Tailor-made Catalysts Immobilised on Silica.
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Continuous, selective hydroformylation in supercritical carbon dioxide using an immobilised homogeneous catalyst

Abstract

A continuous process for the selective hydroformylation of higher alkenes in supercritical carbon dioxide (scCO₂) is presented; the catalyst showed high selectivity and activity over several hours and no decrease in performance was observed over several days.

5.1 Introduction

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 and industrially most 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 that 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 that combines a good catalytic performance with facile product separation and from 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.\(^3\)

The use of scCO\(_2\) is becoming increasingly important as a reaction medium in metal catalysed reactions.\(^4\) 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 (Chapter 1, section 1.4.2). However, homogeneous catalysts often require modification in order to increase their solubility in scCO\(_2\)\(^5\) (a notable exception is the use of rhodium trialkylphosphine complexes).\(^6\) 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 hydrogenations\(^7^,\)^\(^8^\), Friedel-Crafts alkylations\(^9^\) and etherification reactions\(^10^\) using heterogeneous catalysts supported on polysiloxane. In this Chapter, it is shown how this technique is effectively applied in the hydroformylation reaction using the immobilised rhodium-diphosphine catalyst that was previously applied in a batch process (Chapter 3 and 4).

5.2 Results and discussion

The catalyst used is the rhodium complex of N-(3-trimethoxysilane-n-propyl)-4,5-bis(diphenylphosphino)-phenoxazine (A) immobilised on silica (particle size 200-500 \(\mu\)m). Typically 1g of silica with a 0.4\% Rh loading, was loaded into a 5 ml supercritical flow reactor.
The catalyst performed well in the hydroformylation of 1-octene with selective production of linear nonanal. The average linear to branched aldehyde ratio was 40:1. 1-Octene conversions of up to 14% were obtained and only a few percent of octene isomers and a trace amount (~1%) of alcohol were observed as byproducts.

Table 5.1: Results from the hydroformylation of 1-octene, values shown are average numbers over a period of 3-6 hours.

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

a Ligand : Rh ratio is 10:1 and the catalysis was performed at 80°C, 120 bar CO₂ at 0.65 l/min flow rate (at 20°C, 1 atm), 50 bar overpressure syngas and an 1-octene flow rate of 0.05 ml/min (substrate:syngas = 1:10) unless otherwise stated. b Average turnover frequencies were calculated as (mol aldehyde/mol catalyst) 1/h. 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. f 0.3 l/min CO₂ flow rate (at 20°C, 1 atm). g 180 bar CO₂. h Reaction temperature is 90°C. i 1-Octene flow rate of 0.03 ml/min. j 1-Octene flow rate of 0.1 ml/min.

At 70°C with an 1-octene flow rate of 0.05 ml/min, the rate of hydroformylation is moderate (39 mol.mol⁻¹.h⁻¹) (Table 5.1, entry 1). The rate increased to 87 mol.mol⁻¹.h⁻¹ with the catalyst bed at 80°C (entry 2) and improved further to 112 mol.mol⁻¹.h⁻¹ on decreasing the syngas pressure from 50 to 25 bar (entry 3). The latter effect is consistent with the negative order in CO pressure that is commonly observed in hydroformylation reactions. A TOF of 117 mol.mol⁻¹.h⁻¹ was observed on increasing the residence time of the substrate in the reactor by decreasing the CO₂ flow rate (entry 4). An increase of the CO₂ pressure resulted in a decrease in
TOF to 44 mol.mol\(^{-1}\).h\(^{-1}\) (entry 5). 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 mol.mol\(^{-1}\).h\(^{-1}\)) was observed at 90°C (entry 6). On decreasing the 1-octene flow rate from 0.1 to 0.03 ml/min we observed an increase in the linear to branched ratio from 23 to 50 (entries 2, 7 and 8). Thus far we have no explanation for this.

As the CO concentration in scCO\(_2\) is relatively high, it is remarkable that the hydroformylation rate is over four times faster than the batch reaction in toluene (Chapter 3) and only half the rate of the homogeneus analogue.\(^5\) The high rate in scCO\(_2\) is probably caused by enhanced mass-transport properties and the lower viscosity of the solvent medium.\(^{12}\)

It was also found that the expansion system in the apparatus facilitated the separation of the aldehyde product from the residual 1-octene. In our preliminary experiments, we were able to remove ca. 90% of 1-octene from the product by simply controlling the 2-step depressurization of CO\(_2\).

The catalyst appears to be very robust, as its performance is constant over at least 30 hours. In Figure 5.1, the turnover number (TON), is plotted against 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 found (detection limit of used technique (AES) is 0.2% of the total amount of rhodium of the catalyst). This demonstrates unambiguously that the rhodium-diphosphine bond in this catalyst remains stable under hydroformylation conditions.

![Figure 5.1: Turnover number (TON) for the hydroformylation of 1-octene in scCO\(_2\) at 70 and 80°C.](image-url)
5.3 Conclusion

We have presented the first example of continuous selective hydroformylation of higher olefins in scCO₂ 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, scCO₂ 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 complete absence of Rh leaching, makes this system an interesting candidate for sustainable processes.

5.4 Experimental section

Materials
N-(3-trimethoxysilane-n-propyl)-4,5-bis(diphenylphosphino)-phenoxazine (A), was synthesized according to Chapter 2. 1-Octene was purified over neutral alumina prior to its use. All other chemicals were purchased commercially and used without further purification. Solvents were dried prior to their use. THF and toluene were distilled from sodium. Triethylamine was distilled from calciumhydride. All manipulations were performed under Schlenk conditions.

General procedure
The flow-reactor is assembled from commercially available units: scCO₂ pump PM101, CO/H₂ 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.

Catalyst preparation
100 mg \((1.40 \times 10^{-4} \text{ mol})\) of N-(3-trimethoxysilane-n-propyl)-4,5-bis(diphenylphosphino)-phenoxazine (Siloxantphos) (Chapter 2) was added to a suspension of 1 g silica \((200-500 \mu\text{m})\) (predried at 140°C for several days) in 25 ml toluene and the mixture was mechanically stirred at 80°C for 20 hours. 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$_3$N. The suspension was mixed for 10 min and 4 mg (3.88.10$^{-6}$ 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.

**Catalysis procedure**

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.

**5.5 References and Notes**