

HOMOGENEOUS CATALYSIS USING IONIC LIQUID/scCO₂ BIPHASIC SYSTEMS

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A chemical process involving reactants and a catalyst is denominated catalysis. If during the process both the catalyst and the reactants are in the same phase (mostly the liquid phase) then, it is called homogeneous catalysis.

Although homogeneous catalysis has some advantages when compared to heterogeneous catalysis, many of the known homogeneous catalytic systems are still not being commercialised because of problems concerning the separation of the catalyst from the product, the retention of the catalyst in the reaction medium and the use of organic solvents.[1,2]

The advantages of homogeneous catalysts over heterogeneous catalysts include their higher specificity, the availability of all the catalytic centres because of the dissolution of the catalyst in a solvent, reproducibility and controllability. Despite this, heterogeneous catalysts can be a cheaper option to the chemical industry because of their higher thermal stability, the lack of need for a large quantity of suitable solvents and, of course, the easy separation of the very expensive catalyst from the product.[3]

The following Table can illustrate better the advantages and disadvantages of homogeneous versus heterogeneous catalysis.

Table 1: Homogeneous versus heterogeneous catalysis. Reproduced from reference [4].

	Homogenous	Heterogeneous
Activity	+++	-
Selectivity	+++	+
Catalyst description	++	-
Catalyst recycling	-	+++
TON	+	+++
Quantity of catalyst	++	+++

Over the last years, the chemical industry has been starting to try to replace common organic solvents by cleaner alternatives in order to decrease the emissions of VOCs to the atmosphere.

Considered as new substitutes for common organic solvents, ionic liquids (IL) are simply defined as liquids composed only of ions. Although they were discovered many decades ago, about 1914, only recently have they started to be studied as possible solvents because of their ionic character, constituting a new class of solvents. Amongst their many properties that make them being considered as 'environmentally friendly' solvents, ILs having a non measurable vapour pressure, which means they do not emit vapours to the atmosphere. [5, 6]

Supercritical fluids (SCFs) represent another option when considering new reaction media because of their environmentally friendly properties, their low costs and the possibility of being recycled after their use. A SCF is a highly compressed gas above its critical temperature (T_c) and critical pressure (P_c). CO_2 is the most common SCF in use because of its very low critical point ($T_c = 31.1\text{ }^\circ\text{C}$, $P_c = 73.8\text{ bar}$) and benign properties. This critical point can easily be accommodated with suitable equipment design. Besides being used as solvents, SCF can be also used for extracting the product from the reaction medium, a process known as Supercritical Extraction (SCE).[7]

Combining the properties of ionic liquids and supercritical fluids, one of us has been involved in developing a continuous flow process using IL/ scCO_2 biphasic system which is being studied as a possible solution to overcome all the homogeneous catalysis problems exposed above with the benefit of being considered as environmentally friendly.[8] These systems combine the good solvating properties of the ionic liquids that are used as reaction media and the properties of scCO_2 , which is used to extract the products.

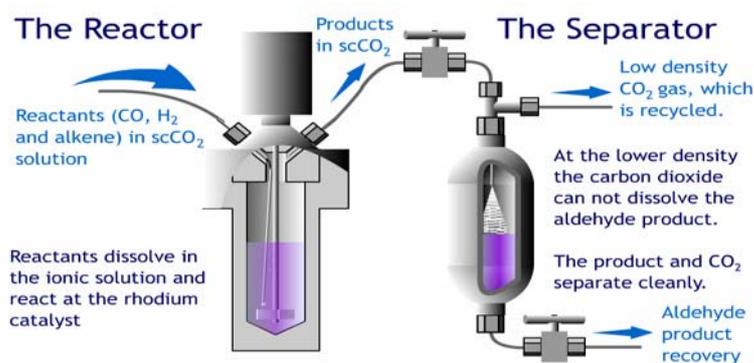


Figure 1: Continuous flow hydroformylation of 1-octene using the IL/ scCO_2 biphasic system. Reproduced from reference [2].

Considered as one of the most important reactions in the chemical industry, the hydroformylation of long chain alkenes has been carried out as a continuous flow reaction using ionic liquids, specifically [octmim][Tf_2N], (octmim = 1-octyl-3-methylimidazolium, Tf = CF_3SO_2) as the reaction solvent and scCO_2 as the mobile phase to extract the products (aldehydes).

In a typical continuous flow hydroformylation reaction, the reactants (CO , H_2 and the alkene) and the CO_2 are introduced into the reactor in a separate and continuous way. Inside the CSTR, which already contains the ionic catalyst dissolved in the ionic liquid, the reactants become dissolved in the ionic liquid solution and react with the Rh catalyst. Both the ionic liquid and the catalyst are insoluble in the scCO_2 but the scCO_2 is soluble in the ionic liquid.

