

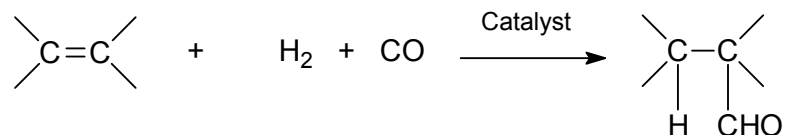
## Biphasic Hydroformylation of Higher Olefins

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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 (>C<sub>6</sub>) olefins due to the difficulty of recovering the high-boiling product aldehyde without simultaneously destroying the catalyst. The hydroformylation of higher olefins (>C<sub>6</sub>) 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%.

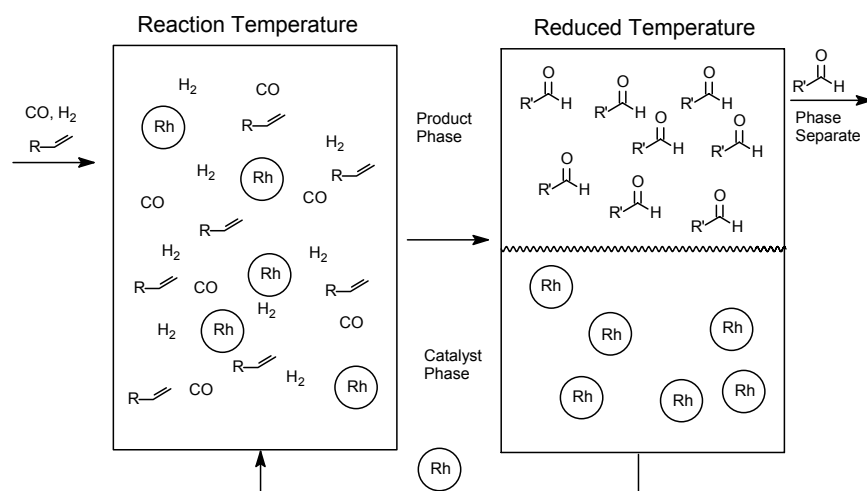


Figure 1. Representation of hydroformylation in a thermomorphic system.

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 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 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. The apparatus is fully automated using OptoControl software and is designed to operate unattended. It has an Autoclave Engineers reactor with a 300 ml capacity that features a bolted closure with a confined gasket for high temperature sealing. 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".

The reactor is a continuous stirred reactor (CSTR) with a catalyst residence time of approximately 30 minutes. 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:H<sub>2</sub>) the phases become miscible and hydroformylation occurs. The contents of the reactor can be sampled from a pressure fed sample tube. The pressurized liquid reactor products exit the reactor through a pressure control valve, which reduces the pressure to atmospheric, and 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.



Figure 2. Bench-scale continuous hydroformylation apparatus.



Now that we have shown that the system works using 1-octene as the higher olefin, we will begin testing 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.

## Conclusions

We have developed a thermomorphic catalyst system for the hydroformylation of higher alkenes. We have built a bench-scale continuous reactor and are using it to determine the long-term performance of the thermomorphic catalyst system. Initial results using 1-octene show that the activity and selectivity of the catalyst are high and the rhodium losses are very low. The next step is to demonstrate the process with the higher olefins dodecene and tetradecene.

## Acknowledgment

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