CONTINUOUS FLOW HOMOGENEOUS HYDROFORMYLATION OF 1-OCTENE OVER SUPPORTED IONIC LIQUID PHASE RHODIUM CATALYSTS USING SUPERCRITICAL CO_2

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Supervisor : Prof D .J. Cole-Hamilton

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The School of Chemistry, the University of St Andrews

I, Zhenxin Gong, hereby certify that this thesis, which is approximately 10,098 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

Date 2010.09.01 Signature of candidate

I was admitted as a research student in September 2007 and as a candidate for the degree of Master of Philosophy in September 2007; the higher study for which this is a record was carried out in the University of St Andrews between 2007 and 2008.

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Abbreviations

acacH	2,4-pentanedione
b/l	Branched / linear ratio
CA	Carbon Aerogels
CO_2	Carbon dioxide
$(DHQD)_2PHAL$	Dihydroquinidine phthalazinediyl diether
DCM	Dichloromethane
HPLC	High Pressure Liquid Chromatograph
ICPMS	Inductively Coupled Plasma Mass Spectroscopy
IL	Ionic liquid
l:b	Linear : branched ratio
NMO	N-methylmorpholine oxide
$[OctMIM][NTf_2]$	1-octyl-3-methylimidazolium bis-(trifluoromethylsulfonamide)
PPh_3	$[PrMIM][Ph_2P(3\text{-}C_6H_4SO_3)]$ Triphenylphosphine (PrMIM = 1-propyl-3-methylimidazolium)
[PrMIM]Br	1-Propyl-3-methylimidazolium Bromine
[PrMIM][TPPMS]	1-Propyl-3-methylimidazolium Diphenyl(3-sulfonatophenyl)-phosphine
Rh	Rhodium
RT	Room temperature
$scCO_2$	Supercritical carbon dioxide

[TPPMS]Na	Mono-sulfonatedtriphenylphosphine Sodium salt
TPP	Triphenylphosphine
TOF	Turnover frequency
TON	Turnover number
β	Beta
ppb	Part per billion (10^9)
J	Coupling constant
℃	Degree Celsius
^{1}H NMR	Proton Nuclear Magnetic Resonance
^{31}P NMR	Phosphorus Nuclear Magnetic Resonance
g	Grams
GC	Gas Chromatography
h	Hours
H_z	Hertz
K	Degree Kelvin
M	Molar concentration, in mole/liter
MeOH	Methanol
mg	Milligram
cm^3	Centimeter cube
mmol	Millimole
mol	Mole
MS	Mass Spectrometry

δ	Chemical shift relative to tetramethylsilane

Abstract

The hydroformylation of 1-octene with supported ionic liquid phase catalyst was demonstrated when using a system involving the substrate, reacting gases and products in CO_2 and N_2 flow over a fixed bed supported ionic liquid phase catalyst (silica gel and carbon aerogels as solid support respectively) at different system pressures. Yields, reaction rates, selectivities and rhodium leaching were all monitored.

A pressure of CO_2 flow just below the critical point of the flowing mixture (106 bar at 100 °C if no 1-octene has been converted) was the best condition for the hydroformylation. It gave the highest acitivity (conversion to aldehyde up to 70 %), fastest reaction (TOF up to 575.3 h^{-1}) and best stable selectivity (l:b ratio reaching 3.37).

The utilization of *sc*CO_2 as reaction media leads to remarkable stability of the catalyst. The supercritical or near critical (expanded liquid) system completely overcame the progressive decrease in activity of catalyst at 50, 75 bar with liquid phase transport and also showed much better results than when using other gas flows such as N_2 flow at 100 bar.

In the high pressure scCO_2 phase, the concentration of 1-octene at the catalyst bed was reduced so that the conversion to aldehyde was reduced.

The pore size and surface groups of the solid support should be suitable for the SILP catalyst consisting of metal complex, excess ligand and ionic liquid. Using microporous carbon aerogels as the supports, whether activated or not, gave disappointing results.

Contents

1 General Introduction

Hydroformylation is the largest homogeneous catalytic process and an important industrial reaction as it provides precursors to detergents and plasticisers. The world-wide production capacity is more than 150 billion U.S. dollars of aldehydes (alcohols) annually [1]. The commercially used catalysts in the hydroformylation industry are complexes of Co or Rh. In addition, the selectivity to linear (normal) or branched (iso) products of the reaction is one of the very important aspects.[2]

Cobalt-catalysed hydroformylation is the more widely used current industrial process, as it has commercial benefits and the catalyst is easy to recover. Compared with it, Rh-catalysed hydroformylation requires less harsh reaction conditions and can be more selective towards the desired linear aldehyde. It will be the favourable method to use instead of the former if the difficulty of separation and recovery of the catalyst can be overcome. [3] Product recovery from the Rh-catalysed hydroformylation is preferably carried out by a distillation step, but the temperature sensitive nature of many homogeneous catalysts means that this is unfeasible, as it would lead to catalyst degradation.[4]

A large number of different methods for affecting product – catalyst separation is being researched [5] [6]. These can involve anchoring the catalyst to a soluble or insoluble support or the use of biphasic systems. Particularly interesting is a new hybrid approach in which the catalyst is immobilized within a thin film of liquid, which is in soluble in the reaction product, adsorbed onto a support such as silica.

Inspired by the early work of Davis et al [7], on supported aqueous catalyst systems, Mehnert reported a new concept of supported ionic liquid phase catalysis (SILP). [8] [9] There are some advantages of ionic liquid media combined with fixed-bed technology through this approach. Solid support materials and the usage of significantly reduced amounts of the ionic liquid are both involved in this concept.

SILP reactions carried out using flowing liquid phases tend to lead to significant loss of catalyst and ionic liquid as well as to problems with gas availability. Once the pores of the support are filled with liquid substrate, gas diffusion to the catalytic centres will be very slow. Reactions carried out in the gas phase are limited to volatile substrates and suffer from catalyst fouling by heavy byproducts, such as aldol condensation products of aldehydes when carrying out hydroformylation reactions [8].

Considering the outstanding work of Brennecke and coworkers concerning CO_2 solubilities in supercritical fluids [10], the combination of SILP catalysis with supercritical carbon dioxide looks very promising. The supercritical fluid should allow rapid diffusion of all the gases and substrates to the catalytic centres, whilst avoiding catalyst leaching. It may also remove heavy byproducts, reducing catalyst fouling.

In this project, the hydroformylation of 1-octene over a SILP catalyst containing a sulfonated phosphine modified rhodium complex is investigated. The performance of the obtained SILP catalysts was tested in continuous flow mode with supercritical CO_2 as transport vector for both substrates and products in a specially designed system to continue the early work of Hintermair, [11] who had used statistical design of experiments to optimise the system.

1.1 Hydroformylation reaction

Hydroformylation is a reaction in which a carbo6n monoxide molecule and a hydrogen molecule are introduced to the double bond of an alkene to form an aldehyde or alcohol depending on the catalyst used (Figure 1.1). Usually the reaction yields two geometric isomers of the product the linear and branched, where the linear version is usually the more desired product.[12]

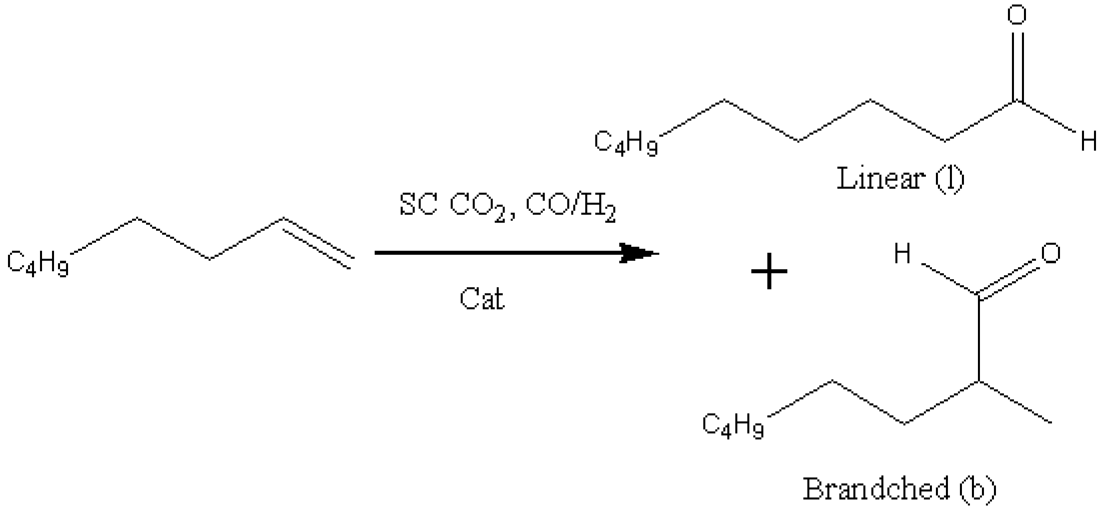


Figure 1.1 *Hydroformylation of 1-octene.*

In 1938, Otto Roelen discovered the first hydroformylation catalysts [13]. They are mainly cobalt carbonyl compounds, such as dicobalt octacarbonyl [$Co_2(CO)_8$]. The mechanism of reaction was outlined by Heck and Breslow [14] (Figure 1.2).

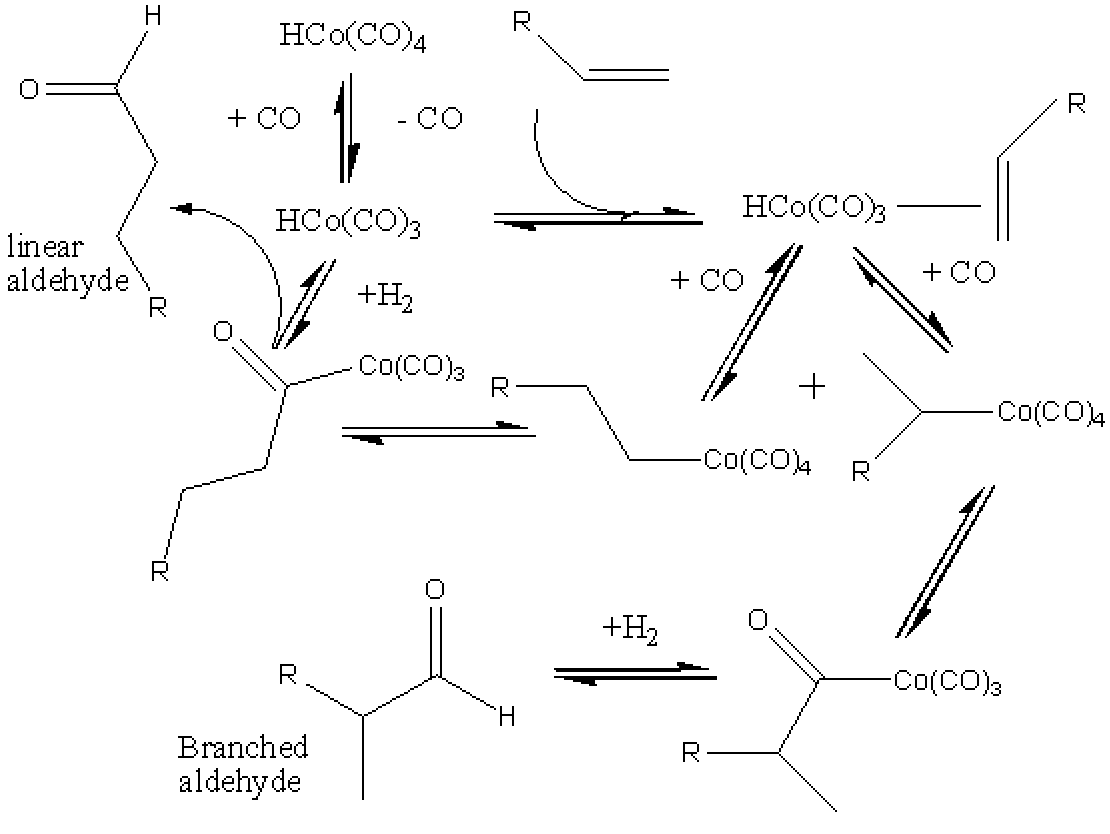


Figure 1.2: *Cobalt catalysed hydroformylation reaction mechanism.*

Reaction condition are harsh (200 – 400 bar and 150 – 200 °C) for this unmodified type of catalysis because of the low activity and stability of the tetracarbonylhydridocobalt(I), [$HCo(CO)_4$] species, which is the active catalyst precursor. In addition, there are some disadvantages of this reactions. For instance the process requires large reactor vessels, this catalyst system gives poor selectivity towards linear product and there are many by-products such as alkanes, ketones, and aldol condensation products.

In the mid-1960s, Wilkinson and co-workers discovered that triarylphophine (TPP) modified rhodium catalysts gave better selectivities to the desired linear aldehyde product and higher activities for alkene hydroformylation under lower temperatures and pressures than the common cobalt catalysts.[15] He suggested the reaction mechanism shown in Figure 1.3.

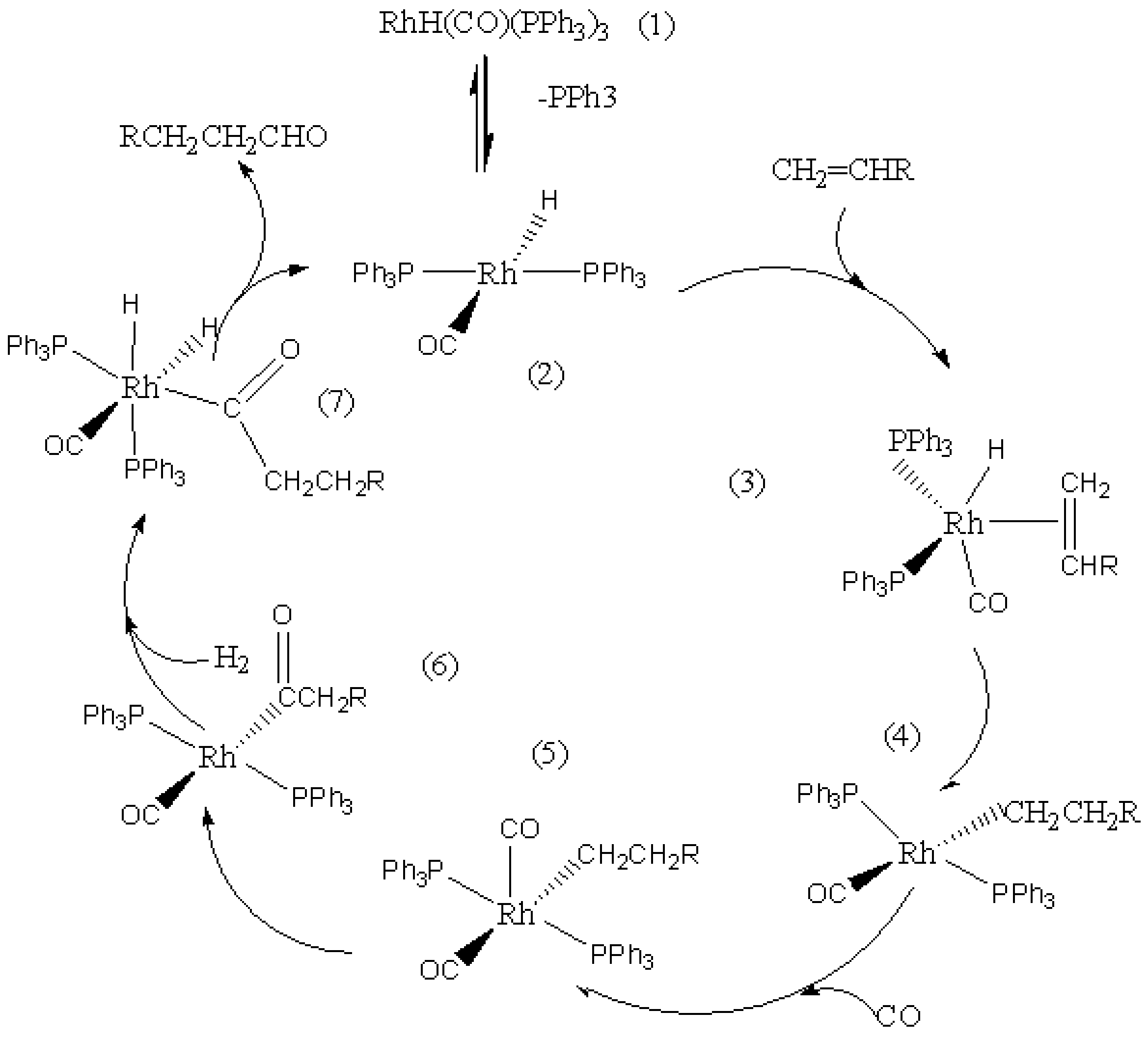


Figure 1.3: *The dissociative mechanism for hydroformylation of an alkene by a triphenylphosphine modified rhodium catalyst.*

The catalyst precursor is usually $[RhH(PPh_3)_3(CO)]$ which is in equilibrium with two active species, $[RhH(PPh_3)_2(CO)_2]$ and $[RhH(PPh_3)(CO)_3]$, under carbon monoxide and hydrogen. The mono-phosphine complex is believed to be less selective towards the linear aldehyde.