The products dissolve in the scCO_2 and pass to the separator, where, by decreasing the pressure, the density of the CO_2 also decreases and the products precipitate from the solution into the collection vessel. The CO_2 can, in principle, be recycled.

The ligand design plays an important part in determining the retention of the Rh catalyst in the reaction medium. Ionic ligands are synthesized by ion exchange between ionic liquids and water-soluble phosphines. Ionic ligands derived from [TPPMS]Na (TPPMS = $[\text{Ph}_2\text{P}(3\text{-C}_6\text{H}_4\text{SO}_3)]^-$) and [TPPTS]Na (TPPTS = $\text{P}(3\text{-C}_6\text{H}_4\text{SO}_3)_3^{3-}$) are being used in this research.

The published work [7] involves the use of [prmim][TPPMS] (prmim = 1-propyl-3-methylimidazolium) ligands and proved to be quite successful at 200 bar pressure and $100\text{ }^\circ\text{C}$. We tested several IL and ionic ligands to check their viability in alkene hydroformylation and the catalyst performance in terms of retention, activity and reaction selectivity to increase the product l:b ratio, obtaining a catalyst activity of over 500 TOF (h^{-1} , similar to rates required in commercial systems), catalyst leaching as low as 12 ppb and several week's stability, [8] However, we have recently discovered that it is also possible to extract the hydroformylation products from the reaction medium using scCO_2 at 100 bar pressure and $100\text{ }^\circ\text{C}$ and so, new experimental conditions started being

developed using the [prmim][TPPMS] and the [pentmim][TPPTS] ligands (pentmim = 1-pentyl-3-methylimidazolium).

Some of the most relevant results are shown in Table 2.

Table 2: Continuous flow hydroformylation of 1-octene catalysed by Rh/[pentmim][TPPTS] (P:Rh = 15:1) in the [octmim][Tf₂N]/scCO₂ biphasic system using a scCO₂ flow rate of 1 nL/min (1 nL = 1 litre at NTP).

Reaction	Pressure (bar)	Temperature (°C)	Conversion to aldehyde (%)	l:b ratio	TOF (h ⁻¹)
TQ66 ^a	100	100	29	3.3	397
TQ67 ^a	150	100	34	3.2	470
TQ70 ^a	150	100	33	3.6	190
TQ71 ^b	150	100	43	3.1	248
TQ83B ^a	150	100	13	1.9	219
TQ89A ^a	150	100	23	2.0	229
TQ89B ^a	150	100	37	2.0	377
TQ78A ^c	200	100	24	2.6	547
TQ80A ^c	200	100	21	2.3	567
TQ83A ^a	200	100	34	2.5	640

^a CO flow rate of 3.77 mmol/min and 1-octene flow rate of 1.89 mmol/min.

^b CO flow rate of 6.6 mmol/min and 1-octene flow rate of 1.89 mmol/min.

^c CO flow rate of 4.2 mmol/min and 1-octene flow rate of 2.65 mmol/min.

All the catalyst performances were quite stable while the system ran at both 150 and 200 bar pressure, as shown in Figures 2 and 3.

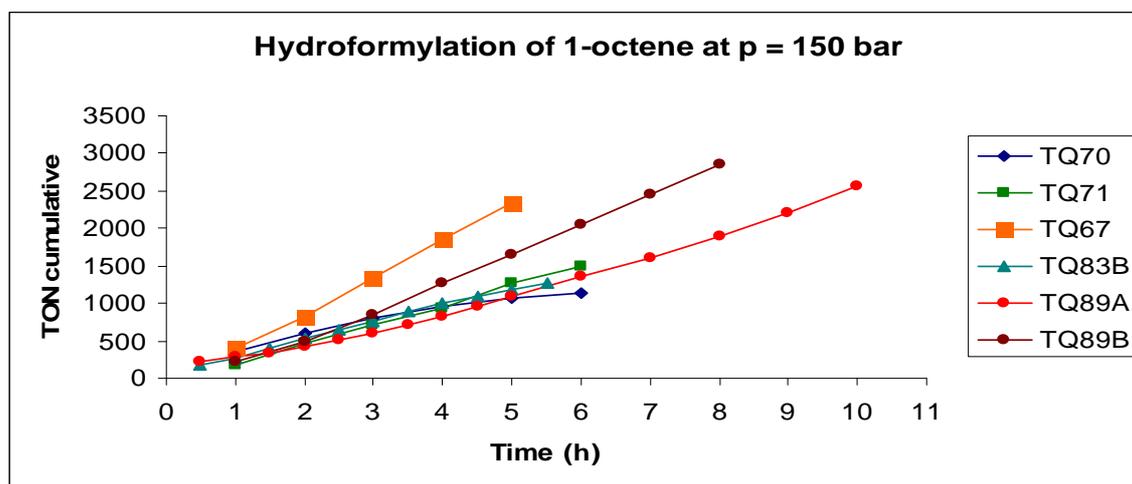


Figure 2: The catalyst stability over time from the reactions ran at p = 150 bar described on Table 2.

