Chapter 5

Hydroformylation of Alkenes with Rhodium Catalyst in Supercritical Carbon Dioxide

1-Octene, 1-decene and styrene have been hydroformylated using a CO$_2$-philic fluorous ligand associated with a rhodium catalyst. The effect of P/Rh molar ratio, partial pressure of CO/H$_2$ and total pressure of carbon dioxide were studied. When 1-octene was used as a substrate, high conversion and selectivity in aldehydes were observed using low rhodium concentration and low P/Rh ratios.

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5.1. Introduction

The hydroformylation of long chain alkenes is an important industrial process. The aldehydes obtained can be converted into plasticizer alcohols and biodegradable detergents [1]. The main disadvantage of this reaction is the difficult separation of the reaction products from the catalyst at the end of the reaction due to the high boiling points of the aldehydes. Several strategies have been developed to solve this problem. The most successful one is to use a multiphase system, consisting of two or more immiscible liquid phases. The catalyst is immobilized in liquid phase while the substrate and the product(s) of the catalysed reaction are in the rest of one of the other phases [2].

In 1984, Rhône-Poulenc/Ruhr-Chemie industries iniciated the first commercial process for the biphasic aqueous hydroformylation of propene [3-5]. This process produces 300.000 tones of butanal per year but it is not viable for long chain alkenes because certain solubility of the alkene in water is needed in order to obtain a high conversion [6].

In 1994, the concept of the fluorous biphase system (FBS) was introduced by Horváth and Rábai and applied to the hydroformylation of 1-decene [7-9]. The FBS is based on the properties of fluorous solvents, which have a low affinity for non-fluorinated compounds. The catalyst, which contains ligands with fluorous chains, is therefore dissolved in the fluorous phase and the products can be separated by a simple decantation. Since then there has been an increasing interest in the development of catalysts that have high affinities for fluorous phase. Although the FBS has many advantages, it has not been applied at industrial level, due to the high cost of the fluorous solvents.

Supercritical carbon dioxide (scCO$_2$) is an attractive green solvent alternative to conventional organic solvents. It is used successfully in industrial extraction processes [10]. ScCO$_2$ can be used as a solvent in homogeneous catalysis [11]. Carbon dioxide has mild critical data (T_c = 31ºC, P_c = 73.8 bar), is both environmentally friendly and relatively inexpensive. Supercritical carbon

dioxide has gas-like properties, and gases such as H_2 and CO are highly soluble in it. For this reason, it is a good alternative solvent, especially in reactions in which reagents are gases. $ScCO_2$ is a non-polar solvent so modifications in catalytic systems are required to increase the solubility of the catalyst in the reaction media. The best results in terms of solubility have been achieved introducing fluorous chains into the ligands [12]. Due to the tuneable properties of carbon dioxide, changing the pressure or the temperature of the system could induce the selective precipitation of the catalyst system. The products and the substrate could then be separated from the catalyst extracting with supercritical carbon dioxide [12, 13].

We recently reported the successful application of Rh catalysts using the fluorous ligand **1** (Figure 1) in the hydrogenation [14] and hydroformylation of [15] alkenes using the FBS concept. The selectivity in aldehydes obtained in the hydroformylation of 1-octene using perfluoromethylcyclohexane was high (96 %) and the activity was up to 1040 h^{-1}. When a biphasic perfluoromethylcyclohexane/toluene system was used, the system could be effectively recycled for two consecutive runs. In this study we report the use of this fluorous monophosphine $P(C_6H_4\text{-}4\text{-}OCH_2C_7F_{15})_3$ (**1**) in rhodium catalytic hydroformylation of model alkenes using supercritical carbon dioxide as solvent.
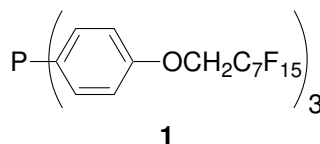

