

Chapter 7. Concluding Remarks

Concluding Remarks

The main objective of this thesis was to study the use of alternative reaction media water and supercritical carbon dioxide for catalysed carbonylation reactions.

Rhodium-catalysed hydroformylation of 1-octene and 1-decene in biphasic aqueous systems was studied using such strategies to increase the mass transfer as adding cationic and anionic surfactants, methanol co-solvents and a dendrimeric molecule. The following conclusions were drawn:

- Adding an anionic surfactant to both systems increases the conversion to 98% (1-octene, Rh/dppbts) and 88% (1-decene, Rh/dppbts). But the selectivity to aldehydes decreases to 31% and 25%, respectively, and the reaction products are mainly isomers.
- Adding cationic surfactants to the systems increases both the activity and selectivity to aldehydes. However, high concentrations of cationic surfactants led to a loss of catalyst in the organic phase. When 1-octene was used as substrate, the regioselectivity to nonanal increased slightly ($n/iso = 79/21$). Using 1-decene and dppbts as a ligand the selectivity to aldehydes was as high as 97% and conversion was 63%. The system could also be recycled without affecting the conversion and selectivity.
- Adding methanol as a co-solvent increases the conversion of the hydroformylation of 1-octene when both ligands dppbts and dpppts (60 and 67 %, respectively) are used. When dppbts was used as a ligand, aldehyde selectivity increased to 90%.
- The use of dendrimer **12** did not improve the results.

The following conclusions were drawn about the hydroformylation of 1-octene in supercritical carbon dioxide:

- New P-donor ligands $\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$ ($n = 1, 2, 3$) containing branched alkyl chains were prepared.
- The cationic rhodium (I) complexes: $[\text{Rh}(\text{cod})(\text{P}(\text{OC}_9\text{H}_{19})_3)_2]\text{PF}_6$, $[\text{Rh}(\text{PPh}(\text{OC}_9\text{H}_{19})_2)_4]\text{PF}_6$ and $[\text{Rh}(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_4]\text{PF}_6$, and palladium neutral complexes: *cis*- $[\text{PdCl}_2(\text{P}(\text{OC}_9\text{H}_{19})_3)_2]$, *cis*- $[\text{PdCl}_2(\text{PPh}(\text{OC}_9\text{H}_{19})_2)_2]$ and *cis*- $[\text{PdCl}_2(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_2]$ were synthesised.
- The X-ray structure of complex $[\text{Rh}(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_4]\text{PF}_6$ was determined.
- In hydroformylation conditions, the catalytic systems $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$ ($n = 1, 2, 3$) in toluene mainly formed the species $[\text{RhH}(\text{CO})\{\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n\}_3]$. Minor amounts of $[\text{RhH}(\text{CO})_2\{\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n\}_3]_2$ were also detected.
- Catalyst precursors $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$ ($n = 1, 2, 3$) were not soluble in scCO_2 .
- The catalytic systems $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$ ($n = 1, 2, 3$) were active in the hydroformylation of 1-octene in supercritical carbon dioxide and in toluene.
- System $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{OC}_9\text{H}_{19})_3$ led to a total conversion of 98% and 86% of aldehyde selectivity in toluene.

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- System $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{OC}_9\text{H}_{19})_3$ at 20 bar of syn gas 1:1, 250 bar of CO_2 at 100°C provided conversion as high as 82% with a selectivity of 89%.
 - Systems $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$ ($n = 2, 3$) in toluene led to conversions as high as 89% and 95% but low aldehyde selectivities of 21% and 38%, respectively. When scCO_2 was used, both systems improved aldehyde selectivity. The system $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}(\text{OC}_9\text{H}_{19})_2$ led to an aldehyde selectivity of 94% and a conversion of 70% in optimised reaction conditions.
 - The catalytic system $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_2\text{C}_7\text{F}_{15})_3$ was found to be soluble in scCO_2 at 10 bar of syn gas (1:1), 200 bar of CO_2 , and 80°C of temperature.
 - Activities (49-76% of conversion) and selectivities (74-86%) were good when the catalytic system $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_2\text{C}_7\text{F}_{15})_3$ was used in scCO_2 at very low rhodium concentrations, $0.48 \cdot 10^{-3}$ M, and low P:Rh = 3 ratios.
 - The system $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_2\text{C}_7\text{F}_{15})_3$ also proved to be active in the hydroformylation of 1-decene and styrene.

The copolymerisation of 4-*tert*-butylstyrene with CO in supercritical carbon dioxide was studied:

- N-donor ligands, bipyridine (bipyR_f) and phenantroline (phenR_f) with perfluorinated chains were synthesised.

- The neutral palladium complexes $[\text{PdCl}(\text{CH}_3)(\text{BipyR}_f)]$ and $[\text{PdCl}(\text{CH}_3)(\text{PhenR}_f)]$, and the cationic palladium $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{Bipy}_f)]\text{BARF}$ and $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{Phen}_f)]\text{BARF}$ were prepared.
- The cationic palladium catalyst precursors were very soluble in supercritical carbon dioxide.
- The application of these cationic complexes to the copolymerisation of *tert*-butylstyrene with CO in scCO_2 and in dichloromethane was studied. The productivities in both solvents are in the range of 10-15 g CP/g Pd but the molecular weight in scCO_2 was twice (≈ 87000 g/mol) the value obtained in CH_2Cl_2 at the same conditions. The polydispersity in scCO_2 was 1.2 in front of 5.3 obtained in CH_2Cl_2 , indicating a narrow distribution of molecular weights in the supercritical solvent.