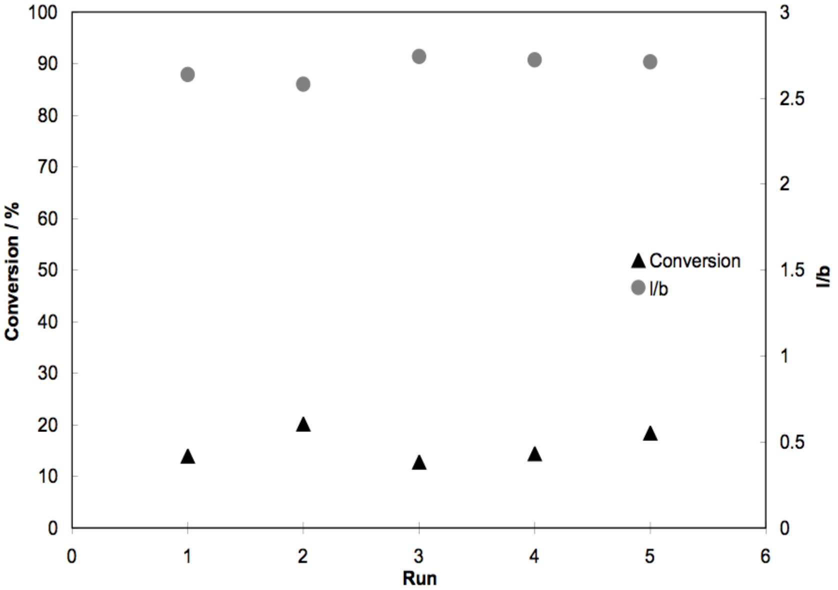

Figure S 4 Repetitive batch experiments for the hydroformylation of 1-octadecene with complex 1 supported onto Amberlyst 26 OH (80°C, pCO$_2$ = 100 bar, CO/H$_2$ = 20 bar, 2.19 mmol 1-octene; S/C = 2000, 20h)