Figure 1. Ligand **1**

5.2. Results and Discussion

Solubility studies

We studied the solubility of the catalytic system Rh/**1** in supercritical carbon dioxide. The solubility studies were performed in a Thar 100 ml autoclave equipped with sapphire windows and the solubility was established by visual inspection. The catalytic precursor [Rh(acac)(CO)$_2$] (0.48.10^{-3} M), the phosphine **1** (P/Rh = 3) and 1-octene (24mmol) were placed in the autoclave, which was then pressurised with CO/H$_2$, 10 bar (1:1) and finally with carbon dioxide. The solubility behaviour was studied by increasing the temperature and the total pressure of carbon dioxide progressively using a syringe pump. The mixture became a solubilized one-phase transparent yellow system at 80°C and 200 bar of total pressure at density of approximately 0.6 g·ml $^{-1}$(Fig. 2a). When the autoclave was cooled down the two phases were recovered without apparent decomposition (Fig. 2b).
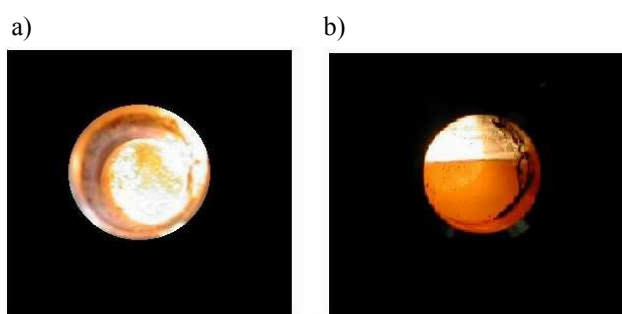
a)   b)
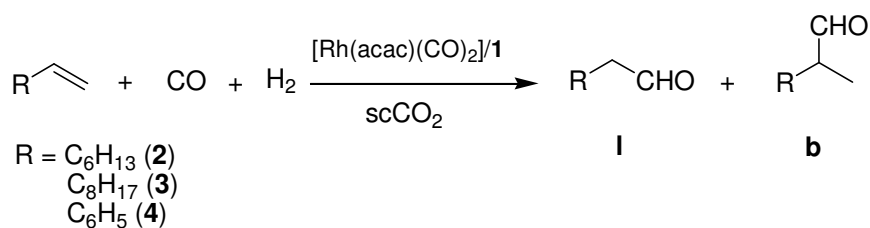

Figure 2. a) Soluble catalyst precursor in one phase system at 80°C and 200 bar b) Precipitation of catalyst precursor at 50°C and 135 bar.

Hydroformylation reactions

To investigate the efficiency of the fluorous phosphine **1** in rhodium catalysed hydroformylation, we choose 1-octene (**2**), 1-decene (**3**) and styrene (**4**) as

model substrates for the hydroformylation of 1-alkenes (Scheme 1) in supercritical carbon dioxide.

$$R\diagup\!\!\!\diagdown\!\!\!\diagup + CO + H_2 \xrightarrow[\text{scCO}_2]{\text{[Rh(acac)(CO)}_2]/\mathbf{1}} R\diagup\!\!\!\diagdown CHO + R\diagup\!\!\!\diagdown\text{(CHO)}$$

$$R = C_6H_{13} (\mathbf{2})$$
$$C_8H_{17} (\mathbf{3})$$
$$C_6H_5 (\mathbf{4})$$

l   **b**

Scheme 1.

Hydroformylation reactions were carried out using the *in situ* formed catalyst precursor [Rh(acac)(CO)$_2$]/**1** at 0.48 mM concentration. Using 1-octene (**2**) as the substrate, we studied the influence of P/Rh ratio, temperature, partial pressure of CO/H$_2$ and total pressure on the activity of the reaction. The results are summarized in Table 1.

At 10 bar of CO/H$_2$, 200 bar of total pressure, 80 °C and with a P/Rh molar ratio of 3 (entry 1, Table 1), conversion was very low, though the system was soluble under these conditions. The selectivity in aldehydes was also very low and the major products obtained were 2-octene isomers. This low conversion may be due to the lack of formation of the active species, since a period of induction, as reported for low donor phosphite systems, was probably needed [16]. Therefore, to form the active species in the supercritical solvent, we decided to conduct an experiment by heating the system at 80 °C, 10 bar of CO/H$_2$ and scCO$_2$ up to 200 bar of total pressure for 1h (entry 2, Table 1). The autoclave was cooled down to –50 °C, depressurised, and the substrate was introduced. CO/H$_2$ and carbon dioxide were again charged, and the reaction was allowed to proceed for 1h. Conversion and aldehydes selectivity increased by up to 49 % and 74 %, respectively.

Increasing the P/Rh molar ratio to 5 (entry 3, Table 1) increased total conversion, but also decreased both aldehydes selectivity and regioselectivity. To prevent the formation of isomerisation products by β-elimination, we decreased the temperature to 60 ° C while maintaining the P/Rh ratio at 5 (entry 4, Table 1). We observed a decrease in conversion, a lower selectivity in aldehydes, and no further improvement in the l/b ratio.

