Continuous, selective hydroformylation in supercritical carbon dioxide using an immobilised homogeneous catalyst

Nicola J. Meehan,[a] Albertus J. Sandee,[b] Joost N. H. Reek,[b] Paul C. J. Kamer,[b] Piet W. N. M. van Leeuwen*[b] and Martyn Poliakoff*[a]

[a] *School of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD.*
E-mail: Martyn.Poliakoff@nottingham.ac.uk
[b] *Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands. E-mail: pwnm@anorg.chem.uva.nl*

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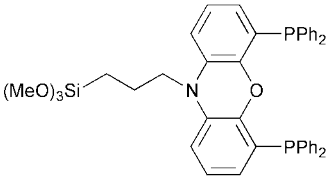
A continuous process for the selective hydroformylation of higher olefins in supercritical carbon dioxide ($scCO_2$) is presented; the catalyst shows high selectivity and activity over several hours and no decrease in performance was observed over several days.

Hydroformylation is one of the mildest and most efficient methods of producing aldehydes and it is therefore widely applied in the petrochemical industry. The cleanest, industrially important hydroformylation process is the aqueous biphasic process, developed by Ruhrchemie/Rhône-Poulenc, affording a straightforward separation of the organic products from the catalyst.[1] The applicability of this system, however, is strictly limited to substrates which are slightly water soluble, such as propene and but-1-ene. In the industrial hydroformylation of higher olefins, the catalyst is separated by either extraction, catalyst destruction or distillation. One of the major challenges in this field is the development of a continuous hydroformylation process combining a high catalytic activity and selectivity with facile product separation, in which catalyst leaching does not occur.[2] To date, no such system has been reported; often at higher CO pressures the ligand on the metal is easily exchanged for CO molecules resulting in rhodium leaching.[3] Recently Van Leeuwen and coworkers reported a promising approach based on rhodium–diphosphine hydroformylation catalysts with a large P–Rh–P bite angle in a multiphase batch process.[4,5]

The use of $scCO_2$ is becoming increasingly important as a reaction medium in metal catalysed reactions.[6–8] The absence of a gas–liquid phase boundary and the ability of $scCO_2$ to support high concentrations of dissolved gases combined with facile product and catalyst separation makes $scCO_2$ a competitive alternative to conventional solvents. However, homogeneous catalysts often require modification in order to increase their solubility in $scCO_2$,[9–12] although unmodified[13] and even insoluble catalysts[14] have demonstrated significant activity in $scCO_2$ systems. The use of an immobilised homogeneous catalyst overcomes both solubility and catalyst recovery problems. At Nottingham, continuous processing in $scCO_2$ has been successfully applied to a wide range of hydrogenations,[15,16] Friedel–Crafts alkylations[17] and etherification reactions[18] using heterogeneous catalysts supported on polysiloxane (Deloxan®, Degussa AG). Here, we show how this technique is effectively applied in the hydroformylation reaction using an immobilised rhodium–diphosphine catalyst containing a large P–Rh–P bite angle.

The catalyst used is the rhodium complex of *N*-(3-trimethoxysilyl-*n*-propyl)-4,5-bis(diphenylphosphino)phenoxazine **A**, immobilised on silica (particle size 200–500 μm).†



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Typically, 1 g of ligand-modified silica was reacted with 4 mg of $Rh(acac)(CO)_2$ and then loaded into a 5 mL supercritical flow reactor.‡

The catalyst performed well in the hydroformylation of oct-1-ene with selective production of linear nonanal. The average linear to branched aldehyde ratio (l : b) was 40 : 1. Oct-1-ene conversions of up to 14% were obtained (Table 1, entries 5 and 7) and only a few percent of octene isomers and a trace amount (*ca.* 1%) of alcohol were observed as byproducts.

Table 1 Results from the hydroformylation of oct-1-ene, values shown are average numbers over a period of 3–6 h[a]

Entry	TOF[b]	Linear aldehyde[c] (%)	Branched aldehyde[c] (%)	Alkene isomers[c] (%)	Linear alcohol[c] (%)	Linear to branched ratio	Oct-1-ene conversion (%)
1[d]	39	96.1	2.4	1.5	0	40	3.6
2	87	92.9	3.0	3.8	0.3	32	9.4
3[e]	112	94.4	2.4	2.5	0.7	40	10.1
4[f]	117	92.6	3.8	2.5	1.0	24	10.3
5[g]	160	93.5	2.8	2.9	0.8	33	14.3
6[h]	44	90.7	4.4	3.7	1.3	21	4.1
7[i]	93	96.0	1.9	1.1	0.9	50	14.3
8[j]	96	91.3	4.1	4.3	0.3	23	4.6

