

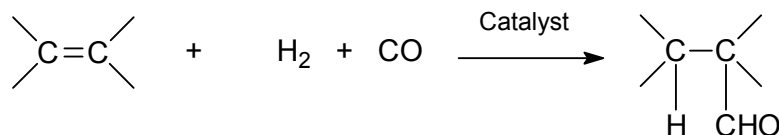
Biphasic Hydroformylation of Higher Olefins

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Introduction

Currently, worldwide production of aldehydes exceeds 7 million tons/year (Billig and Bryant 1995). Higher aldehydes are important intermediates in the synthesis of industrial solvents, biodegradable detergents, surfactants, lubricants, and other plasticizers. The process, called hydroformylation or more familiarly, the Oxo process, refers to the addition of hydrogen and the formyl group, CHO, across a double bond.



For lower aldehydes, homogeneous rhodium-phosphine catalysts are used because they have by far the best activity and selectivity. In this case the aldehyde product is recovered by distillation before the catalyst is recycled. The process used for conventional hydroformylation of short-chain alkenes cannot be applied to higher (>C₆) olefins due to the difficulty of recovering the high-boiling product aldehyde without simultaneously destroying the catalyst. The hydroformylation of higher olefins (>C₆) is done with less efficient cobalt catalysts at high temperatures and pressures.

One approach that has been successfully used to separate the catalyst from the product aldehyde is to use a biphasic system in which the rhodium catalyst is soluble in water and the product soluble in an organic phase. This approach is used by Hoechst/Rhône-Poulenc to produce more than 600,000 t/year of butyraldehyde (a lower aldehyde) (Baker and Tumas 1999). Unfortunately, this process cannot be used to produce higher aldehydes because the water solubility of the higher olefins that are the feedstock is very low, which dramatically reduces the reaction rate.

To eliminate the need to recover the product by distillation, thermomorphic solvent mixtures are proposed. These mixtures are immiscible at room temperature but become miscible at reaction temperature, enhancing conversion rates by promoting contact between the rhodium catalyst and the olefin. After the reaction is complete, the reaction mixture is cooled and the phases completely separate. The product can be simply recovered by decantation and the catalyst can be recycled. Thermomorphic mixtures can result in dramatic energy and cost savings because the fraction of feedstocks converted to the desired product could be increased from 60 to 85%.

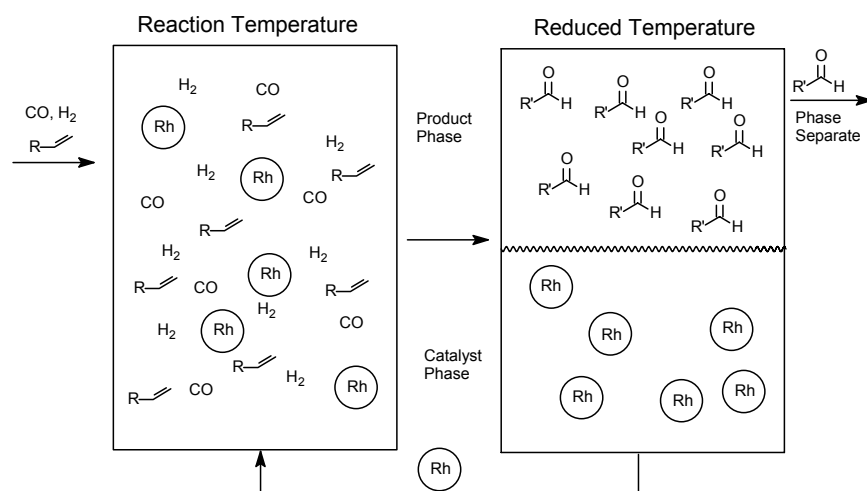


Figure 1. Representation of hydroformylation in a thermomorphic system.