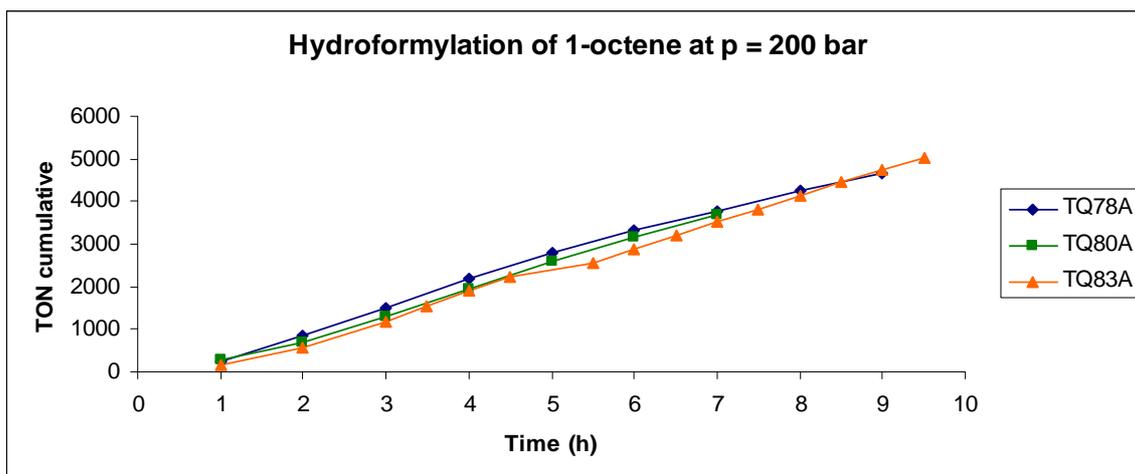


Figure 3: The catalyst stability over time from the reactions ran at $p = 200$ bar and $T = 100$ °C described on Table 2.

ICPMS analysis, used to check the Rh leaching from the reaction medium shows leaching results between 0.1 and 0.5 ppm.

Continuous flow hydroformylation of 1-octene “without gases” – a supported homogeneous system

Continuous flow hydroformylation of long chain alkenes (1-octene) have also been carried out in a supported homogeneous system using a SILP (Supported Ionic Liquid Phase) catalyst, where a thin layer of ionic liquid catalyst is immobilized at the surface of an inert solid support, for instance, silica. SILP catalysts have the ability to combine the advantages from both homogeneous and heterogeneous catalysts. By using a fixed bed reactor in a homogeneous system, it is possible to achieve a better catalyst/product separation and still expect the same performance in terms of selectivity as a “normal” homogeneous catalyst.[9, 10] In some cases they have been used with transport being effected by flowing $scCO_2$, with high rates, low Rh leaching and good catalyst stability.[11]

Some of us have been involved in developing systems in which catalytic reactions are carried out under high pressures of gas, but in the absence of gas cylinders; the “without gases” approach. Much of the work has involved generating hydrogen and CO_2 from formic acid [12], but in this application we have generated CO/H_2 *in situ*. Syn gas is obtained by decomposing formaldehyde at 450 °C (in a first reactor installed in the rig). The syn gas then flows into the second reactor where the hydroformylation reaction is carried out. The products can either be extracted using $scCO_2$ flow or the reactions can be carried out in the liquid phase in a downwards flow reactor. In the later case, the products are forced through the catalyst bed and into the collecting vessel using the pressure of syn gas.

Several runs were carried out using SILP catalysts with either 14 or 44% of ionic liquid loading (related to the mass of silica) at different pressures and different 1-octene flows. All the SILP catalysts prepared show good activity under the different conditions applied. Preliminary results suggest that the Rh leaching is < 1 ppm.

Some of the results obtained are shown in the Table 3.

Table 3: Continuous flow hydroformylation of 1-octene using SILP based catalyst Rh/[pentmim][TPPTS] (P/Rh = 10:1) and [octmim][Tf₂N] (loading of 44% w/w relative to the silica. Both runs were carried out for 12 h.