Table 1. Hydroformylation of **2**-**4** using [Rh(acac)(CO)$_2$]/**1** in scCO$_2$[a]

Entry	Alkene	P/Rh	t(h)	P(CO/H$_2$) (atm)	T °C	P$_{tot}$ (atm)	Conv (%)[b]	S$_{ald}$ (%)[c]	l/b	S$_i$ (%)[d]
1	**2**	3	1	5/5	80	200	4	50	70/30	41
2[e]	**2**	3	1	5/5	80	200	49	74	76/24	26
3[e]	**2**	5	1	5/5	80	200	66	64	68/32	36
4[e]	**2**	5	1	5/5	60	200	29	57	66/34	43
5[e]	**2**	3	1	10/10	80	200	66	86	76/24	14
6[e]	**2**	3	1	10/10	100	200	47	60	77/23	40
7[e]	**2**	3	1	10/10	80	250	40	72	73/27	28
8[e]	**2**	3	1	10/10	100	250	73	74	76/23[f]	26
9[e]	**2**	3	1	20/20	80	200	76	74	72/23	26
10[g,h]	**2**	5	1	20/20	80	40	68	96	74/26	4
11[e,h]	**2**	5	1	20/20	80	200	32	38	64/36	61
12[i]	**2**	5	1	20/20	80	40	97	98	73/23	2
13[e]	**3**	3	3	10/10	80	200	94	60	71/29	40
14[e,j]	**4**	3	3	10/10	80	200	31	87	28/62	-

[a] Reaction conditions: V= 25 ml, [Rh(acac)(CO)$_2$] = 0.48·10^{-3} M, 1-octene:Rh = 500. [b] % Conv = total conversion of alkene; [c] % S$_{ald}$ = selectivity in aldehydes; [d] %S$_i$ = selectivity in isomerized products; [e] Preactivation of catalyst; [f] less than 0.5% of ethylhexanal was detected; [g] solvent = C$_7$F$_{14}$ see reference [15]; [h] [Rh(acac)(CO)$_2$] = 1,6·10^{-3} M, S:Rh = 2000. [i] solvent = toluene, ligand = PPh$_3$, see reference [15]; [j]13 % ethylbenzene was also formed.

We studied the effect of partial pressure of CO/H_2 at P/Rh ratio of 3. Increasing the partial pressure to 20 bar (1:1) increased the selectivity in aldehydes (86%) and conversion (66 %) (entry 5 *vs* entry 2 , Table 1). When we increased the temperature to 100 °C (entry 6, Table 1) while keeping the other parameters constant, we observed a drop in both conversion and aldehydes selectivity.

The total pressure of carbon dioxide and the temperature can also affect the reactivity of the system, since these parameters also affect the density [11, 17]. At the same partial pressure of 20 bar of CO/H_2, and by increasing the total pressure of carbon dioxide to 250 bar at 80 °C (entry 7 *vs* entry 5, Table 1), we observed a decrease in conversion and in aldehydes selectivity. Increasing the temperature to 100 °C (entry 8 *vs* entry 6, Table 1) and applying a higher pressure of carbon dioxide led to better conversion (73 %) and aldehydes selectivity (74 %). The approximate calculated density of the system at 250 bar and 100 °C (entry 8, Table 1) was 0.6 $g \cdot ml^{-1}$, whereas the density at 200 bar and 100 °C (entry 6, Table 1) was 0.5 $g \cdot ml^{-1}$. When we compared these densities with those calculated for the system at 200 bar and 80 °C (d = 0.6 $g \cdot ml^{-1}$) (entry 5, Table 1) and at 250 bar and 80 °C (d = 0.7 $g \cdot ml^{-1}$) (entry 7, Table 1), we found that the best conversions and aldehydes selectivity were obtained when the density of the system was around 0.6 $g \cdot ml^{-1}$.

Increasing the partial pressure of CO/H_2 up to 40 bar (1:1) (entry 9, Table 1) gave higher conversion but slightly decreased aldehydes selectivity.

Optimisation of the conditions therefore showed that the best results (66 % conversion and 86 % selectivity in aldehydes) were obtained at P/Rh molar ratio of 3, 20 bar of CO/H_2 and 200 bar total pressure.