In the triphenylphosphine modified rhodium catalysed hydroformylation, low phosphine concentration results in a low linear to branched ratio (approximately 3:1) [16].

1.2 Homogeneous catalyst

Homogeneous catalysts have much more important advantages than heterogeneous catalysts such as high activity and selectivity. For most homogeneous catalysts, the catalytic sites are accessible due to the dissolved metal complex being usually used as catalyst. In addition, the enantioselectively, regioselectivity, and /or chemoselectivity of the catalyst are often possibly tunable for homogeneous catalysts [5].

Some of the properties of catalysts are collected in Table 1, where heterogeneous and homogeneous catalysts are compared.

Table 1 *Comparison of homogeneous and heterogeneous catalysts* [6].

	Heterogeneous	Homogeneous
Catalyst form	Solid, often metal or metal oxide	Metal complex
Mode of use	Fixed bed or slurry	Dissolved in reaction medium
Solvent	Usually not required	Usually required – can be product or byproduct
Selectivity	Usually poor	Can be tuned
Stability	Stable to high temperature	Often decompose < 100℃
Recyclability	Easy	Can be very difficult
Special reaction	Haber process, exhaust clean up etc	Hydroformylation of alkenes, methanol carbonylation, asymmetric synthesis etc.

A main obstruction for homogeneous catalysts to be commercial is that it is difficult to separate the catalyst from the products and the solvent, because of thermally stable temperature of the most homogeneous catalyst below 150 °C.[17] [18]

To solve the separation problems, lots of methods beside distillation for recycling the catalysts [19,20] have been investigated. There are two main new processes considered widely.

Firstly, the soluble or insoluble supports are used to anchor the catalysts, and filtration is applied for separation. These reactions were referred to as heterogenizing homogeneous catalysts. Two more modern examples of these methods are briefly explained below. First, a supported ionic liquid phase (SILP) catalyst is a good choice.

Second, because they are large spherical molecules with coordinating groups grafted in well defined positions on the dendrimer's exterior, dendrimers are another choice for use as the support. Their dimensions are suitable for them to be removed from solution by ultra filtration. [6]

The second approach to immobilization involves designing the catalyst to be solubilized in a solvent, which is not miscible with the product under some conditions. These reactions are mostly referred to as biphasic systems. Two of these methods are briefly explained as follows. Firstly, in fluorous biphasic systems, the substrates and products are in a special organic solvent which is immiscible with a fluorous solvent and the catalyst is designed to be soluble in the fluorous phase in the same reaction condition. The selection of fluorous phase and organic solvent can make the system monophasic at the reaction temperature, which enhances the access of the substrate to the catalyst, but the phases separate at room temperature. [21] Secondly, supercritical fluids have gas-like properties, so they are miscible with other gases and can solubilise many compounds with low to medium polarity [14], due to their sufficient densities. They are considered as ideal solvents for catalytic reactions because they are easily removable as a result of a phase change on lowering the pressure.

1.3 Supported Aqueous Phase (SAP) Catalysis

A "supported aqueous- phase catalyst" (SAPC) developed by Davis and Hanson in 1989, combines a hydrophilic organometallic catalytic complex and a hydrophilic liquid on a solid support (Figure 1.4) [22]

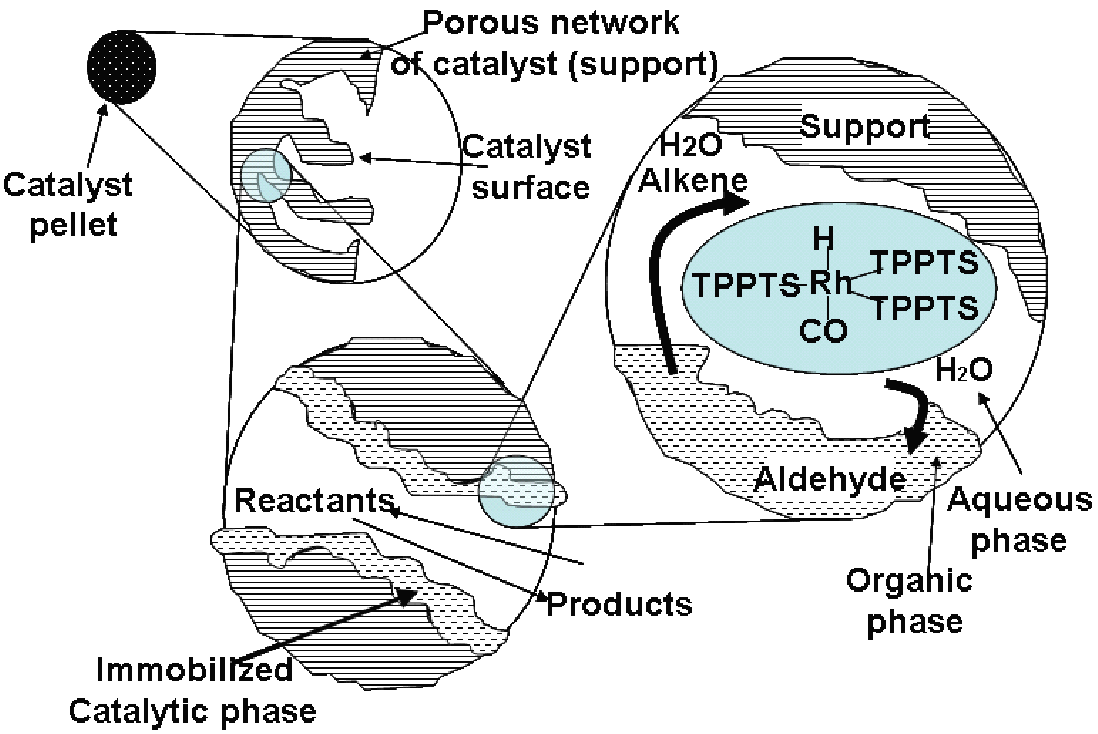


Figure 1.4 *The illustration of a supported aqueous-phase catalytic system (SAPC)* [6].

In order to increase the interface in aqueous biphasic catalysis they used a high surface area hydrophilic support. These materials were covered with a thin film of water clinging on the surface, which can dissolve the water soluble catalyst. The supported catalyst has a very large interfacial area, which results in very efficient catalysis for organic substrates. In addition, the catalysts are anchored on the support surface.[23]

The water thickness can impact the performance of the catalyst systems enormously [24]. If the layer is very thin the catalyst mobility decreases, it causes the activity of the catalyst to be much lower. If the layer is very thick the rate increases, but then drops again after an optimal thickness is reached because substrate diffusion through the water film becomes rate determining.[25] [26]

The activity of the SAPC were impacted by the volume of water in the system strongly, which was observed by Mortreux and co-workers, who compared the activity of SAPC catalysts with that of the homogeneous analogue in the hydroformylation of methyl acrylate [27]. Furthermore, the activities of the homogeneous systems were lower than that of SAPC. This effect was ascribed to the polar interactions between the substrate and the silica support.

Under optimal conditions, the solubility in water did not influence the activity [28]. Water obviously leaches if the SAPC is used in a continuous flow system, which, in a practical application, should be compensated for by using water-saturated organic solvents.

1.4 Supported Ionic Liquid Phase (SILP) Catalysis

Supported Ionic Liquid Phase (SILP) catalysis involves the heterogenisation of a homogeneous catalyst system by confining an ionic liquid solution of catalytically active complexes on a solid support [8]. This concept results in improvement on the concept of SAPC. A relatively quite short diffusion distances for the reactants and a highly efficient utilization of the ionic liquid were established. The results were compared to those of an ionic-liquid catalyst phase used in conventional two-phase systems.

These catalysts have been examined for the Friedel-Crafts reaction[29], hydroformylation [30,8], hydrogenation [31], and hydroamination [32].

In a thin film of the ionic liquid, transition-metal complex catalysts were dissolved and anchored on a porous solid with high surface area. Immobilisation takes place through covalent anchoring, tethering or physisorption. (Figure1.5)

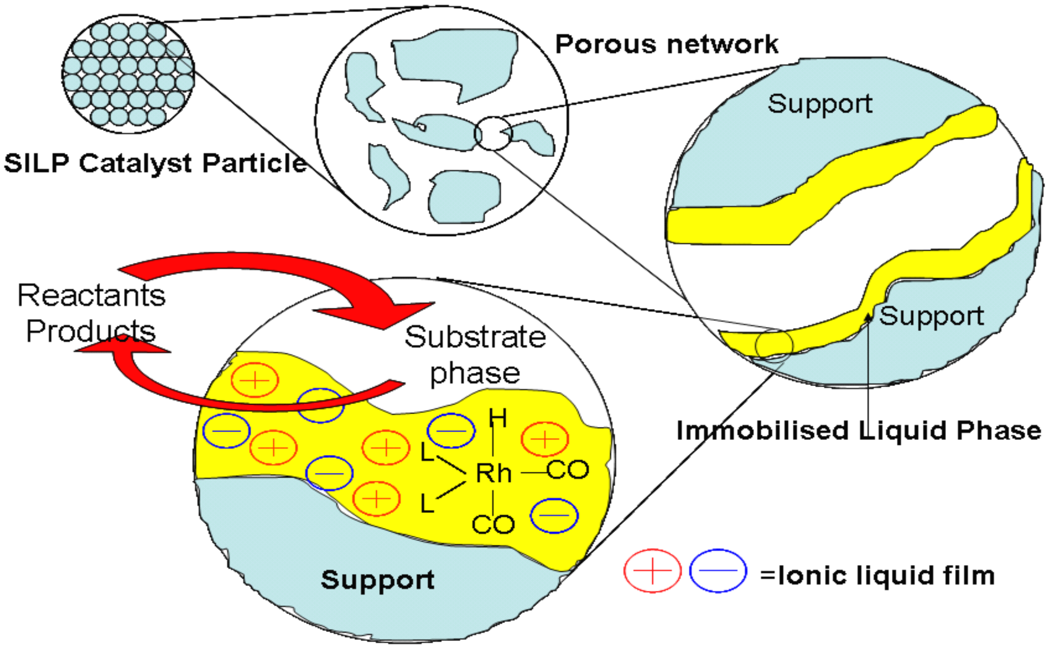


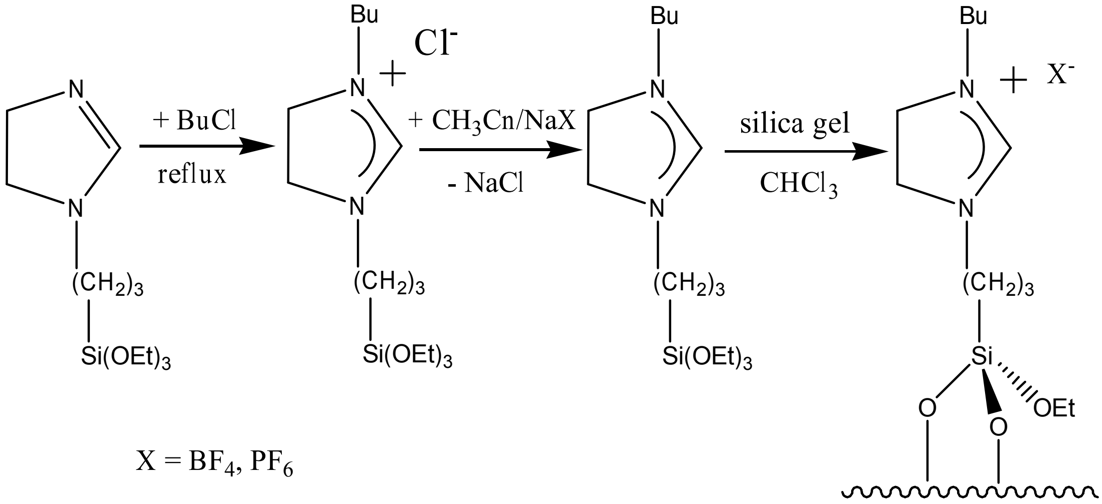
Figure 1.5: *The illustration of a SILP catalyst with Rh complexes in the ionic liquid film and anchored within a porous solid.* [6]

Although the catalyst is a solid it performs as a homogeneous catalyst, i.e. reaction happens in the very highly dispersed ionic liquid. Furthermore, a variety of cation / anion combinations can be used to change the solvent properties of the ionic liquid strongly. SILP catalysts are highly suitable for continuous processes, because of the thermal stability of the solvent, which was maintained by thermal stability of ionic liquids, the negligible vapor pressure and the large liquid range.[33]

The SILP concept can overcome some of the major disadvantages of the utilization of ionic liquids in catalysis, such as relatively high viscosity leading to slow mass transfer and the high price of ionic liquid. In the SILP concept only very thin films of the ionic liquids are used in a highly efficient manner. Thus the small size of the diffusion layer can allow all the rhodium atoms to be catalytically active. This results in a large amount of the precious catalyst metal being utilized during the reaction.

There are two ways which the SILP concept can be used to sort out the problem that the liquid immobilization phase is easily removed from the carrier by evaporation in SLP and SAP concepts.

Firstly, the approach is that the ionic liquid phase is designed to be fixed to a support by chemical bonds between either the cation or the anion and the support [8]. For example, the first SILP-catalysis applied for Rh-catalysed hydroformyaltion involved a covalently anchored ionic liquid fragment and a surface modified silica gel. (scheme 1.1) [35]



Scheme 1.1: *Preparation of surface anchored ionic liquid phases.*

Secondly, impregnation, in which physisorption fixes the ionic liquid onto the support, has be used by Riisager and Fehrmann.[34] They used the SILP concept in continuous Rh-catalysted hydroformylation of propene in a gas-phase reaction. The ligand and [Rh(acac)(CO)$_2$] under investigation were dissolved in dry methanol together with either [BMIM][PF$_6$] or [BMIM][n-C$_8$H$_{17}$OSO$_3$]. The silica gel 100 (BET surface area 297.5 m^2, mean pore diameter 13.7 nm, pore volume 1.015 cm^3) was added as support. Finally the methanol was removed by evaporation [30].

1.5 Supercritical Fluids (SCFs)

1.5.1 Definition and a brief description of SCFs

A supercritical fluid occurs when an element, compound or mixture, is above its critical temperature (Tc) and critical pressure (Pc). [35]

It combines both properties of liquid and gas, such as dissolving materials like a liquid and diffusing through solids like a gas. The property of the fluid is very changeable close to the critical point, due to the huge changes in density caused by small differences in pressure or temperature, which tune many properties of the fluid.