[a] Ligand : Rh ratio is 10 : 1 and the catalysis was performed at 80 °C, 120 bar CO_2 at 0.65 L min^{-1} flow rate (at 20 °C, 1 atm), 50 bar overpressure syngas and an oct-1-ene flow rate of 0.05 mL min^{-1} (substrate : syngas = 1 : 10) unless otherwise stated. [b] Average turnover frequencies were calculated as mol aldehyde (mol catalyst)$^{-1}$ h^{-1}. [c] Determined by means of GC analysis using decane as an internal standard. [d] Reaction temperature is 70 °C. [e] Syngas overpressure is 25 bar (substrate : syngas = 1 : 5). [f] 0.3 L min^{-1} CO_2 flow rate (at 20 °C, 1 atm). [g] Reaction temperature is 90 °C. [h] 180 bar CO_2. [i] Oct-1-ene flow rate of 0.03 mL min^{-1}. [j] Oct-1-ene flow rate of 0.1 mL min^{-1}.

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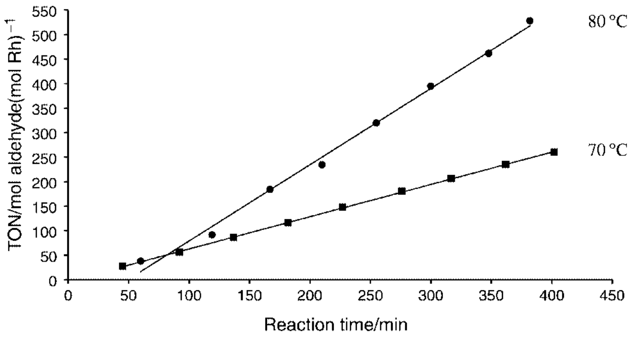

Fig. 1 Turnover number (TON) for the hydroformylation of oct-1-ene in $scCO_2$ at 70 and 80 °C.

The rate of hydroformylation is moderate (39 h^{-1}) at 70 °C with an oct-1-ene flow rate of 0.05 mL min^{-1} (Table 1, entry 1). The rate increased to 87 h^{-1} with the catalyst bed at 80 °C (Table 1, entry 2) and improved further to 112 h^{-1} on decreasing the syngas pressure from 50 to 25 bar (Table 1, entry 3). This improvement in rate is consistent with the negative order in CO pressure that is commonly observed in hydroformylation reactions.[19] A TOF of 117 h^{-1} was observed on increasing the residence time of the substrate in the reactor by decreasing the CO_2 flow rate (Table 1, entry 4). An alternative method of increasing the residence time is to increase the CO_2 pressure, however this resulted in a decrease in TOF (Table 1, entry 6). This may be explained as a higher pressure results in a higher density of CO_2 which will alter the transport properties in the reactor. The highest TOF (160 h^{-1}) was observed at 90 °C (Table 1, entry 5). Varying the oct-1-ene flow rate was found to have an effect on the l:b ratio but not on the TOF (Table 1, entries 2, 7 and 8). As the CO concentration in $scCO_2$ is relatively high, it is remarkable that the hydroformylation rate is over three times faster than the batch reaction in toluene (TOF = 35 h^{-1}) and only half the rate of the *homogeneous* analogue (TOF = 283 h^{-1}) under comparable reaction conditions (80 °C, 50 bar syngas).[5] The high rate in $scCO_2$ is probably caused by enhanced mass-transport properties and the lower viscosity of the solvent medium.[20]

It was also found that the expansion system in our apparatus facilitated the separation of the aldehyde product from the residual oct-1-ene. In our preliminary experiments, we were able to remove *ca.* 90% of oct-1-ene from the product by simply controlling the two-step depressurization of CO_2.

The catalyst appears to be very robust, as its performance is constant over at least 30 h. Fig. 1, shows a plot of the turnover number (TON) *vs.* reaction time. The TON increased linearly with time at both 70 and 80 °C. Moreover, we were able to continue using the catalyst for six non-consecutive days with no observable decrease in either activity or selectivity. Furthermore, no rhodium leaching was detected (detection limit of used technique (AES) is 0.2% of the total amount of rhodium of the catalyst). This demonstrates that the rhodium–diphosphine bond in this catalyst remains stable under hydroformylation conditions.

