Catalytic supercritical fluid extraction: selective hydroformylation of olefin mixtures using $scCO_2$ solubility for differentiation†
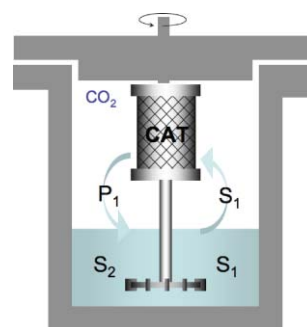
Timo J. Koch,[a] Simon L. Desset[a] and Walter Leitner*[a,b]

A new reaction concept that allows one to control the substrate selectivity of a catalytic reaction by supercritical fluid extraction is demonstrated for the hydroformylation of long-chain olefins as a prototypical example.

Catalysts can usually discriminate between reactive substrates based on the functionality of the compound, or the shape and/or size of the compound. However, for substrates bearing identical reactive functions and being of similar shapes, the catalyst alone is sometimes not able to achieve acceptable levels of differentiation. The integration of mass separation processes and catalytic reactions provides a possible approach to address this challenge and examples based on reactive extraction and reactive distillation are currently being explored.[1] In reactive extraction, the discrimination is based on differences in solvation (typically polarity), whereas reactive distillation exploits differences in vapour pressures at sufficiently high temperature. In the present communication, it is demonstrated that supercritical fluid extraction, SFE, provides an alternative approach that can be efficiently coupled with transition metal catalysed transformations, allowing the selective conversion of substrates with almost identical polarities at temperatures far below their boiling points.

The intrinsic solubility of a compound in compressed carbon dioxide, *i.e.* its "CO_2-philicity", depends largely on a combination of its volatility and polarity.[2] Moreover, the extent of solubility can be tuned by adjusting the density of the carbon dioxide.[3,4] Therefore, by contacting a mixture of substrates with compressed CO_2 and immobilising a catalyst in a separate compartment in the CO_2 phase, only those constituents of the mixture displaying significant solubility in the CO_2 phase at a given density would be converted (Fig. 1).

The hydroformylation of long-chain olefins was chosen as a prototypical example to validate this concept. It is well established that molecular rhodium phosphine catalysts exhibit high chemo- and regioselectivity, but show no significant differentiation in rate for different terminal olefins above C_5.[5] For example, when a mixture of linear terminal olefins, namely 1-hexene, 1-octene and 1-decene (1:1:1 mixture) is hydroformylated in hexane, the corresponding aldehydes are

[a]*Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 1, 52074, Aachen, Germany.
E-mail: leitner@itmc.rwth-aachen.de; Fax: +49 (0)241 80 22177; Tel: +49 (0)241 26480*
[b]*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Mülheim an der Ruhr, Germany*
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Fig. 1 Schematic representation of the concept for selective reaction of a substrate mixture in a CO_2 biphasic system (S = substrate; P = product) – S_1 has a higher "CO_2-philicity" then S_2 allowing its selective transportation to the catalyst, where it is converted to P_1.

typically obtained in equimolar proportions indicating that there is no differentiation from the Rh/PPh_3 catalyst between the substrates under conventional homogeneous conditions.[6,7]

Rhodium phosphine catalysed hydroformylation of long-chain olefins in supercritical CO_2 ($scCO_2$) has been widely studied under homogeneous[8] and multiphasic conditions.[9] In particular, compressed carbon dioxide has been used as the mobile phase for continuous hydroformylation, transporting the dissolved olefin to the reactor containing a catalyst immobilised on solid supports.[10] However, for all these systems, only pure alkenes, especially 1-octene, have been used as substrates. Given the high selectivity of SFE we speculated that it should be possible to identify suitable conditions where CO_2 could act as a selective mass separation vector for olefins of different chain length.

To identify suitable conditions for the differentiation, the continuous extraction of an equimolar mixture of 1-octene and 1-octadecene at 80 °C and different pressures of CO_2 was investigated (Table 1). The extractions were carried out using a standard high pressure reactor connected to a constant pressure CO_2 feed line.‡ The flow was controlled by adjusting the opening of a thermostatted decompression needle valve at the outlet of the reactor. The outlet flow passed through two successive traps, one at ambient temperature and the second at −73 °C, and finally through a rotameter before being vented to the atmosphere. The extractions were carried out for 8 h and the weights and compositions (GC analysis) of the extracts were determined every hour. The material balance of the extractions was determined by gravimetry and found to be ≥95%.