The solubility of material in the supercritical fluid is impacted by pressure and temperature. It increases with the density of the fluid at constant temperature. Since density increases with pressure, the solubility increases with pressure as well. Solubility will increase with temperature at constant density. However, the density can drop sharply with a slight increase in temperature close to the critical point. Therefore, solubility can drop with the increase of temperature close to the critical temperature , then rise up again. [36]

Supercritical fluids are considered as the best way to provide both the closest attachment of reagents and catalyst during the reaction and a maximum of discrimination at the separation step for immobilized organometallic catalysts. [37] [38]

1.5.2 Supercritical Carbon dioxide

Supercritical carbon dioxide ($scCO_2$) offers many advantages over conventional organic solvents, including increased reaction rates, higher selectivities, and facile separation of reactants, catalysts, and products after the reaction [39].

Carbon dioxide ($scCO_2$) is the most widely used supercritical fluid due to its mild critical properties (T_c = 31.1°C, p_c = 73.8 bar, d_c = 0.437 g/ml) and because it is nontoxic, non-flammable and can be handled safely on laboratory and industrial scales [39].

Figure 1.6 shows an experiment carried out by Rayner and co-workers in which liquid CO_2 is heated in a closed view cell. They describe what is observed as follows "Under low temperature and pressure condition, the separate phases (Liquid and gas) of carbon dioxide can be observed easily due to the clear meniscus. With temperature increasing, the meniscus starts to diminish. Increasing the temperature further, the densities of the gas and liquid become more similar. The meniscus starts to be less easily observed but still exists. Once the critical temperature and pressure are reached the two distinct phases of liquid and gas are not visible. The meniscus is not observed either. Then the homogenous phase called the "supercritical fluid" phase is formed and shows properties of both liquids and gases." [41]

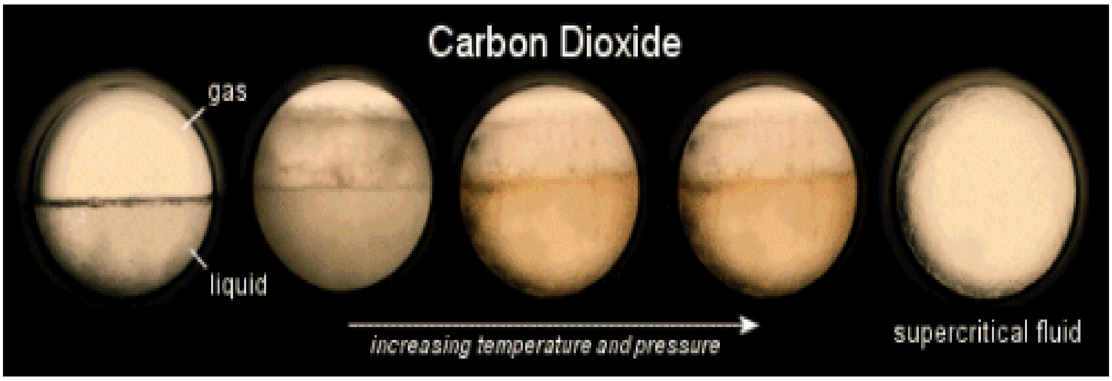


Figure 1.6 *The observation of the phase behaviour of CO_2 with temperature and pressure increasing [40].*

The application of supercritical fluids is considered as a viable technique with environmental friendly benefits. They deliver pure product in the recovery of products from ionic liquids and supercritical fluid extraction. [41] The combination between volatile and nonpolar $scCO_2$ and nonvolatile and polar ILs results in different two-phase systems. So the product recovery process is based on the observation that $scCO_2$ is soluble in ILs, not the other way round [42].

There was a successful example of the application of supercritical fluids to take substrates through and take products away from supported ionic liquid phase catalysts, which was carried out by Ulrich Hintermair in 2007 [11] . A rapid hydroformylation of 1-octene with the high stability of catalyst and with very low rhodium leaching levels was demonstrated under a system involving a supported ionic liquid phase catalyst with supercritical CO_2 flow.

In the continuous flow reactions which are explained in this thesis, we report further studies of the operation factors on the performance of the hydroformylation, such as different pressure of CO_2 flow, different flow gas (N_2 compare to CO_2) and different solid support (carbon aerogels compared to silica gel).

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2 Experimental section

2.1 Measurements

2.1.1 NMR Spectra

NMR spectra were recorded on a Varian 300 spectrometer using protio impurities of the deuterated solvent as a reference for ^{1}H and ^{13}C chemical shifts, with tertramethylsilane at 0 ppm. ^{31}P chemical shifts are reported to high frequency of external 85% H_3PO_4.

2.1.2 Gas chromatography measurement

All samples from catalytic runs were analyzed by Gas Chromatography on a Hewlett-Packard 5890 series gas chromatograph equipped with both a flame ionisation detector (GCFID for quantitative analyses) and a mass selective detector (GC-MS for qualitative analyses). The gas chromatograph was interfaced with a Hewlett-Packard Chemstation for the determination of peak areas by electronic integration. The GC-MS and GC-FID methods employed a Supelco^{TM} Meridian MDN-35 low polarity, cross-linked phase comprised of a (35% phenyl)-methylpolysiloxane fused silica capillary column (30 m x 0.25 mm x 0.25 mm).

2.1.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

All trace analyses of recovered fractions (i.e. Rh leaching) were measured by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500a instrument.The instrument was modified for direct analyses of the organic fractions by using O_2 as a makeup gas to prevent carbon deposition on the sample and skimmer cones. Platinum cones were used together with a self-aspirating nebulizer held at -5

°C. Samples were diluted by 10% in a mixture of xylene and toluene (50:50) and ion counts were referenced against calibration curves obtained from standard solutions of $[Rh(acac)(CO)_2]$ (acacH is 2,4-dimethylpentanedione) in xylene/toluene (50:50). Standard solutions were run intermittently between samples to ensure that there were no drifts in instrument response and that the rate of aspiration was constant.

2.1.4 Porosimetry measurement

The characteristics of the different SILP catalyst before and after hydroformylation reactions, BET surface area, pore volume and pore size were measured by porosimetry on a N_2 BET system (ASAP 2020 V 3.00H, Micrometritics Co.) Considering the strict requirement for dryness of the sample, all SILP catalyst samples were dried at 100 °C under vacuum at least for 4 days to remove the solvent and products nearly completely.

2.2 Materials

2.2.1 1-Propyl-3-methylimidazolium Diphenyl (3-sulfonatophenyl)- phosphine ([PrMIM][TPPMS]) [1]

[PrMIM]Br (2.3g, 11.2 mmol) was added dropwise to a rapidly stirred solution of sodium diphenyl-(3-sulfonatophenyl)phosphine dihydrate (4.7g, 11.7 mmol) in degassed THF (40 cm^3), with vigorous stirring, resulting in immediate formation of a fine white precipitate. The solution was stirred at room temperature for a further 24 h, filtered through diatomaceous earth, and the solvent removed by evaporation. The resulting residue was dissolved in the minimum volume of acetone and layered by diethyl ether. The solution containing a white precipitate was kept in the fridge overnight. The solvent was removed in vacuo. Then the product was afforded as colourless rhomboidal crystals.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ= 0.99 (3H, t, CH_3), 1.92 (2H, sext, CH_2CH_3), 3.97 (3H, s, NCH_3), 4.20 (2H, t, NCH_2), 7.43 (14H, m, $Ph_2PC_6H_4SO_3$), 7.92, 7.96 (2H, 2 _ d, NC(H)C(H)N), 9.71 (1H, s, NC(H)N) ppm.

^{31}P NMR (121.4 MHz, CD_2Cl_2, 298 K) δ= - 4.10

2.2.2 [OctMIM][Tf_2N]

[OctMIM][Tf_2N] 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonamide) was synthesised in the laboratories by a fellow student, Tania Quintas Martins. It was further purified by stirring over charcoal, passing over a short silica column, washing with water and in-depth drying. Additionally, the IL was degassed for two hours at 100 °C prior to every use. [OctMIM][Tf_2N] was selected as the ionic liquid because it was the best of several ionic liquids for the hydroformylation of 1-octene using the same catalyst in a bulk biphasic system consisting of [OctMIM][Tf_2N] and $scCO_2$.[1] 1-Octene is highly soluble in [OctMIM][Tf_2N] and the presence of $scCO_2$ is known to improve the solubility and mass transport of the permanent gases into the ionic liquid.[2] Even though $scCO_2$ is very soluble in [OctMIM][Tf_2N], the ionic liquid and the ionic catalyst are essentially insoluble in $scCO_2$, so that they are not dissolved by the flowing supercritical CO_2 phase.[1]

2.2.3 Silica Gel

The Silica Gel was purchased from Merck (Silica Gel 100, grade 10184, 60-230 mesh) and thermally pre-treated by heating at 500 °C in air for 15 h. It was stored under N_2 over P_4O_{10} at room temperature. [3]

2.2.4 Methanol

Pure methanol was used for the impregnation of the SILP catalysts. It was dried and purified prior to use by distillation from magnesium methoxide and stored under N_2 at room temperature [4].

2.2.5 Purification of 1-octene

Ammonium ferrous sulphate was dissolved in degassed water. 1-octene was also degassed by bubbling argon for 3 min. The 1-octene was added to the ammonium ferrous sulphate solution by cannula and shaken vigorously. The mixture was allowed to separate in the Schlenk tube and the organic layer removed by cannula, passed though an alumina column and collected under argon.

2.3 Methods

2.3.1 Catalyst preparation

2.3.1.1 Supported ionic liquid phase Rh-catalyst with Silica Gel

[PrMIM][TPPMS] was used with the precursor dicarbonyl(2,4-pentanedioato)rhodium(I) ([Rh(acac)$(CO)_2$]). As the solubility of liquid substrates in RTILs is known to be determined by the cation while gas solubility is mainly influenced by the anion [5]. [OctMIM]NTf_2 was used as IL.

Considering the very low thickness of the IL layer and the resulting sensitivity for impurities, all compounds used were synthesized and thoroughly purified using a completely grease-free Schlenk system. Commercial Silica Gel as a non-toxic and easily available mesoporous support was thermally pre-treated prior to the impregnation. All prepared SILP catalysts were slightly lemon yellow, homogeneous, dry and free flowing powders.

A typical preparation of the SILP catalyst (14% w/w IL loading) was performed by dissolving the precursor [Rh(acac)$(CO)_2$] (0.04g, 0.15 mmol) , the ligand

[PrMIM][TPPMS] (0.738g, 1.5 mmol) , to give a ligand : Rh ratio of 10.2 and the degassed [OctMIM]NTf$_2$ (0.285g, 0.6 mmol) in purified methanol (40 cm^3 , 10 cm^3 per gram of silica). After one hour of stirring at room temperature, the pre-treated silica gel (3.27g) was added, and the mixture was stirred for a further two hours. Then the methanol was very slowly removed at 35°C under reduced pressure, and the residual powder was dried for six hours at 100°C under vacuum. Every catalyst was synthesized just prior to use, and not stored for longer periods.

2.3.1.2 Supported ionic liquid phase Rh-catalyst with Carbon Aerogels (CA)

The SILP catalyst (14% w/w IL loading) was formed by dissolving the precursor [Rh(acac)(CO)$_2$] (0.04g, 0.15 mmol) , the ligand [PrMIM][TPPMS] (0.738g, 1.5 mmol) , to give the ligand : Rh ratio of 10.2 and the degassed [OctMIM]NTf$_2$ (0.285g, 0.6 mmol) in purified methanol (40 cm^3 , 10 cm^3 per gram of carbon aerogels). After one hour of stirring at room temperature, the CA (from Fernando Pérez-Caballero, details shown in Table 1) [6] was added, and the mixture was stirred for a further two hours. Then the methanol was very slowly removed at 35 °C under reduced pressure, and the residual powder was dried for six hours at 100 °C under vacuum. Every catalyst was synthesized just prior to use, and not stored for longer periods.

Table 1. *Properties of Carbon Aerogels after activation. Note: sample ACT 2 was used in reaction; ACT : activated sample, na: not assessed, Mic. Area, S BET : m^2/g; Density: g/cm^3; V Mic, Total pore V : mm^3/g*

Sample	Dried	Blank	ACT 1	ACT 2	ACT 3	ACT 4
ACT Time	-	0	0.5	1	1.5	2
V mic	0	82.92	263.19	290.73	472.48	261.15
Total pore v	na	na	812.91	na	na	1253.32
Mic Area	0	235.34	746.96	825.114	1340.97	741.18
S BET	295.48	475.53	1028.28	969.42	1589.88	1655.8
% Mic	0	49.49108	72.64169	85.11446	84.34357	44.76238
Density	0.2061	0.303	0.245	0.217	0.178	0.158

2.3.2 Catalytic Reactions

2.3.2.1 Hydroformylation of 1-Octene over SILP Catalysts with CO_2 or N_2 flow

The catalytic reactions were carried out on a specially designed rig (Figure 3) using a stainless steel tubular reactor with a volume of 8.8 ml. Glass wool was used to fix the catalytic bed and prevent it being flushed from the reactor. All reactions were carried out with the tubular reaction held vertical and with the flow being from bottom to top.

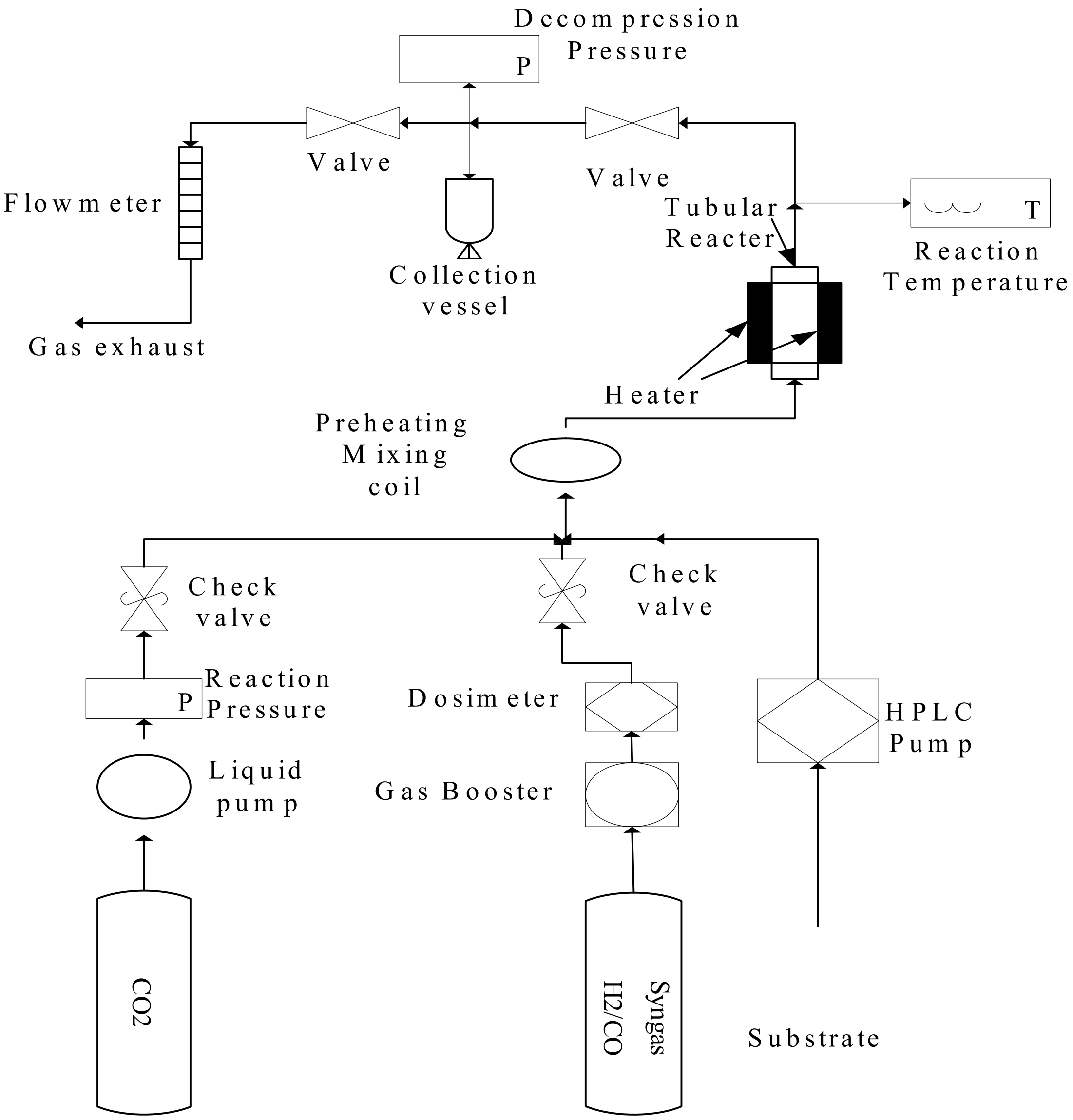

Figure 1: *Illustration of the rig for supercritical continuous flow hydroformylation reactions.*