A thermomorphic system is characterized by solvent pairs that reversibly change from being biphasic to monophasic as a function of temperature. Many solvent pairs exhibit varying miscibility as a function of temperature. For example, methanol/cyclohexane and *n*-butanol/water are immiscible at ambient temperature, but have consolute temperatures (temperatures at which they become miscible) of 125°C and 49°C, respectively (Halpern and Gozashti 1988).

The use of thermomorphic systems has recently been studied as a way of achieving catalyst separation in homogeneous catalysis. For example, a biphasic hydroformylation catalyst system was developed to take advantage of the unusual solvent characteristics of perfluorocarbons combined with typical organic solvents. Fluorous mixtures such as perfluoromethylcyclohexane (PFMCH)/toluene are immiscible at ambient temperature but become a single-phase solution upon heating (Hildebrand and Cochran 1949; Scott 1948; Dorset 1990). This characteristic is very useful for homogeneous catalysis because the reaction can be performed at an elevated temperature where the mixture becomes one-phase, overcoming any rate limitations due to mass transfer. Upon reaction completion, the solution is phase separated by cooling and the products are simply decanted. Unfortunately, the expense of the solvents and the ligands make the fluorous biphasic system impractical for industrial application. Other thermomorphic systems studied rely on exotic phosphine ligands for their use. Again, these are not used industrially because of their high cost (Bergbreiter et al 1998, Bianchini et al 1995).

Our approach is that to use the inexpensive ligands that are already used industrially as well as conventional solvents. The goal of this project is to develop a thermomorphic approach to rhodium-catalyzed hydroformylation of higher olefins ($>\text{C}_6$) that enhances conversion rates and ease of product recovery while minimizing catalyst degradation and loss.

Thermomorphic solvent mixtures have been tested for hydroformylation of 1-octene, 1-dodecene and tetradecene to determine the ease of product recovery and catalyst recycling. Using a small scale Parr pressure reactor, we demonstrated the efficacy of a biphasic, thermomorphic, system that had the following advantages:

- Suitable for conversion of higher olefins to higher aldehydes.
- High conversion rates and selectivity
- Recovery of the product aldehyde by simple room temperature decantation rather than high temperature distillation.
- Little to no catalyst leaching and high catalyst recyclability.
- More than 30% saving in feedstock and energy costs.

Results

In Table 1 is shown examples of hydroformylation reactions using thermomorphic catalysts. For direct comparison we did all the reactions under the same conditions. The reactions were carried out in a batch reactor with 1:1 molar mixture of H₂/CO with a combine pressure of 500 psi at 100°C for 2 h. After the reaction mixture was cooled and allowed to separate the product was analyzed by GC. In all cases the linear to branch aldehyde selectivity was very high and as expected, the rate of conversion drops as the chain length of the alkene is increased (Hanson et al. 1998).

Table 1. Thermomorphic hydroformylation results.

Sample	1-Alkene	Conversion (mol %)	L/B ratio
1	Octene	16	6.0
2	Dodecene	7	3.9
3	Tetradecene	3	4.2

Reaction conditions: Alkene/Rh (molar ratio) = 426, CO/H₂ (molar ratio) = 1, P(CO/H₂) = 500 psi, T = 100°C. Reaction time = 2h.

We have found that the rhodium loss to the product phase in batch reactions is very low. For example, cycling a thermomorphic catalyst solution three times showed a rhodium loss below the 0.1 ppm as measured by atomic absorption. At this time we believe the rhodium loss due to leaching of catalyst into the product phase is minimal and should not be a problem. When we do long-term studies in our continuous bench scale reactor we will get a better understanding of this issue.

In order to do long term studies, we have built a bench-scale continuous hydroformylation apparatus. Figure 2 is a picture of the apparatus built at TDA and Figure 3 depicts the P&ID for the apparatus. It has an Autoclave Engineers reactor with a 300 ml capacity that features a bolted closure with a confined gasket for sealing at even very high temperatures. It is designed to withstand a maximum allowable pressure of 3800 psig at 538°C. The contents of the reactor are mixed with an overhead mixer designed specifically for use with the pressure vessel. Two thermocouples measure the internal and external temperature of the reactor wall and a pressure gauge monitors the internal reactor pressure. A rupture disk designed to withstand up to 1000 psig is mounted on the top of the reactor. All process lines to and from the reactor are unheated 1/8" 316 ss tubing with a wall thickness of 0.3".