When the extraction was carried out at low pressure, *i.e.* p_{CO_2} ≤ 90 bar, very high selectivity toward the shorter olefin was observed (1-octene selectivity > 97%). By raising the pressure at constant temperature, *i.e.* raising the CO_2 density, the extraction

Table 1 Continuous extraction of a 1-octene/1-octadecene mixture (1 : 1) with compressed CO_2 at 80 °C[a]

p_{CO_2} (bar)	C_8 Selectivity (%)[b]
50	99.9
70	99.6
90	97.4
110	91.7
130	87.2

[a] 80 °C, 8 h, 50 cm³ min⁻¹ (STP); [b] (mole 1-octene)/(mole 1-octene + mole 1-octadecene), determined by GC, average over 8 h extraction.

selectivity was found to decrease. This was anticipated since the solvent power of compressed CO_2 is directly linked to its density. Thus at high density, CO_2 becomes a "better" solvent hence decreasing its discrimination ability toward the two different olefins. The very high selectivities observed for the extraction at $p_{CO_2} \leq 90$ bar indicated that under these conditions CO_2 could, *a priori*, be used as a selective transport vector to bring one of the components of the mixture to an immobilised catalyst that is located in a separated compartment above the liquid substrates.

An additional prerequisite for the successful combination of SFE and catalytic reaction was therefore the efficient compartmentalisation of the catalyst from the liquid substrate phase. In other words, the catalyst must be efficiently immobilised onto a support so that no catalyst is transported to the liquid phase where it would catalyse the non-selective reaction and override the selectivity gained trough SFE. Ionic compounds usually exhibit very little solubility in CO_2. Therefore the well known ionic water-soluble hydroformylation complex [HRh(CO)(TPPTS)$_3$], **1**, (TPPTS = triphenylsphosphine trisulfonic acid trisodium salt) was immobilised on various supports and the obtained catalysts were tested for the hydroformylation of olefins in homogeneous supercritical phase. Two different types of supports were used: controlled pore glasses following the concept of supported aqueous phase catalysts (SAPC),[11] and anion exchange resins where the catalyst is maintained on the support by ionic interactions between the cationic groups from the surface and the negatively charged ligand.[12] The catalysts were prepared by wet impregnation of the supports with an aqueous solution of complex **1** under a syngas atmosphere. Filtration and drying afforded the supported catalysts as free flowing yellow coloured solids.

For controlled glass supports, the catalysts were active for the hydroformylation reaction but deactivated rapidly upon recycling. Moreover, very low linear-to-branched ratio, l/b, were observed (0.5 < l/b < 1.5). Deactivation might occur either by leaching of the catalyst or by change of the hydration level of the support which was shown to have a dramatic effect on the catalyst performances.[13] In any case, the poor robustness of the system under supercritical conditions was not suitable for the present application.

When using the anion exchange resins Dowex Marathon A2 and Amberlyst 26 OH as supports, active catalysts were obtained and the activity remained stable over 4 consecutive recyclings. Linear-to-branched ratios of 2.7, typical for rhodium triphenylphosphine type catalysts, were observed. The maximum rhodium leaching, measured by ICP, after reaction over a wide range of CO_2 pressure never exceeded 1.5% of the initial rhodium

charge (15 ppm). Moreover, when testing the crude product phases for blind activity, no further conversion was observed.

Owing to the stability exhibited by the catalysts supported on ion exchange resins, the use of complex **1** immobilised on Amberlyst 26 OH for the hydroformylation of a mixture of long-chain olefins under selective SFE conditions was investigated. The catalyst was held in a basket placed in the top part of the reactor ensuring there was no direct contact between the liquid substrate phase and the catalyst in absence of CO_2. Using this reaction set-up, the hydroformylation of a mixture of 1-octene and 1-octadecene (1 : 1) under 20 bar of syngas at different partial pressures of CO_2 was conducted (Fig. 2). As expected, no conversion of any of the substrates was observed when the reaction was carried out in the absence of CO_2. In the presence of compressed CO_2 at low density, only 1-octene was converted to the corresponding aldehydes (24% conversion, l/b = 2.7) leaving the 1-octadecene unreacted. Further increase of the CO_2 pressure to 110 bar led to higher conversions (octene conversion = 32, 48 and 52% at 72, 92 and 107 bar, respectively), presumably due to more efficient transport of the substrate to the catalyst, but again almost exclusively 1-octene was reacted with the same levels of regio-selectivity (2.7 < l/b < 2.9). Only for CO_2 pressures above 110 bar, the conversion of the C_{18} olefin started to become significant (22% conversion at p_{CO_2} = 135 bar) and at 160 bar the same levels of conversion were observed for both substrates (38% conversion).
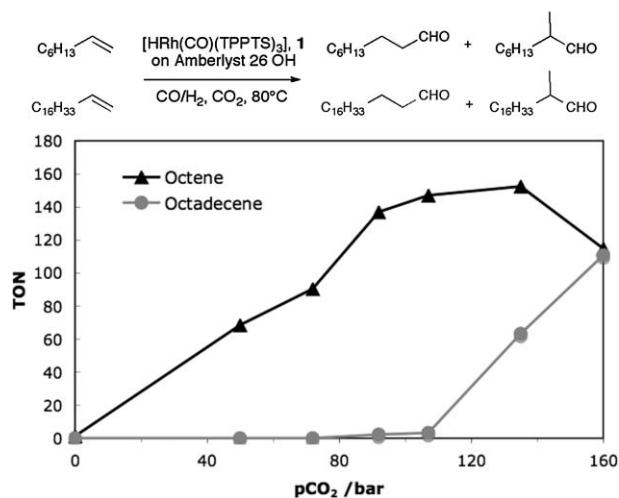
Fig. 2 Hydroformylation of a 1-octene/1-octadecene mixture (1 : 1) at different pressures of CO_2.