The catalyst (made following the method described above, *ca.* 4.5 g) was loaded into a tubular reactor (8.8 ml) in a glove box to avoid air. The tubular reactor was fitted into the rig (Figure 1) with CO_2 purging. The tubular reactor was pressurized with CO/H_2 (1:1, 40 bar) through a gas booster, for which the internal pressure is 80 bar above the system pressure, and heated to 100 °C for 7 h. This process allows the preformation of the active catalyst. The system was then pressurized with CO_2 using an air operated liquid pump to the desired overall pressure. Following equilibration, 1-octene was injected directly into the flowing CO_2 just before the preheating coil using an HPLC pump, with the other flows being maintained. The total flow was controlled using the decompression valve. The liquid in the collecting vessel was removed every hour, weighed to check mass balance and analysed by GC (organic products) and ICPMS (Rh content). Turnover frequency (TOF / mol of product (mol of catalyst h)$^{-1}$ and cumulative turnover number (mol product (mol catalyst)$^{-1}$) were plotted against time on stream.

Numerous factors influence the activity and selectivity of phosphine modified rhodium complexes in hydroformylation [7]. As Wasserscheid et al. have proven the pure homogeneous character of hydroformylation using SILP catalysts for gas phase reactions some well-established data could be transferred. The molar ligand/rhodium ratio was always 10, and the syngas composition was 1:1 hydrogen : carbon monoxide. The catalyst loading was 14 wt % of IL loading in all cases, but experiments were carried out at 50, 75, 100, 130, 150, 180 and 200 bar reaction pressure at 100 °C respectively. CO_2 and N_2 flow were continued for at least 10 hours in continuous flow reaction.

2.3.2.2 Continuous flow dihydroxylation

$(DHQD)_2PHAL$ (Hydroquinidine 1,4-phthalazinediyl diether) and potassium osmate , to give the ligand : Rh ratio of 10.2 were mixed in the ionic liquid [Octmim][NTf_2] by Dr Ana Serbanovic and charged into the reactor. The mixture was made on a 44 w/w % basis relative to the amount of ionic liquid used and supported in silica gel, which had been heated at 500 °C for 15 h, cooled under vacuum and kept under N_2. The system was sealed, heated and pressurised with CO_2 to the required pressure and temperature. The liquid substrate (1-hexene) mixed with morpholine-N-oxide MNO was delivered into the system using a HPLC pump at a fixed rate.

The system was run in a continuous flow mode with the products being extracted and sampled at regular intervals. These reactions were run at 100 bar, 50 bar and 150 bar each for 10 h at 40 °C. Unfortunately, I left before the end of this experiment, when I was there it seems that there were traces of products observed, but the further detail data and analyse was not passed through by Dr Ana Serbanvic so far.

2.3.2.3 Phase behaviour studies

This system was run following the same procedure as the continuous flow SILP hydroformylation reactions, the only difference being that the tubular reactor was replaced by an autoclave with a sapphire window as its bottom plate and no catalyst was used. The phase behaviour inside the reactor could be observed through the sapphire window in the bottom of the autoclave. During this phase behaviour study, the autoclave was pressuriseed from 50 bar up to over 100 bar very slowly, to find the critical point of the flowing mixture. The flows of 1-octene, CO/H_2 and the overall flow were the same as in the catalytic reactions at the different pressures. These studies give information on the critical point of the mixture when only 1-octene is present (i. e. at the entrance to the reactor). The critical point is expected to occur at a higher pressure when aldehydes replace 1-octene since they are more polar and higher boiling.

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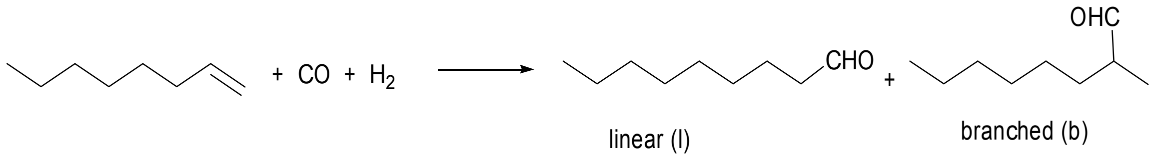
3 Results section

Supported ionic liquid phase catalysts, consisting of a rhodium complex made in situ from [Rh(CO)$_2$(acac)] and [PrMIM][Ph$_2$P(3-C$_6$H$_4$SO$_3$] (PrMIM = 1.proply-3-methylimidazolium) dissolved in a thin film of the ionic liquid [OctMIM]Tf$_2$N (OctMIM = 1-octyl-3-methylimidazolium, Tf = CF$_3$SO$_3$) supported within the pores of silica or carbon aerogels,have been synthesised. Reactions were carried out in a continuous flow system with the catalyst packed into a vertical tubular reactor with the direction of flow being from the bottom to the top. The system was tested using the hydroformylation of 1-octene (Scheme 1) as a model reaction. Some preliminary experiments had been carried out by Ulrich Hinternaier [1] , who had shown that high conversions could be obtained using this system over periods of up to 40 h with minimal rhodium leaching (0.5 ppm). There was little dependence of the rate on film thickness, but there was some doubt about the phase behaviour during his reactions.



Scheme 1. *The hydroformylation of 1-octene to linear and branched products used as a test reaction in this thesis.*

Reactions were carried out in the presence of nitrogen (liquid flow) or CO$_2$ at different pressures. The phase behaviour was monitored by replacing the tubular reactor with an autoclave the bottom plate of which was a sapphire window and observing visually how many phases were present when flowing substrate, syngas and CO$_2$ through the system under conditions identical to thise used for the catalytic reactions.

3.1 Porosimetry measurements

Important parameters of porous catalysts are their surface area, pore size and pore volumes. It is also important to know how these change on activation of the catalyst and as a result of the catalytic reaction. Porosity measurements were used to monitor these features of the catalysts. [2] [3]

Considering the very low thickness of the IL layer and the resulting sensitivity for impurities, all compounds used were synthesized and thoroughly purified using a completely grease-free Schlenk system. [4] Commercial Silica Gel as a non-toxic and easily available mesoporous support was thermally pre-treated prior to the impregnation. All prepared SILP catalysts yielded slightly lemon yellow, homogeneous, dry and free flowing powders.

The molar ligand/rhodium ratio was always 10, the [Rh(acac)$(CO)_2$] loading of catalyst was always 14 wt % and the Syngas composition was 1:1 hydrogen and carbon monoxide in all experiments. All experiments were carried out at 100°C but at different pressures between 50 and 200 bar .

The performance of SILP catalysts may depend on the nature of the supporting solids. Here, in addition to silica gel, the SILP catalyst was supported on carbon aerogels (from Fernando Pérez-Caballero) instead of silica gel. [5] Unlike the results obtained using silica gel, the SILP catalysts with Carbon Aerogels as support did not show conversion to aldehyde in the reactions.

The characteristics of the different SILP catalysts measured both before and after hydroformylation by porosimetry are listed below. (Table 1)

Table 1: *The porosimetry results of different experiments.*

Sample	**Reaction condition**			**BET surface area**	**Pore volume**	**Pore Size**
	Pressure / bar	**gass**	**T /°C**	**m^2/g**	**cm^3/g**	**nm**
Silica Gel C	—	—	—	332.47	0.99	10.21
Silica Gel D	—	—	—	322.63	1.00	9.57
Catalyst	—	—	—	156.67	0.53	5.38
G12	50	CO_2	100	—	—	—
G14	75	CO_2	100	225.41	0.71	5.32
G11	100	N_2	100	—	—	—
G8	100	CO_2	100	225.10	0.70	5.20
G13	130	CO_2	100	217.17	0.69	5.28
G9	150	CO_2	100	203.31	0.65	5.22
G7	180	CO_2	100	200.93	0.64	5.11
G10	200	CO_2	100	204.83	0.65	5.13
FGCB	—	—	—	536.10	2.90	22.01
FGCA	—	—	—	963.18	2.92	18.48
FG1	—	—	—	132.74	1.73	27.09
FG1R	100	CO_2	100	155.36	1.75	24.92
FG3R	150	CO_2	100	151.57	1.50	19.17
FG2	—	—	—	214.88	1.93	18.00
FG2R	100	CO_2	100	237.57	2.10	19.91

1. The uncoloured data were for SILP catalysts on pre-treated Silica Gel 100 (grade 10184), in different experiments.

2. These data coloured by □ were SILP catalysts on Carbon Aerogels (from Fernando Pérez-Caballero) in different experiments. FGCB means the crude carbon aerogels; FGCA means the pre-treated Carbon Aerogels; FG1 means the SILP catalyst on the crude Carbon Aerogels; FG1R means the SILP catalyst on the crude Carbon Aerogels after reaction in 100 bar CO_2 ; FG3R means the SILP catalyst on the crude Carbon Aerogels after reaction in 150 bar CO_2; FG2 means the SILP catalyst on the pre-treated Carbon Aerogels; FG2R means the SILP catalyst on the pre-treated Carbon Aerogels after reaction in 100 bar CO_2. " — " means no data.

3. "Silica Gel C" means commercial Silica Gel; "Silica Gel D" means dehydroxylated. "Catalyt" means: the SILP catalyst before reaction. "G+number"means: the catalyst after reaction , such as G7.

The SILP catalysts after reaction at 50 bar in CO_2 flow and at 100 bar in N_2 flow were very difficult to dry completely to remove the solvent even after 6 days, so porosimetry measurements were unsuccessful. The wet nature of these catalysts after reaction suggests that significant amounts of product remain in the catalyst and are not removed by the mobile phase.

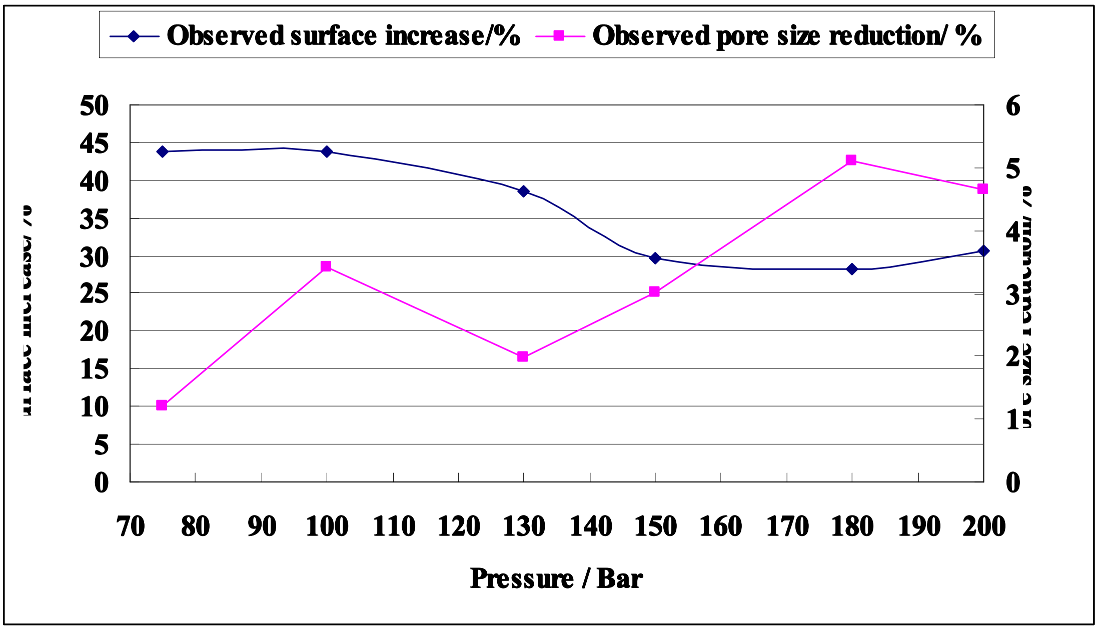


Figure 1: *The difference trend of BET surface area increase % at left hand side y axis and Pore Size reduction % at right hand side y axis for the catalyst before and after reactions in different pressures. SILP catalysts on pre-treated silica Gel 100 (grade 10184) 14 wt % IL loading.*

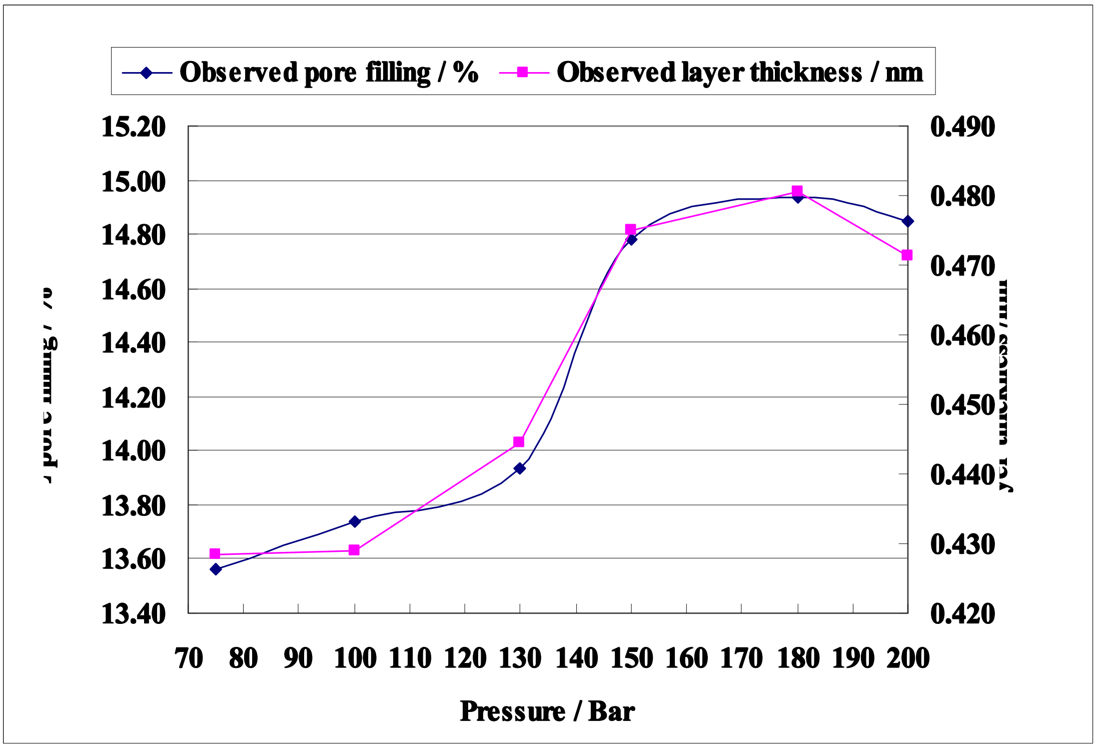


Figure 2: *The observed pore filling at left hand side y axis and observed layer thickness of catalyst after reactions at right hand side y axis at the different pressures after reactions. SILP catalysts on pre-treated silica Gel 100 (grade 10184) 14 wt % IL loading. The IL pore filling of catalyst was 10.2% and the layer thickness of catalyst was 0.35 nm before reactions.*

According to the curves shown in Figures 1 and 2, it seems that the IL and ligand were better retained within the pores of the silica after the high pressure reactions. Here we assume that no solvent is left in the catalyst during the porosimetry analysis.