In conclusion, we have presented the first example of continuous selective hydroformylation of higher olefins in $scCO_2$ using an immobilised homogeneous rhodium catalyst. The process is potentially interesting in the manufacture of fine chemicals and our approach has several advantages compared to conventional homogeneously catalysed reactions. Firstly, $scCO_2$ is a clean, environmentally benign medium which can be easily separated from the organic phase. Secondly, the application of an immobilised homogeneous catalyst in the flow reactor provides a direct and quantitative separation of the products from the catalyst and avoids any solubility limitations of homogeneous catalysts. Finally, the robustness of the catalyst and absence of Rh leaching, makes this system an interesting candidate for sustainable processes.

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Notes and references

† *Catalyst preparation*: 100 mg (1.40×10^{-4} mol) of *N*-(3-trimethoxysilyl-*n*-propyl)-4,5-bis(diphenylphosphino)phenoxazine (Siloxantphos) was added to a suspension of 1 g silica (200–500 μm) (predried at 140 °C for several days) in 25 ml toluene and the mixture was mechanically stirred at 80 °C for 20 h. After cooling to room temperature, the liquids were removed from the residue and the silica was washed with three portions of toluene. The ligand-on-silica was dried *in vacuo* and was then suspended in a mixture of 5 mL THF and 1 mL Et_3N. The suspension was mixed for 10 min and 4 mg (1.55×10^{-5} mol) $Rh(acac)(CO)_2$ was then added. The mixture was mechanically stirred for 15 min, after which the THF was removed and the catalyst was further washed with three portions of THF. The catalyst was dried *in vacuo* and was either used directly or stored under argon at −20 °C.

‡ The substrate + internal standard, supercritical CO_2 (P_c = 73.8 bar, T_c = 31.1 °C) and CO/H_2 are brought together in a heated mixer, passed through the reactor containing catalyst, and then expanded to separate the fluid product from the process-stream. The reactor is assembled from commercially available units: $scCO_2$ pump PM101, CO/H_2 compressor CU105 and Expansion Module PE103 (all from NWA GmbH, Lörrach, Germany), a high pressure mixer (Medimix) and a Gilson 305 pump (for the organic substrate). **CAUTION**: Flow reactors have a comparatively small volume under pressure. Nevertheless, equipment with the appropriate pressure and temperature rating should always be used for high pressure experiments.

1 E. G. Kuntz, *Chemtech*, 1987, 570.
2 W. A. Herrmann and B. Cornils, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1048.
3 M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpainter, *J. Mol. Catal. A*, 1995, **104**, 17.
4 A. J. Sandee, V. F. S. Slagt, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Chem. Commun.*, 1999, 1633.
5 A. J. Sandee, L. A. van der Veen, J. N. H. Reek, P. C. J. Kamer, M. Lutz, A. L. Spek and P. W. N. M. van Leeuwen, *Angew. Chem., Int. Ed.*, 1999, **38**, 3231.
6 R. Noyori, *Chem. Rev.*, 1999, **99**, 475.
7 J. A. Darr and M. Poliakoff, *Chem. Rev.*, 1999, **99**, 495.
8 B. M. Bhanage, Y. Ikushima and M. Shirai, *Chem. Commun.*, 1999, 1277.
9 S. Kainz and W. Leitner, *Catal. Lett.*, 1998, **55**, 223.
10 D. Koch and W. Leitner, *J. Am. Chem. Soc.*, 1998, **120**, 13 398.
11 D. R. Palo and C. Erkey, *Ind. Eng. Chem. Res.*, 1998, **37**, 4203.
12 D. R. Palo and C. Erkey, *Organometallics*, 2000, **19**, 81.
13 I. Bach and D. J. Cole-Hamilton, *Chem. Commun.*, 1998, 1463.
14 M. F. Sellin and David J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 2000, 1681.
15 M. G. Hitzler and M. Poliakoff, *Chem. Commun.*, 1997, 1667.
16 M. G. Hitzler, F. R. Smail, S. K. Ross and M. Poliakoff, *Org. Proc. Res. Dev.*, 1998, **2**, 137.
17 M. G. Hitzler, F. R. Smail, S. K. Ross and M. Poliakoff, *Chem. Commun.*, 1998, 359.
18 W. K. Gray, F. R. Smail, M. G. Hitzler, S. K. Ross and M. Poliakoff, *J. Am. Chem. Soc.*, 1999, **121**, 10 711.
19 J. A. Moulijn, P. W. N. M. van Leeuwen and R. A. van Santen, *Catalysis: an integated approach to homogeneous, heterogeneous and industrial catalysis*, Elsevier, Amsterdam, 1993.
20 A. Baiker, *Chem. Rev.*, 1999, **99**, 453.