The system Rh/**1** was also used in the rhodium catalysed hydroformylation of 1-octene (**2**) in fluorous systems [15]. The best results in FBS were obtained at P/Rh ratio of 5 and a rhodium concentration of $1.6.10^{-3}$ M (entry 10, Table 1). To compare both solvents as reaction media, we performed a catalytic

experiment in scCO$_2$ using the same conditions than as those in FBS. Under the same conditions, the fluorous system provided better results. However, when we compared the best results for both systems (entry 5 *vs* entry 10, Table 1), we noticed that similar conversion and regioselectivity can be obtained using scCO$_2$ but with the added advantage that the catalyst concentration, P/Rh molar ratio and CO/H$_2$ partial pressure can be much lower. The selectivity in scCO$_2$ was about 10 % lower. When we compared the results obtained using the catalyst precursor [Rh(acac)(CO)$_2$]/PPh$_3$ in toluene (entry 12, Table 1), though conversion and selectivity were lower in scCO$_2$, we found that under suitable conditions this solvent can replace toluene.

The catalytic system Rh/**1** was also applied to the hydroformylation of 1-decene (**3**) and styrene (**4**) (entries 13 and 14, Table 1). When 1-decene (**3**) was used as the alkene, conversion was high but selectivity in aldehydes was moderate. The n/iso ratios were similar to those obtained with 1-octene (**2**) under the same reaction conditions. Styrene (**4**) was also hydroformylated with low conversion (31 %) although aldehydes selectivity was high (87 %) and the l/b ratio was moderate.

5.3. Conclusions

Ligand **1** associated with [Rh(acac)(CO)$_2$] afforded an active catalyst in the hydroformylation of olefins in scCO$_2$. The results showed that the system was more active at low rhodium concentrations with low P/Rh ratios. At low CO/H$_2$ pressure, conversions were low. However, increasing the partial pressure up to 20 bar led to high conversion. Higher partial pressures slightly decreased the aldehydes selectivity. The density of the system clearly influences the conversion and selectivity in aldehydes. The best results were obtained at density values close to 0.6 g·ml^{-1}. Comparative results showed that scCO$_2$ can replace fluorous systems and, though conversion and

selectivity were lower than when $[Rh(acac)(CO)_2]/PPh_3$, this system could be also used as a catalyst precursor.

5.4. Experimental

Solubility studies

The solubility studies were carried out in a Thar reactor (100 cm^3) equipped with sapphire windows and magnetic stirring. The autoclave was charged with ligand **1** (0.144 mmol), $[Rh(acac)(CO)_2]$ (0.048 mmol) and 1-octene (24 mmol). The reactor was pressurised with syn-gas and CO_2, the system was heated and the total pressure was increased using a syringe pump. Solubility was monitored by visual inspection.

Catalysis in supercritical carbon dioxide

Hydroformylation experiments were carried out in a Parr autoclave (25 cm^3) with magnetic stirring. The autoclave was equipped with a liquid inlet, a gas inlet, a CO_2 inlet and a thermocouple. An electric heating mantle kept the temperature constant. The complex $[Rh(acac)(CO)_2]$ (0.012 mmol) and the ligand (0.036 or 0.06 mmol) were placed in the autoclave. The autoclave was then evacuated, and the substrate 1-octene (6 mmol) was then added. The system was pressurised with CO/H_2 (1:1), and liquid CO_2 was introduced until a total pressure of 60 bar. The autoclave was heated to the desired temperature. When thermal equilibrium was reached, the total pressure was adjusted with a Thar syringe pump. After the reaction time, the autoclave was cooled down to –50 °C and carefully vented. The final mixture was analysed by GC. The products were identified by GC-mass spectrometry.

To preactivate the catalyst, $[Rh(acac)(CO)_2]$ and the ligand **1** were placed in the autoclave, the system was evacuated and pressurized with syn gas and carbon dioxide, the system was heated to the desired value, and then more carbon dioxide was added. The system was stirred for 1h, cooled down to –50

°C and depressurised. The substrate was then added and the system was pressurized again. All preactivations were carried out under the same reactions conditions.

Gas chromatography analyses were performed in a Hewlett-Packard 5890A in an HP-5 (5 % diphenylsilicone/95% dimethylsilicone) column (25 m x 0.2 mm Ø) for the separation of the products.

Acknowledgements

5.5. References

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