For normal and activated Carbon Aerogels, the pore size increased after SILP reactions. The opposite behaviour was observed for silica gel. It seems that the IL and ligand may drain from the carbon based materials during the reaction.

3.2 Phase Behavior influence

The rates of the reactions carried out under CO_2 flow may depend on the different phases of sc CO_2 present under different conditions. [6] [7] [8] In practice faster rates were observed when a two-phase system was present in the reactor than when a homogeneous, one phase situation was present. [9] The phenomenon was attributed to the fact that sc CO_2 can dissolve extensively in the liquid reactant, leading to the formation of an " expanded liquid " , which can dissolve large quantities of hydrogen[1] and presumably CO.[10] At the same time it allows good contact between the substrate and the catalyst.

The experimental conditions were designed with different total pressures and different compositions of carrier gas shown as Table 2.

Table 2: *Experimental matrixs designed for different pressure and flow gas.*

Exp number	Total pressure (bar)	Flow gas	IL loading [wt%]	Substrate injection rate [ml/min]	Syngas /Substrate ratio	Total flow rate ml/min at SATP
G12	50	CO_2	14	0.24	10	893.22
G14	75	CO_2	14	0.24	10	865.13
G8	100	CO_2	14	0.24	10	1113.8
G11	100	N_2	14	0.24	10	2204.39
G13	130	CO_2	14	0.24	10	1181.88
G9	150	CO_2	14	0.24	10	1584.6
G7	180	CO_2	14	0.24	10	1602.92
G10	200	CO_2	14	0.24	10	2160.07

.

The responses studied were selectivity (l:b ratio), activity (Conversion to aldehydes) and turnover frequency (TOF).

In addition, phase behaviour observations were made by replacing the reactor with an autoclave fitted with a sapphire window in place of the bottom plate and observing the number of phases present under the conditions of Table 2, but using only 1-octene. Below 106 bar, two phases were present, but above it only one phase could be seen. The critical point of supercritical CO_2/1-octene/CO/H_2 mixtures in the tubular reactor in the experiments was thus found to be 106 bar at 100 °C. A pressure of 100 bar led to a higher rate of reaction than the other pressures conditions (See Figures 3-5).

3.3 Catalytic reactions under flow conditions [11] [[12] [13]

3.3.1 Activity

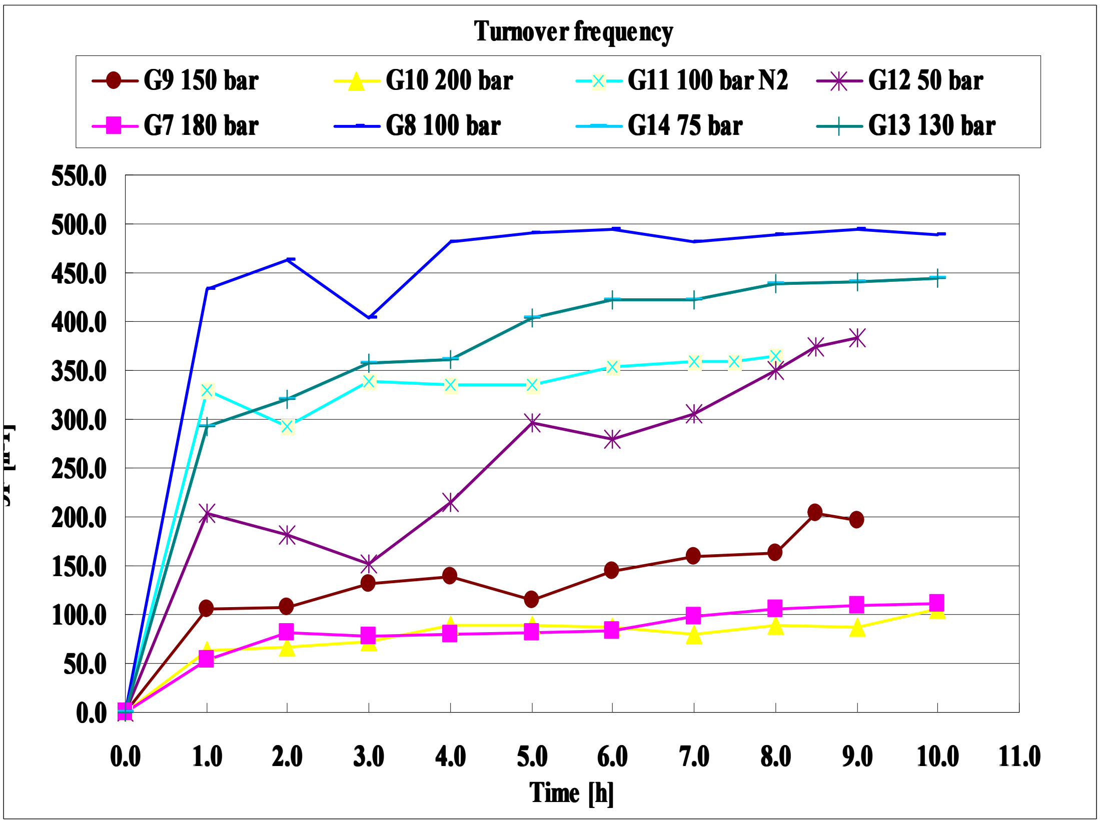


Figure 3: *Turnover Frequencies of the 14 wt % IL catalyst under different pressures and different carrier gases.* N_2 *as suffix means in* N_2 *flow; others without* N_2 *as suffix mean in* CO_2 *flow. The trends of G14 and G 13 were similar.*

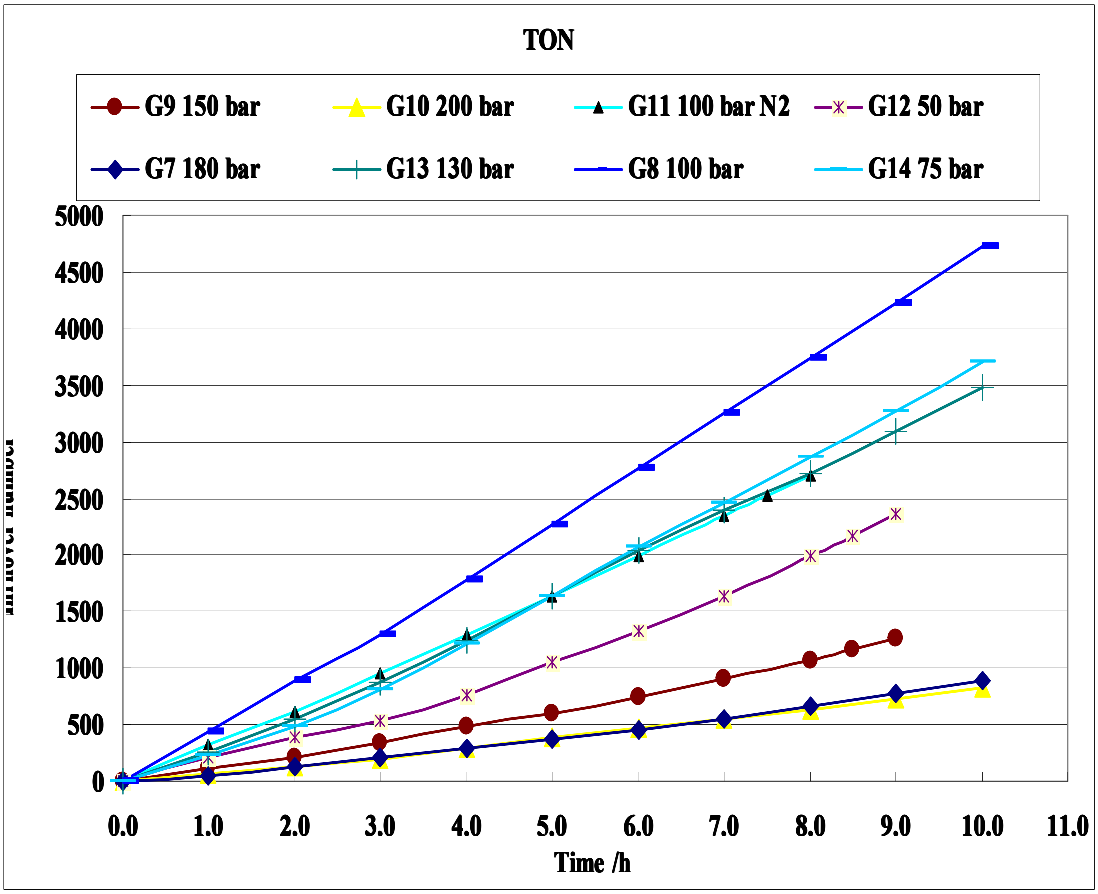


Figure 4: *Turnover number of the 14 wt % of IL catalyst under different conditions. N_2 as suffix means in N_2 flow; others without N_2 as suffix mean in CO_2 flow.*

A series of catalytic reactions for the hydroformylation of 1-octene was carried out at different total pressures. [11] The rate of injection of the substrate and of the syngas were held constant, whilst the pressure was altered by varying the rate of CO_2 addition. Samples were taken every hour and analysed by GC. Turnover frequencies were calculated form each of the GC samples. The data are collected in Figure 3 and cumulative turnover frequencies are shown in Figure 4. In general, the reaction rates were stable after the initial period of 1-2 h. The corresponding percentage conversion to aldehyde for each sample is shown in Figure 5.

At system pressures below 100 bar, where 2 phases were present, conversions to aldehyde were about 60% at 50 bar and 70 % at 75 bar. The conversions at the low pressures were not very stable during the first 7 to 8 h. In particular, the rate rose significantly over the entire period of the reaction. This may be because phosphine ligand was being washed away by the liquid phase present. It is known that hydoformyaltion reactions using catalysts of the kind used here often display negative order in [phosphine]. At system pressures above 100 bar , where only one phase is present, the conversions to aldehyde were about 72% at 130 bar, 32 % at 150 bar, 19 % at 180 bar and 13 % at 200 bar. The conversions at the higher pressures were during at least the last 2 to 4 h. Note: the arithmetic mean of the last two values of each step was used when plotting the steady-state turnover frequency.

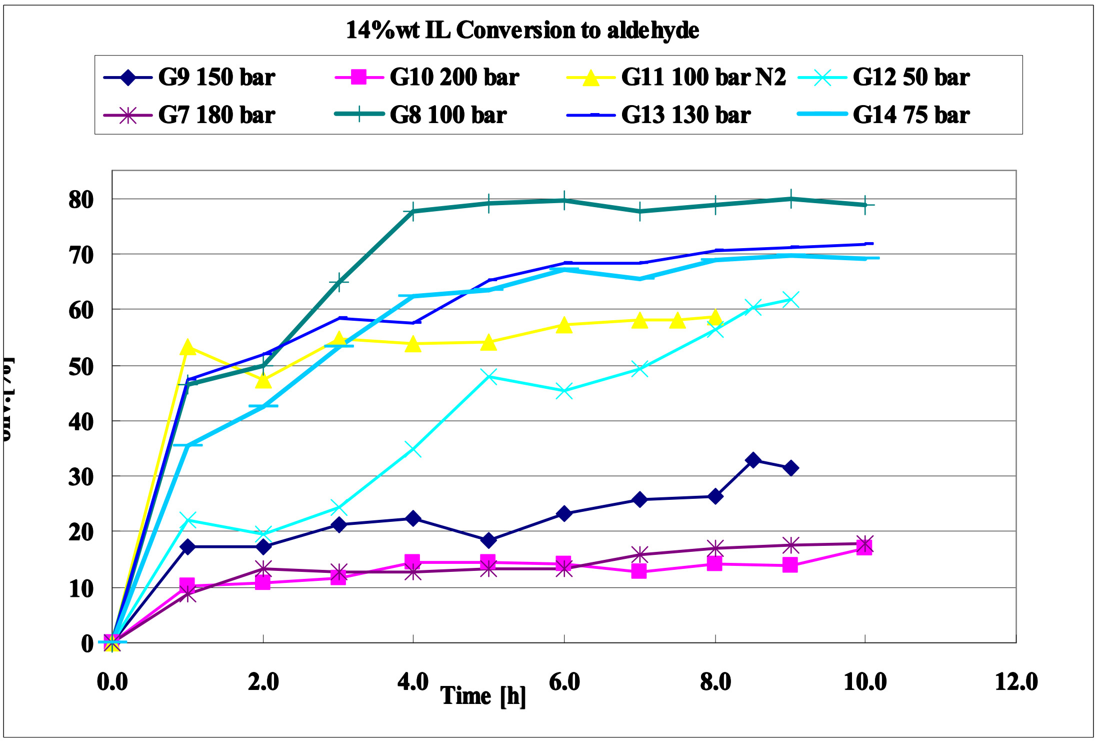


Figure 5: *Conversion to aldehydes of the 14 wt % IL catalyst under different pressures and using different carrier gases. N_2 as suffix means in N_2 flow; others without N_2 as suffix mean in CO_2 flow.*

Different flow gases may also affect the reaction rates. [12] The turnover frequency of the reactions in N_2 was less than that of reaction in CO_2, both at 100 bar. (Figure 3) This is probably because the liquid substrate sits on the catalyst bed (note that the reactor is used with the flowing passing from bottom to top). This will cause the liquid to fill the pores of the catalyst and hence prevent the gaseous reagents (CO and H_2) from diffusing towards the catalyst. Only the gas already dissolved will be available for the reaction and so low rates of reaction are expected.

As indicated above, different pressures will change the phase behaviour of the CO_2 rich flowing medium and might be expected to have significant influence on the reaction rates. (Figure 3-5). The effect of system pressure on the steady state reaction rate is shown in Figure 6.

At pressures lower than 100 bar a liquid phase was observed but the rate increased as the CO_2 pressure was increased from 50 bar. In the light of the discussion above, it would seem that the gases should once again be prevented from gaining access to the catalyst because of the presence of the liquid. However, CO_2 acts to expand organic liquids as it approaches its critical pressure and the solubility of the gases in the expanded liquids is greatly increased compared with those in pure organic liquids. [14] We propose that this increased gas solubility is responsible for the observed increase in reaction rate, despite the fact that the substrate concentration will decrease the more expanded the liquid becomes.