To ensure that the reaction was taking place in the CO_2 phase and not catalysed in the liquid substrate phase by leached catalyst, all crude reaction mixtures were analysed by ICP-AES for rhodium and phosphorus. Rhodium concentrations were below the detection limit (< 1 ppm) and the highest concentration of phosphorus detected was 10 ppm (1% of the initial charge) which is fully in line with the batch reactions. Very interestingly, the octene selectivities observed for the reaction and for the extraction at different pressures followed very similar trends (Fig. 3).

This observation, together with the very low levels of rhodium leaching supports the conclusion that the reaction is genuinely
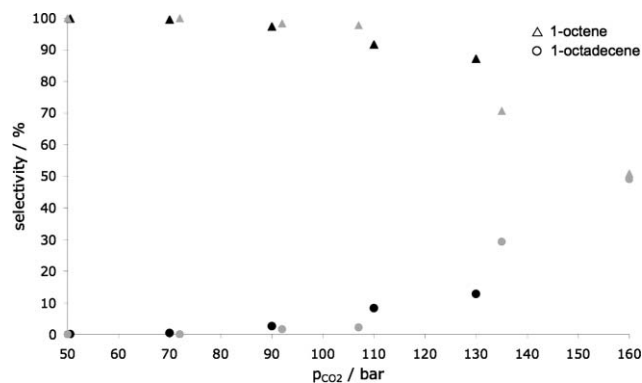
Fig. 3 1-Octene (triangle) and 1-octadecene (circle) selectivity during extraction (black) and hydroformylation (grey).

taking place in the CO_2 phase, in which density acts as the differentiating agent between the reactive substrates.

In summary, we have demonstrated that the selective catalytic transformation of one compound from a mixture of substrates could be achieved using the solubility in CO_2 as a discrimination tool. This constitutes a new approach in combining catalysed transformations with mass separation processes in reactive multicomponent systems. Extension of this concept to other relevant mixtures and transformations appears promising for integrated catalytic processes.

Notes and references

‡ Extraction: in an autoclave (100 cm³) equipped with a CO_2 inlet, a CO_2 outlet connected to two successive traps and a flowmeter, a mechanical stirrer, a heating jacket, a pressure gauge and a thermocouple, the olefin mixture (1-octene/1-octadecene (1 : 1), 7.7 g) was introduced. The autoclave was heated to 80 °C, stirred (500 rpm) and the CO_2 was introduced at the desired pressure. The extraction was started by opening the needle valve to the CO_2 outlet and adjusting the flow to 50 cm³ min⁻¹. The traps were changed every hour, the content were weighted and analyzed by GC. The extraction was stopped after 8 h, the reactor was cooled and vented. The liquid phase remaining in the autoclave was weighed and analysed by GC. Catalyst preparation: the dried support was impregnated by suspension in an aqueous solution of [HRh(CO)(TPPTS)₃], **1**, (prepared according to ref. 14) for 12 h with gentle bubbling of syngas. After filtration and drying under vacuum, the supported catalyst was obtained as a slightly yellow, free flowing solid. Hydroformylation: under inert atmosphere, the basket, loaded with catalyst (300 mg, 7.34 wt% of [HRh(CO)(TPPTS)₃]), **1**, was introduced into the autoclave (20 cm³) and mounted in the upper part. The autoclave was sealed, heated to 80 °C and pressurized with syngas (20 bar). The olefin mixture (1-octene/1-octadecene (1 : 1), 1.5 cm³), was introduced at the bottom of the autoclave through a valve

connected to an HPLC pump ensuring there was no contact between the catalyst and the substrate. The magnetic stirrer was switched on and the autoclave pressurized with CO_2 to the desired pressure. After 20 h, the autoclave was cooled down and the bottom valve connected to a cold trap (acetone/dry ice). The content of the reactor was emptied by gently opening the valve to the cold trap. The content of the cold trap was analysed by GC for organics and by ICP-AES for rhodium and phosphorus.

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