CO flow (mL/min)	1-octene flow (mL/min)	Temperature (°C)	Conversion to aldehyde (%)	l:b ratio	TOF (h ⁻¹)	TON cumulative
1,0	0,1	100	96	3	194	1272
1,0	0,1	100	94	3	189	1221

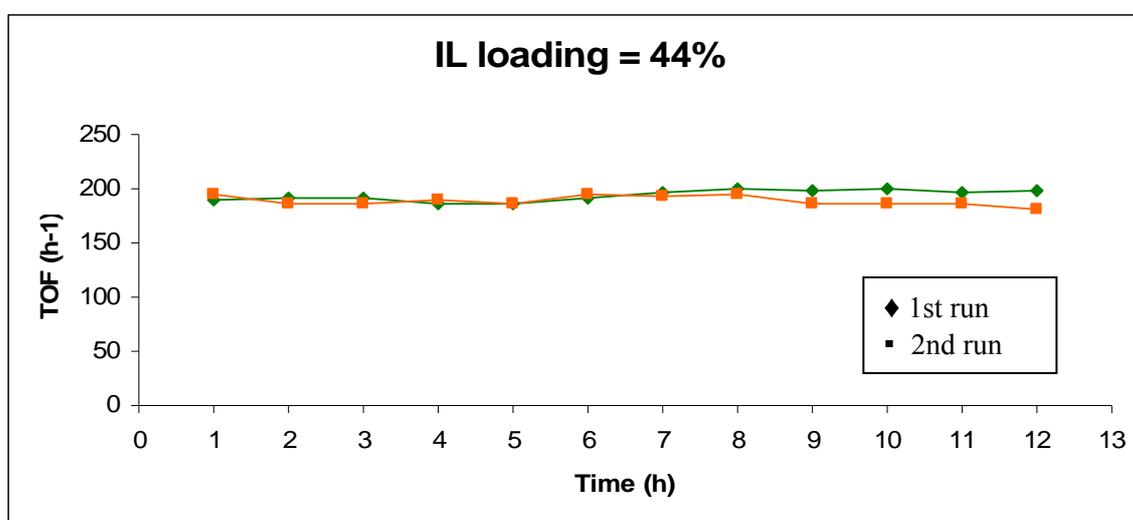
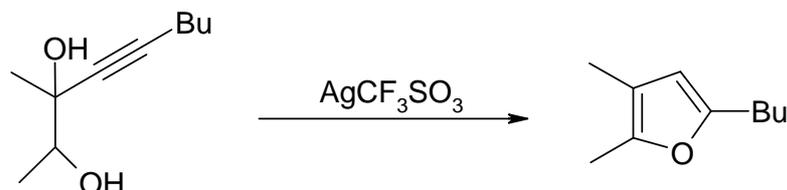


Figure 4: The catalyst activity over time from the reactions on Table 2.

Continuous flow silver catalysed heterocyclisation

The IL/scCO₂ system was applied to the heterocyclic synthesis shown in Scheme 1, in which a dihydroxyalkyne is cyclised to a substituted furan. This reaction has been carried out in conventional solvents, but catalyst recovery and reuse can be a problem.[13] The catalytic system involves silver salts and the reaction was carried out in [octmim][Tf₂N] or [octmpyr][Tf₂N] (Octmim = 1-octyl-3-methylimidazolium; Octmpyr = 1-octyl-3-methylpyridinium and Tf = CF₃SO₂). The results of a number of batch and continuous flow reactions are shown in Table 4.



Scheme 1: Silver catalysed synthesis of substituted furans.

The results obtained show that [octmpyr][Tf₂N] is more suitable for as a solvent for this system in that yields > 70 % (very little starting material was observed, but the collection efficiency was < 80 %)

were sustained for the 2 h of the reaction, even at a total pressure of 100 bar. Ag[CF₃SO₃] proved to be a better catalyst than AgNO₃ probably because of the higher solubility of Ag[CF₃SO₃] in the ionic liquids. The catalyst leaching in this medium was also low at < 1 ppm. The results demonstrate that heterocyclic synthesis may be carried out successfully using a proper IL/ scCO₂ continuous flow system, showing its versatility.

Table 4: Continuous flow heterocyclic synthesis catalysed by AgCF₃SO₃.

Reaction	Procedure	Pressure (bar)	Temperature (°C)	Ionic liquid	% Product
1	Batch	100	50	[octmpyr][Tf ₂ N]	46
2	Batch	200	50	[octmpyr][Tf ₂ N]	95
3	Flow	100	50	[octmpyr][Tf ₂ N]	> 60
4	Flow	125	50	[octmpyr][Tf ₂ N]	>70
5	Flow	150	50	[octmpyr][Tf ₂ N]	>70
6	Flow	150	75	[octmpyr][Tf ₂ N]	~ 50
7	Flow	200	80	[octmim][Tf ₂ N]	~ 50

NOTE: The reactor was charged with a 10% IL/silver catalyst solution (12 mL) and the products were extracted using a 1 nL/min scCO₂ flow rate, on both batch and continuous flow experiments. The flow rate of the substrate varied between 0.05 and 0.2 mL/min.

In conclusion, continuous flow IL/scCO₂ biphasic systems provide an efficient approach to the problem of catalyst separation. Such systems can now be run under pressure conditions which are accessible to a wide range of chemical industries.

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