The highest rate was observed at a system pressure of 100 bar, just below the critical pressure of the mixture, 106 bar. At pressures much higher than 100 bar, where a single supercritical phase is present over the catalyst, the contact of the substrate with the catalyst is reduced. The reaction rate reduces as the pressure is increased because of the decrease in the concentration of substrate in the reactor and because the better solubilising power of the higher pressure scCO_2 decreases the partitioning of the substrate into the ionic liquid, where the catalyst resides. [15]

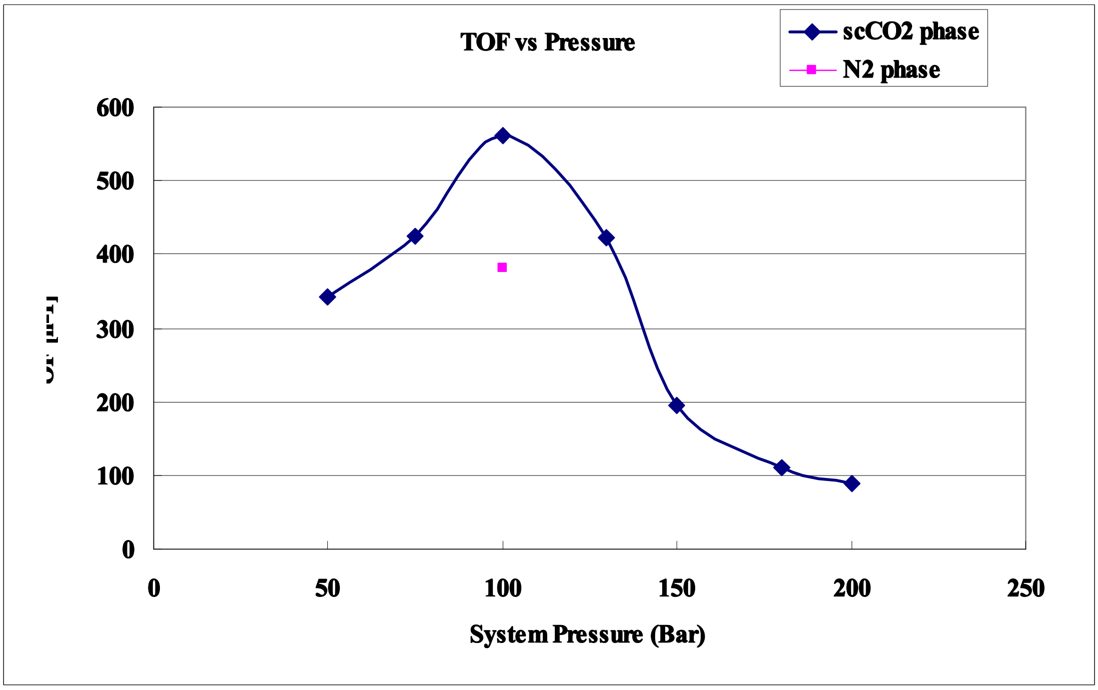


Figure 6: *Steady state Turnover Frequencies at different pressure and under different carrier gases. The TOF data were the arithmetic mean of those obtained during the last two hours of reaction.*

3.3.2 Selectivity

The reaction under sc CO_2 at 100 bar and at 180 bar, 100 °C, shows the most stable linearity. The linear : branched ratio of aldehyde is about 3.2. The remaining reactions, especially those carried out at lower pressures show a dramatic decrease of linear: branched ratio after the peak at the first hour. (Figure 7) A good linear selectively was not observed under any of the conditions studied, perhaps because the phosphine: Rh ratio was not high enough.

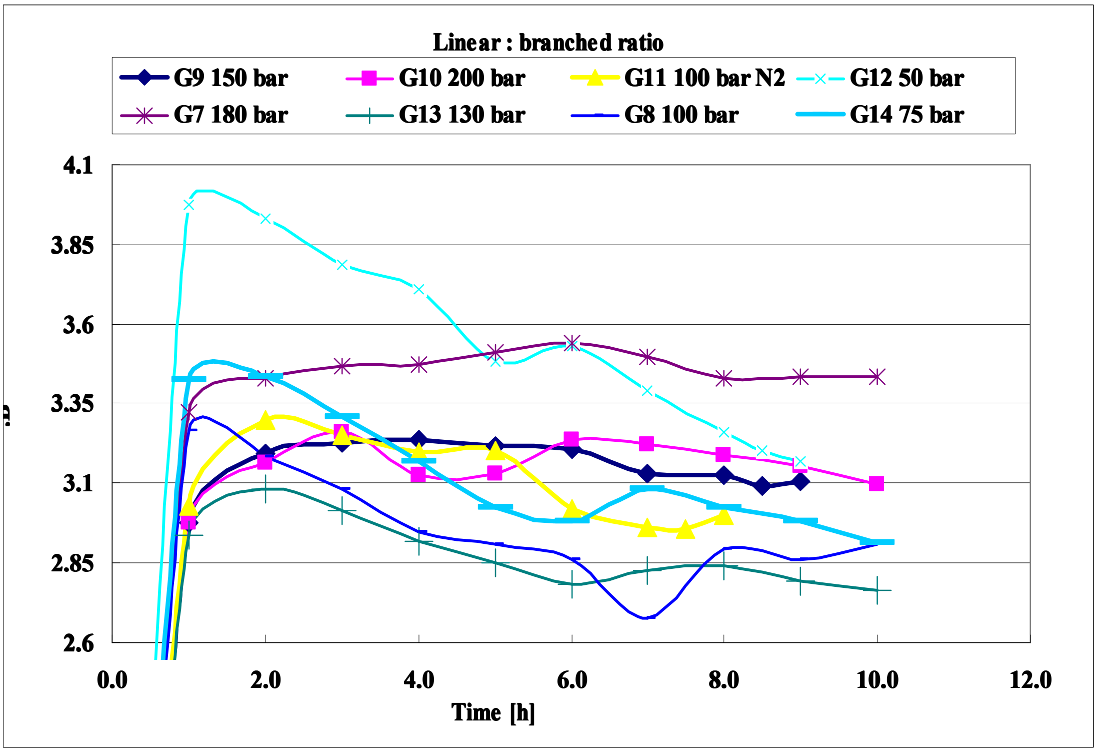


Figure 7: *Linear : branched ratio of the 14 wt % IL catalyst under different conditions. N_2 as suffix means in N_2 flow; others without N_2 as suffix mean in CO_2 flow.*

3.3.3 Total flow

In an attempt to keep the residence time within the reactor constant, despite the changes in pressure, the total flow rate was increased as the pressure increased. [12] The total flow mix gas through decompression valve after the reactor assumed only syngas and CO_2 to be present with different mole ratios. (Figure 8) The total flow is measured using a float metre, so the rate is not only related to the height of the float, but also to the density of the gas, which is dependent upon the ratio of syngas : CO_2. The amount of syngas in the flowing medium was calculated allowing for that used up as a result of the reaction. There was an increase of the total flow rate at NTP with increasing pressure to make the residence time approximately constant in the all cases. (Figure 9 and Table 2)

The flow meter was actually calibrated for pure CO_2 only and thus the flow of a mixture of gases having different density than pure CO_2 has to be recalculated. The calculation started from the assumptions that there was negligible substrate (or product) concentration in the gas phase and a linear correlation between mole fraction and density. While the amount of substrate in the gas phase depends on the total flow rate and consequently might have an effect on the density at higher flows.

The calculation of flow rate was as follows: [10]

It assumes that at 1 bar CO, H_2 and CO_2 are ideal gases.

d = density, m = mol fraction, f = flow

f(meas) is the flow rate obtained from the graph of flow travel against flow rate

f(act) is the actual flow rate

f(syn) is the syngas flow rate

d(act) = d(syn) x m(syn) + d(CO_2) x m(CO_2)

f(act = [f(meas) x d(CO_2)]/[d(syn) x m(syn) + d(CO_2) x m(CO_2)]

rearranging and remembering that [f(act) x m(syn)] = f(syn) and [f(act) x m(CO_2)] = f(CO_2),

d(syn) x f(syn) + d(CO_2) x f(CO_2) = d(CO_2) x f(meas)

Since all the terms in this equation were known, f(CO_2) could be calculated.

Here f(CO_2) was calculated from the amount of syngas and conversion of aldehyde, which was initially guessed on the basis of previous reactions under similar conditions. The flow travel required for the desired flow rate was calculated and used in the reaction. The actual flow rate was calculated once the products had been analysed by GC.

The detailed steps were the following:

1) determine the partial pressure of CO_2 and of Syngas required in the

experiment

2) calculate the total flow rate and the dosimeter settings which would give the desired partial pressures

3) with the catalyst and substrate concentration a conversion was estimated. This tells how much Syngas will roughly be consumed by the reaction

4) with the amount of Syngas left, it was possible to calculate the density of the gas mixture after the reacto, which was used to calculate the real flow and the flow travel.

At some points, they were guessed, because the density of outlet gas was not known correctly in advance.

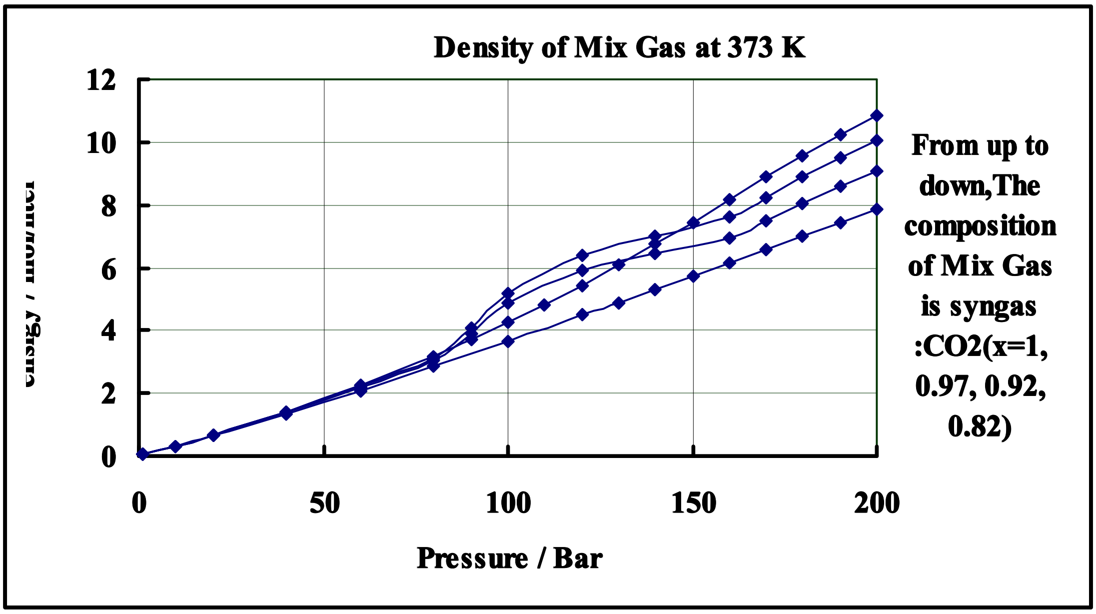


Figure 8: *The density of the composition of mix gas for the total flow passing through the reactor in all experiments. Note: x= syngas:* CO_2 *mole ratio.* [10]

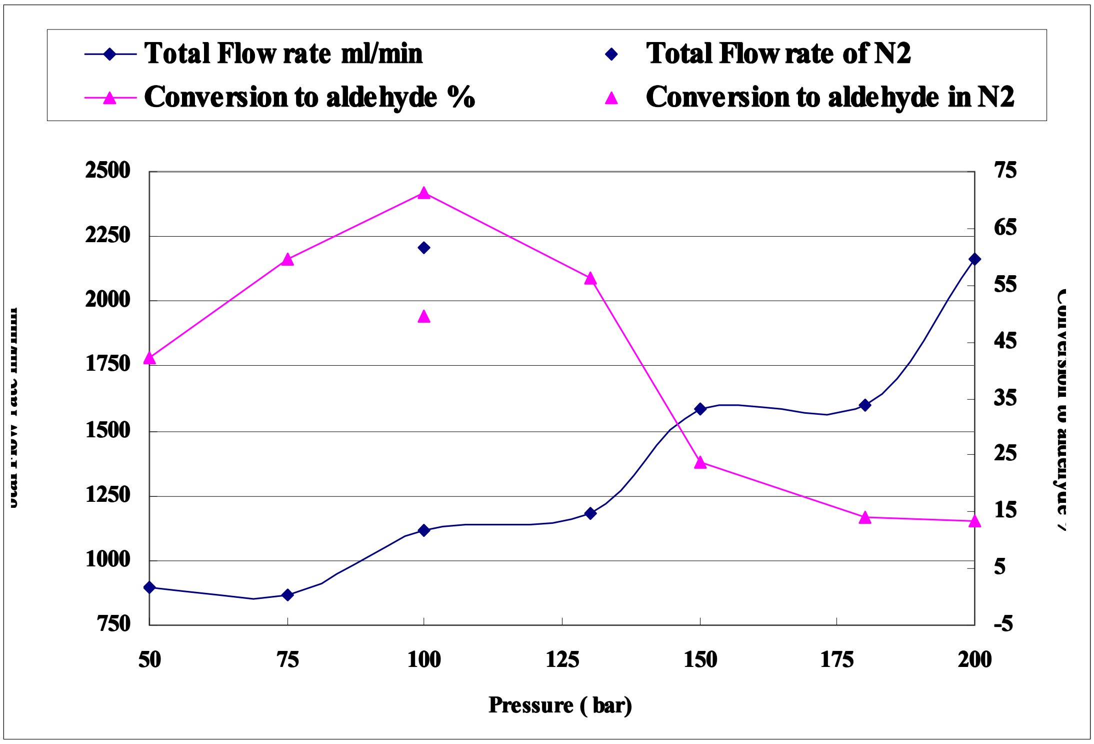


Figure 9: *The relation between total flow rate and the conversion to aldehyde at different pressures.*

3.4 Catalysts

3.4.1 Silica supported catalysts

Leaching is a major problem in SILP systems when using liquid phase substrate in the reaction. [14] This is expected to be a serious problem when using the designed ionic liquid, which was miscible with the substrate, in the reaction. 1-octyl-3-methylimidazolium triflamide was used as the ionic liquid in the hydroformylation of alkenes because this ionic liquid has been designed to be miscible with 1-octene so as to reduce problems associated with mass transfer. [16] Mechanical losses may also occur due to the flowing system. Catalyst losses may occur because the ionic liquid dissolved in the flowing substrate / product will increase the solubility of the catalyst in the flowing medium.

Leitner and Brennecke [17] [18] found the solubility of many ionic liquids in

$scCO_2$ is very low during the study of sc CO2 / IL. IL leaching is expected to be low in the supercritical flow system, although physical abrasion may still be a problem, especially at higher pressures.

The presence or absence of ionic liquid in the product samples was confirmed and quantified by ^{1}H NMR spectroscopy. Rhodium leaching was measured by ICPMS with the results being presented in Figures 10 and 11.