Two separate 2.1L reservoirs contain the catalyst and product phases and the contents are fed into the reactor through a standard liquid mass flow controller. Under reaction

conditions, (100°C and 500 psig CO:H₂) the phases become miscible and hydroformylation occurs. The contents of the reactor can be sampled from a pressure fed sample tube. After a prescribed residence time the pressurized liquid reactor contents are continuously sampled by a standard liquid mass flow controller, and after the solution exits the reactor a pressure control valve reduces the pressure of the sampling line to atmospheric level, the liquid contents are delivered to a continuous decanter where the phases separate. The catalyst phase then settles to the bottom where it is drained for recycle and reuse, while the product phase is collected into a 4.2L reservoir where it is sampled for GC analysis. As the reaction progresses and the linear alkene substrate (i.e., 1-octene) is slowly consumed, it can be replenished through the 2.1L liquid reservoir.

The apparatus is fully automated using the OptoControl software package is designed to operate unattended. Scanning and safety charts will monitor the vital parameters of the system, initiating a shutdown if the reactor exceeds 160°C and 550 psig. A flammable gas monitor is also located near the apparatus and when tripped the apparatus will be automatically shut down.



Figure 2. Bench-scale continuous hydroformylation apparatus.

We are starting using 1-octene as the olefin and once we have worked out the process conditions for 1-octene, we will also test the higher olefins 1-dodecene and 1-tetradecene. From the results of the tests in this continuous reactor system, we hope to have data strong enough to convince potential commercial partners of the advantage of our process compared to conventional cobalt-based hydroformylation of higher olefins.

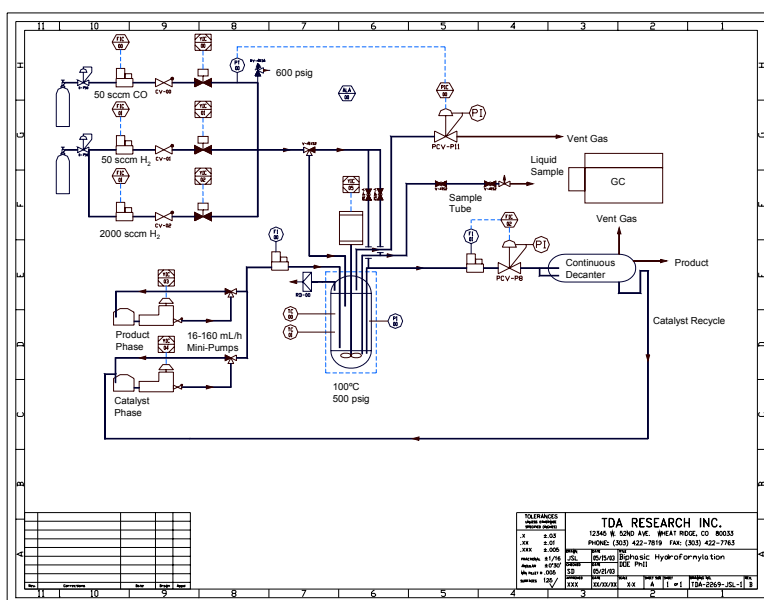


Figure 3. P&ID of bench-scale continuous reactor.

Conclusion

We have developed a thermomorphic catalyst system for the hydroformylation of higher alkenes. We have shown that the system works in batch reactions and that the rhodium losses are very low. We have built a bench-scale continuous reactor and are using it to determine the long-term performance of the thermomorphic catalyst systems in hopes of generating data that will convince potential commercial partners of the advantage of our process compared to conventional cobalt-based hydroformylation of higher olefins.

Acknowledgment

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