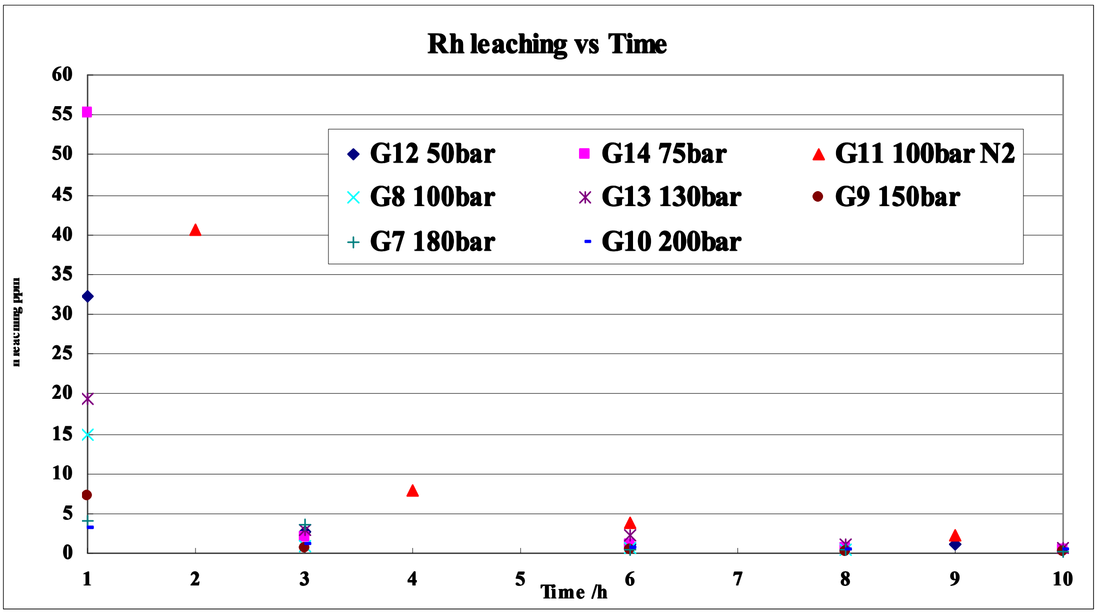


Figure 10: *Rh leaching of different experiments involving SILP catalysts with silica gel over time.*

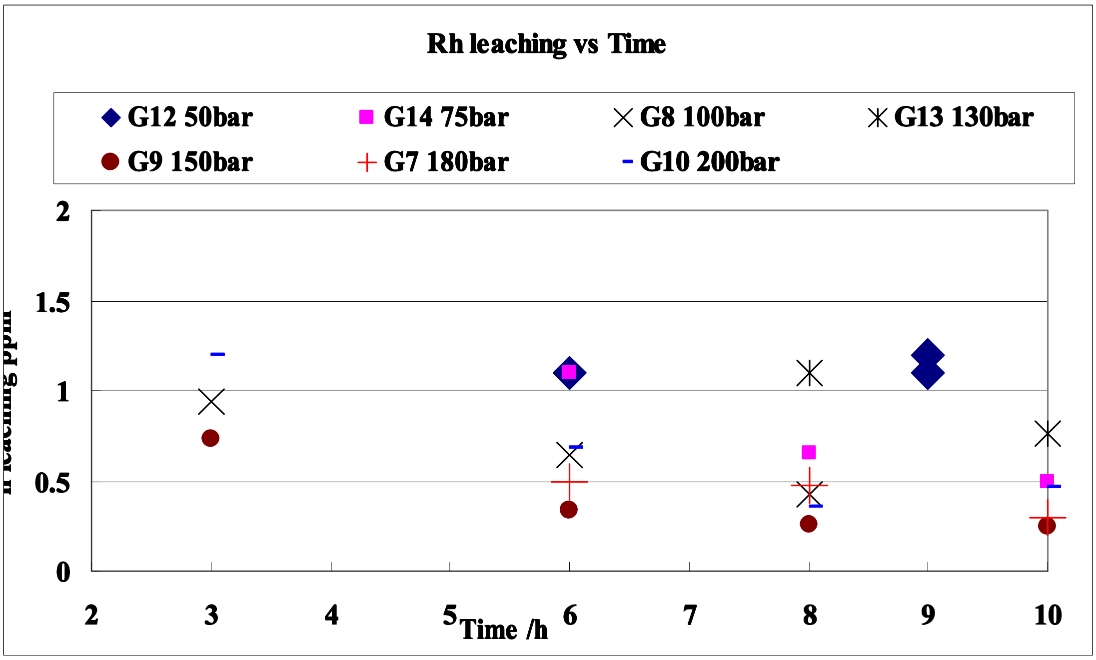


Figure 11: *Rh leaching of different experiments involved SILP catalysts with silica gel over time from 2nd to 10th h.*

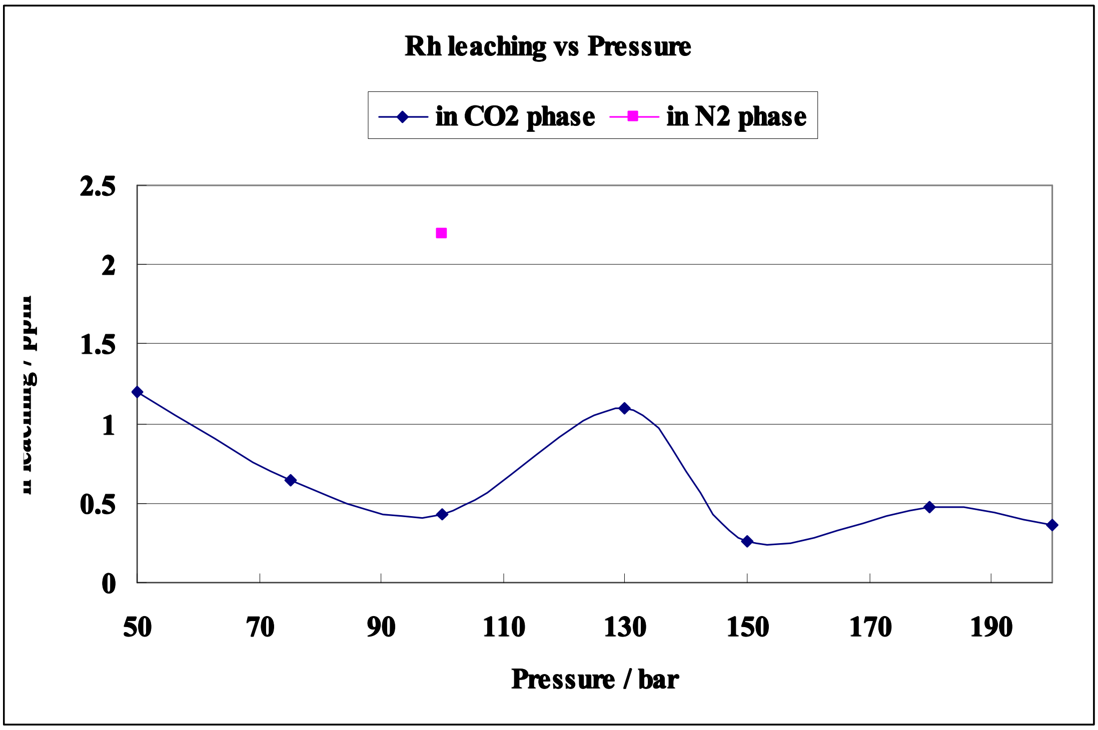


Figure 12: *The relation between Rh leaching at 8 h and different pressures, in CO_2 phase and N_2 phase respectively.*

In general, high rhodium leaching levels are observed after the first hour of reaction, but the level drops dramatically thereafter, then falling slowly over the rest of the reaction period. When using N_2 as the transporting gas (liquid phase reaction, the leaching is high and remains above 2 ppm throughout the reaction (Figure 10). With the exception of the reaction carried out at 130 bar, where the leaching appears to be anomalously high, the rhodium leaching after 8-9 h of reaction decreases as the pressure is increased, levelling off at round 0.1-0.2 ppm at pressures above 100 bar (Figures 11 and 12). This suggests that the leaching is caused by dissolving of the catalyst in the flowing phase when there is a liquid or expanded liquid present, but more probably by abrasion when the single phase is reached, although the small increase in rhodium leaching at higher pressures may be attributable to the better solvating power of the flowing medium. Increased leaching at higher pressures is observed in the bulk SCF-IL system using the same, catalyst and ionic liquid [15].

Ionic liquid is found (NMR evidence) in the some of the products after decompression of the CO_2. For experiments carried out at 75, 100 and 130 bar in $scCO_2$ flow and that at 100 bar in N_2 flow ionic liquid was present during the first three hours only. On the other hand, for the experiments at 50, 150, 180 and 200 bar in $scCO_2$ flow ionic liquid was not found in the products. N_2 flow gave larger leaching than CO_2 flow. (Figure 12) In general (once again the data at 130 bar appear anomalous), higher rhodium leaching corresponded with greater leaching of the ionic liquid into the products, suggesting that the mechanism of loss of both is related. （Figure 13）

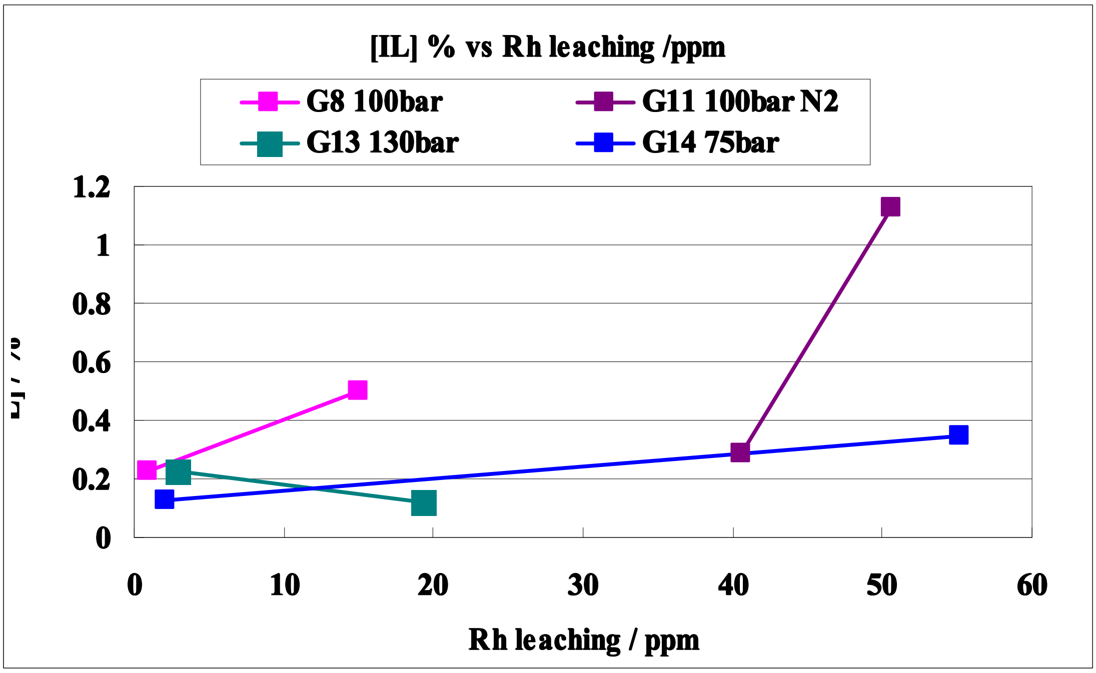


Figure 13: *The relation between Rh leaching and the amount of Ionic liquid in the products from the different experiments. Note: [IL] % means of the amount of ionic liquid in every sample after reaction in mol/mol %. The data of the 1st h and 4th h are plotted and joined by a line. Leaching in the first hour was higher than in the 4th.*

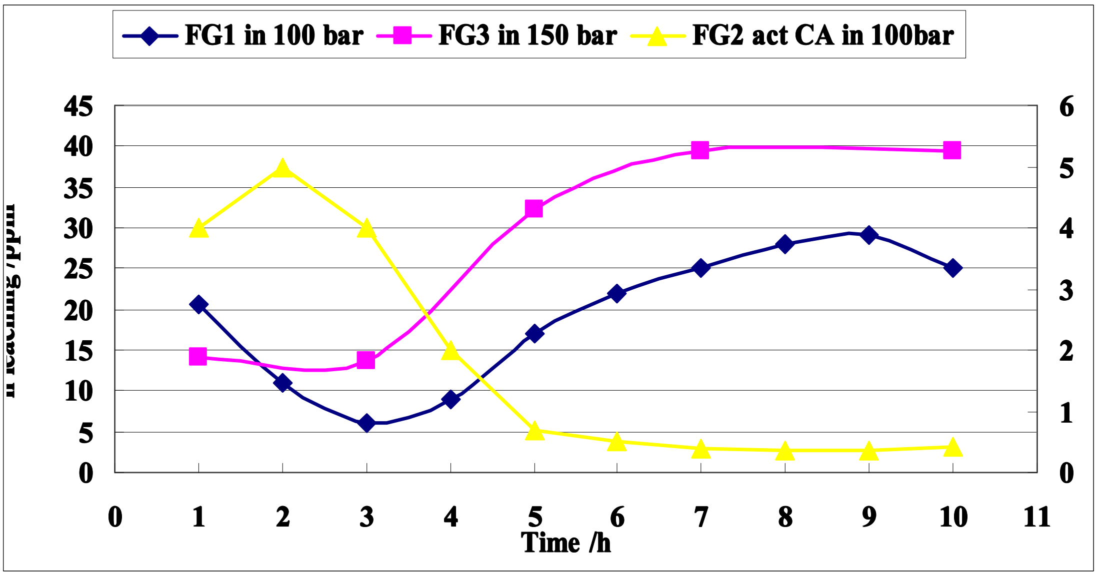


Figure 14: *Rh leaching of different experiments involved SILP catalyst with carbon aerogels. Notes: The data FG2 act CA in 100 bar is plotted using the secondary y-axis， rest of them are plotted in the primary y-axis; FG1 means the SILP catalyst with unactivated carbon aerogel in 100 bar reaction with* CO_2 *flow; FG3 means the SILP catalyst with unactivated carbon aerogles in 150 bar reaction with* CO_2 *flow; FG2 act CA means the SILP catalyst with activated carbon aerogel (heated at 900 °C for 1 hour) in 100 bar reaction with* CO_2 *flow.*

3.4.2 Catalysts supported in carbon aerogels [5]

The rhodium leaching measured by ICPMS during the SILP hydroformylation of 1-ocetene using carbon areogels as supports, which showed very low conversions, are shown in Figure 14. Rh leaching tended to increase with time and pressure for the SILP catalyst with unactive carbon aerogels. This trend is opposite to that found with silica gel, where the leaching is 2 orders of magnitude lower. This suggests that the catalyst is not immobilised well within the pores of the aerogel. This may be because of poorer surface interactions, but may also be associated with the larger pore size. The activated carbon aerogels retained the catalyst much more effectively than the unactivated ones and the leaching reduced to levels similar to those observed when using silica as the reaction proceeded. (Table1, Chapter 3) This suggests that the surface is more important than the pore size since the pore size for the activated carbon aerogels is similar to that of the unactivated material but much higher than that for the silica (Table 1). The effects on the carbon aerogels on activation by heating at 900 °C in nitrogen flow are illustrated Figure 15.1, 15.2 and 15.3. [5] Material is lost from the carbon aerogels whilst the surface area and porosity increase, and the porosity drops again after prolonged heating. Presumably some material is lost from within the pores, increasing the pore diameter and surface area.

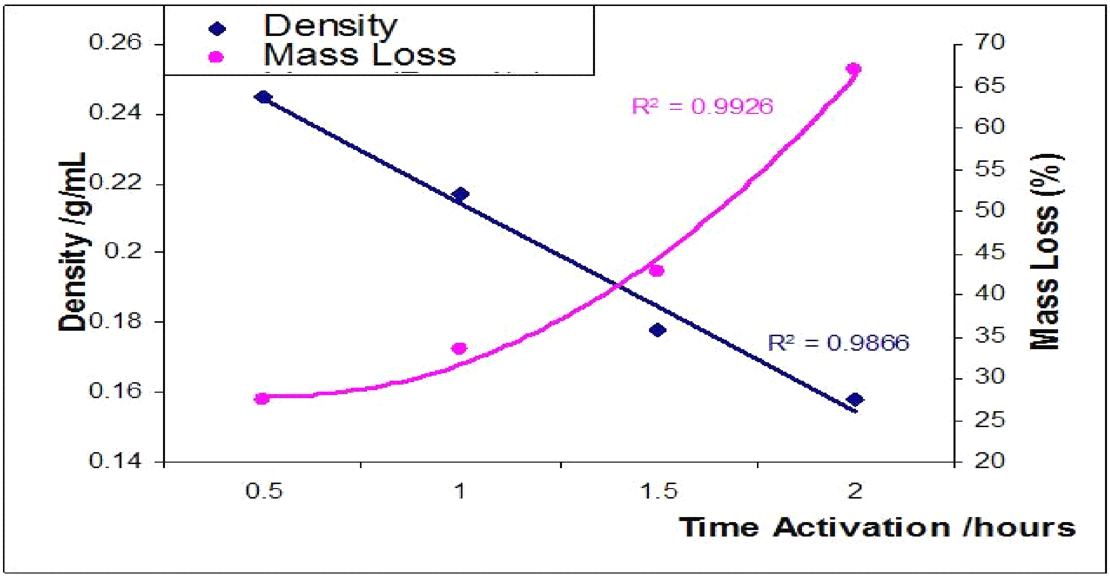


Figure 15.1 *Change on Density of carbon aerogels with Activation time (Act.T.)*

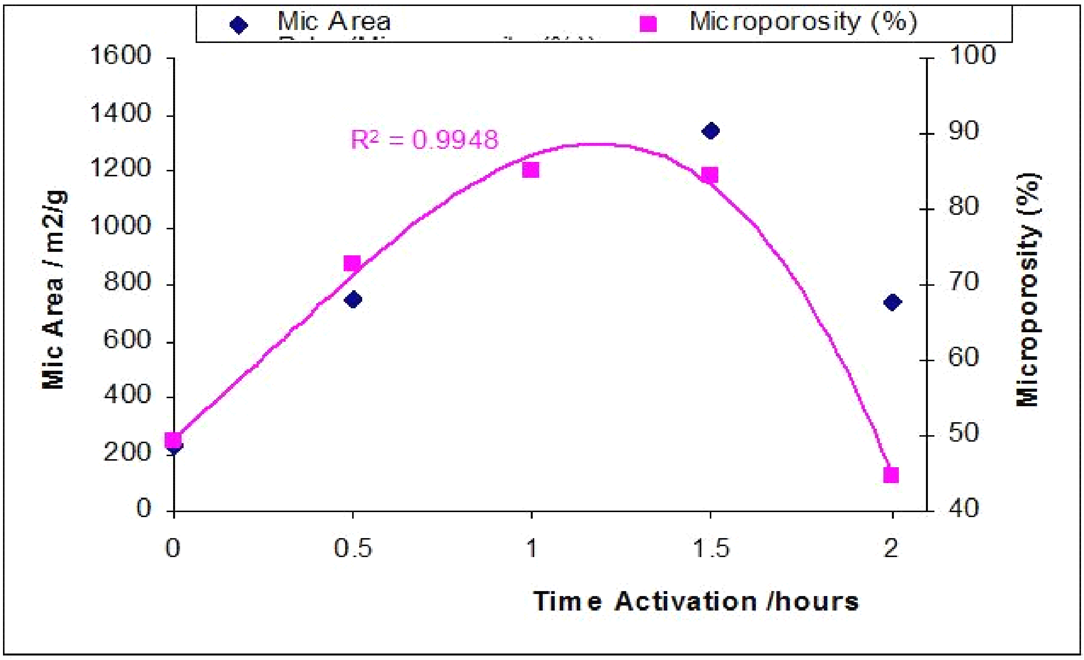


Figure 15.2 *Change on porosity of carbon aerogels with Activation Time.*

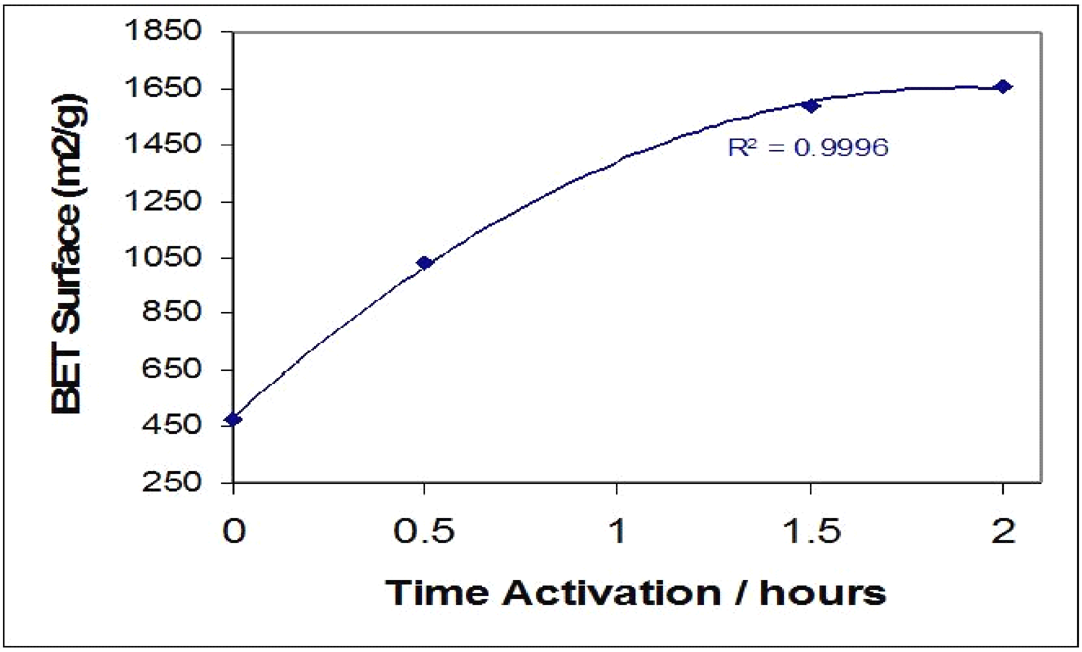


Figure 15.3 *Change on BET specific surface area of carbon aerogel with activation time.*

In addition to the nature of the support, there were two operational factors, which may determine the amount of ionic liquid present in the products in the different experiments. [11] They are pressure and conversion to the aldehyde, with their effects being shown in the Figure 16. They did not show a clear straight trend such as decreasing or increasing. This may be because of the different phase behaviour of CO_2 at the different pressures. Loss of ionic liquid increases from 75 to 100 bar , perhaps because of increased conversion to aldehyde making the expanded liquid a better solvent. It then reduces as the pressure is increased to 130 bar , presumably because the supercritical solution is overall a much less good solvent.

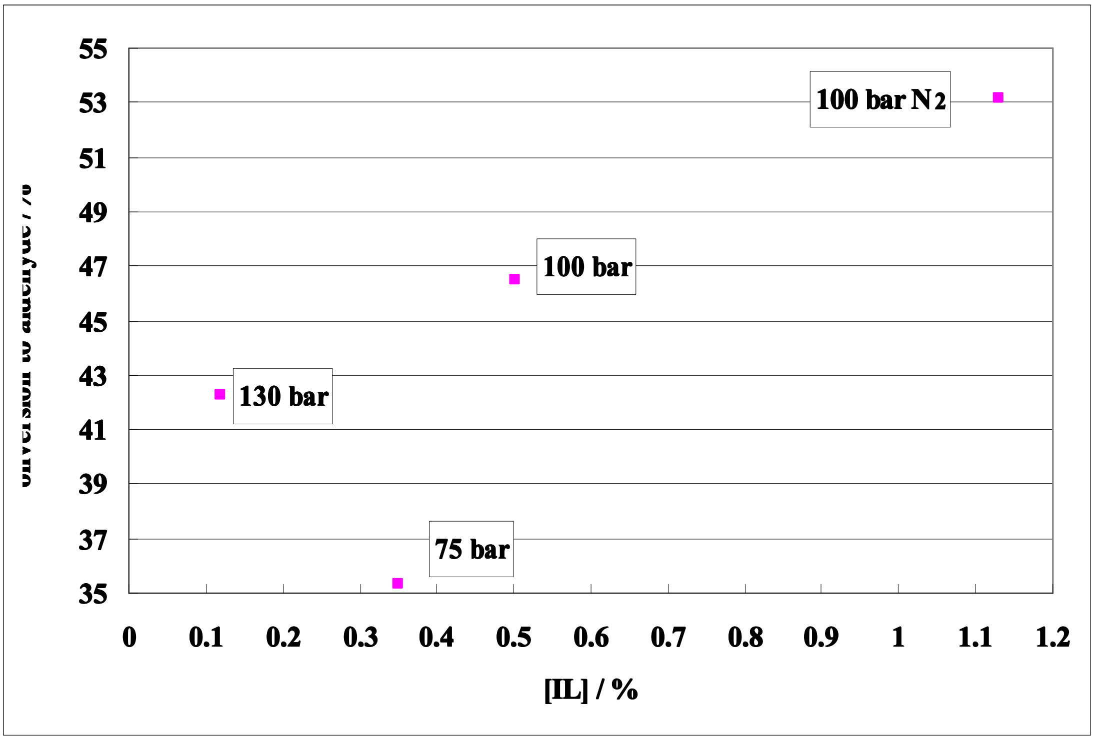


Figure 16: *The dependence of IL in the product (mol %) upon conversion to aldehyde at different pressures. The data of the first one hour was taken as the result due to the [IL] % was only found in the first 1 and 2 hour during reaction time for the cases.*

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4 Conclusion and Future Perspectives

From the experimental results obtained in the hydroformylation of 1-octene using a SILP catalyst with a flow of CO_2, a pressure just below the critical point of the flowing mixture (106 bar at 100 °C if no 1-octene has been converted) was the best condition for the hydroformylation. It gave the highest acitivity (conversion to aldehyde up to 70 %), fastest reaction (TOF up to 575.3 h^{-1}) and most stable linear selectively (l:b ratio reaching 3.37).

Another striking advantage of the utilization of *sc*CO_2 as reaction medium is the remarkable stability of the catalyst, while the SILP hydroformylation experiments carried out in the (expanded) liquid phase at 50 and 75 bar show a progressive decrease in activity of catalyst, probably as a result of catalyst and ionic liquid removal by the flowing phase. The supercritical or near critical (expanded liquid) system almost completely circumvented these problem and also showed much better results than when using a pure liquid flow propelled by N_2 flow at 100 bar.

Even through the CO_2 flow can expand the liquid substrate so that catalyst leaching is reduced and can increase the solubility of syngas into the IL phase, so that gas starvation problems are reduced, there was a requirement that the pressure should not be too high. In the high pressure scCO_2 phase, the concentration of 1-octene at the catalyst bed and partitioning of the substrate into the IL was reduced so that the conversion to aldehyde was reduced.

The solid support chosen was a factor on the performance of the SILP catalyst. The pore size and surface groups of the solid support should be suitable for the SILP catalyst consisting of metal complex, excess ligand and ionic liquid. Using microporous carbon aerogels as the supports, whether activated or not, gave disappointing results. Since the pore size is similar to that in the microporous silica, which was also involved, we impute the poor performance to weaker interactions between the surface and the ionic liquid. Much higher Rh leaching supports this conclusion.

The practical advantages of the continuous flow system obviously represent a very economic and “green” process. Most notably, no catalyst separation step is necessary because simple decompression of the flowing phase gives the product / substrate mixture without any cross contamination. Furthermore, no organic solvent is employed removing problems with the handling of volatile organic compounds and again decreasing separation cost.

Through working in an expanded liquid rather than fully homogeneous supercritical flowing phase, it is possible to reduce the operating pressure to within the range that is commercially attractive. Such an approach is not possible when using bulk ionic liquid – supercritical fluid biphasic systems because the reactor would fill and the expanded liquid containing the catalyst and the ionic liquid would flow out with the substrate / product mixture. This problem is overcome when the catalyst and ionic liquid are immobilised within the pores of silica gel. The expanded liquid is also favoured over the pure supercritical condition, because the concentration of substrate at the catalyst bed is higher and so higher reaction rates are observed. This is because the partition between the mobile and the ionic liquid phase removes more 1-octene from the ionic liquid, where the catalyst resides at higher system pressures.[1]

The disadvantage of pure liquid flow is that gas transport to the catalyst is inhibited because of the high aspect ratio of the pores within the silica and because the solubility and diffusion rate of the gases in the liquid substrate are both low. Once the gas initially dissolved in the liquid has been used, the rate reduces dramatically because of mass transport limitations on gas supply to the catalytic centres. In addition, the ionic liquid has been designed to be miscible with the 1-octene, so that substantial amounts are removed, along with some catalyst when only liquid flow is used. Because neither the ionic liquid nor the catalyst is soluble in CO_2, the expanded liquid has a much lower affinity for removing the ionic liquid or the catalyst from the system. Since CO and H_2 are fully miscible with CO_2, their solubility in the expanded liquid is enhanced relative to that in the pure liquid substrate and their transport to the catalytic centres is increased. Their solubility in the ionic liquid is also increased.[2] Finally, rates of diffusion in the expanded liquid are expected to be significantly faster than those in the pure liquid so that access to the catalyst for the substrate and for the reacting gases will be improved.

The effects of the pressure on the phase behaviour, the solubilities of different components in the ionic liquid film and in the flowing phase, as well as on the rates of diffusion, the reaction rate and the leaching of catalyst and ionic liquid are shown in Figure 1.

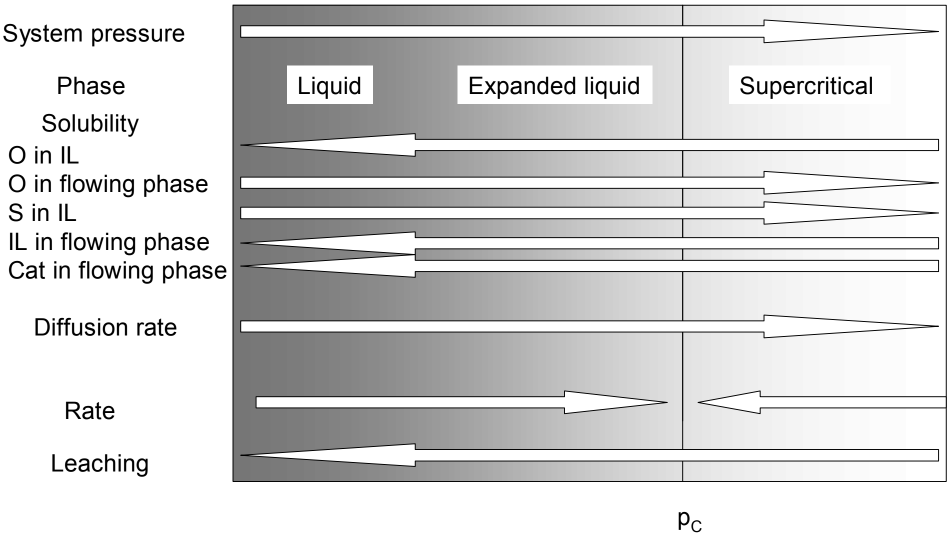

Figure 1. Effects of system pressure on various parameters of the system. The direction of the arrow indicates an increase. S = Syngas, O = 1-octene, IL = [OctMIM]NTf$_2$, cat = catalyst and excess ligand.[3]

In future investigations, it would be interesting to see if the process can still be efficiently run at lower temperatures and lower pressures, within the near critical region of CO$_2$. Industrial chemical engineers will be very happy to run the long time continuous flow reaction in a huge plant with minimum energy expenditure. Low temperatures and pressures, very low catalyst leaching and easy product separation are all essential for this. The SILP process with expanded liquid flow comes close to achieving all of these objectives.

In order to overcome the IL and Rh leaching, two factors should be checked. If the solubility phenomenon is caused by the substrate itself, lower injection rates might produce relief. If physical abrasion is the problem, it could be reduced by lower volumetric flows at lower total pressures. A redesign of the reactor in order to minimize the stream together with better methods for retaining the catalytic bed might lower the depletion of IL as well.

The SILP catalyst with $scCO_2$ flow approach could also be applied to other catalytic reactions like carbonylation or hydrogenation. In principle, every homogeneous catalytic reaction that is practicable in ILs and employs rather non polar substrates and products can be transferred to the SILP catalyst with CO_2 flow system.

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