Biphasic Hydroformylation of Higher Olefins

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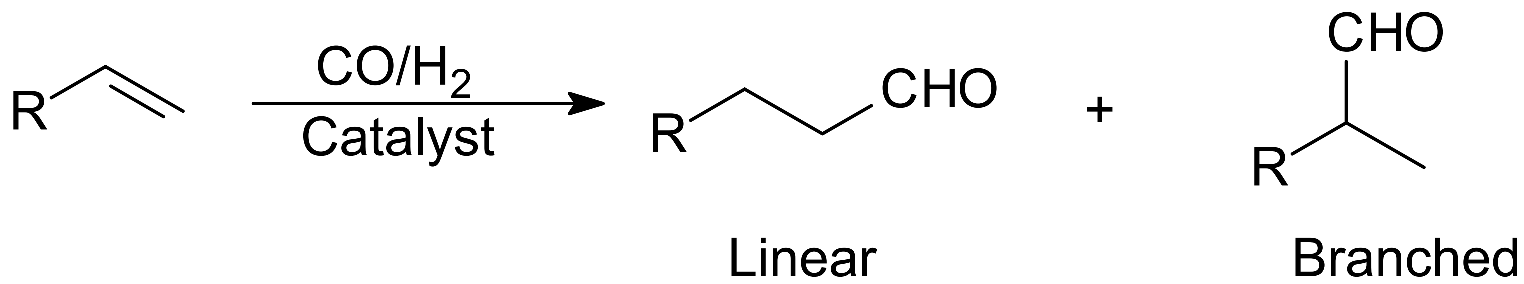
Project Summary

- **Objective: Develop improved hydroformylation process to produce higher aldehydes based on:**
  - Thermomorphic solutions using conventional solvents
  - Rhodium phosphine catalysts
  - Higher olefins (octene through tetradecene)
- **Process produces aldehydes with good (high) ratio of linear to branched products**
- **Low loss of expensive rhodium catalyst during recycle**

Hydroformylation

- **Largest commercial application of homogeneous catalysis**



- **Worldwide production of aldehydes exceeds 7 million tons/year**
- **Higher aldehydes (>C_6) are important intermediates for solvents, detergents, surfactants, lubricants and plasticizers**

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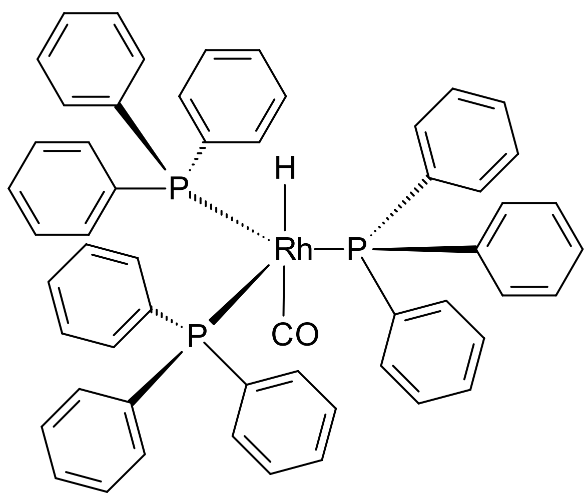
Aldehyde Production

- Rhodium and cobalt catalysts can be used
- Rhodium phosphine catalysts have replaced cobalt catalysts for lower aldehydes (<C_6) because of their higher activity and selectivity
- Because of the high cost of rhodium, catalyst losses have to be very low



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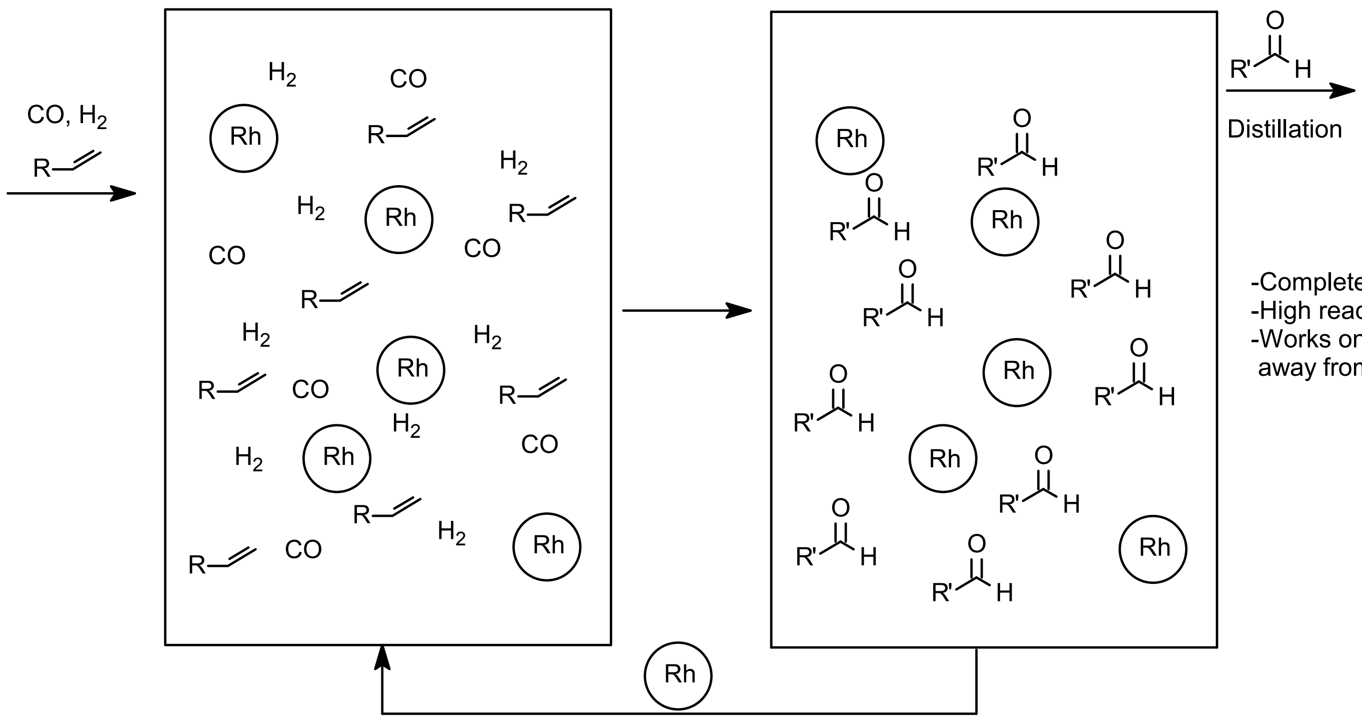
Single-Phase Homogeneous Hydroformylation (lower aldehydes)



-Complete mixing
-High reaction rates
-Works only if product can be distilled away from catalyst, i.e. butylaldehyde

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Higher Aldehydes

- The higher boiling points of higher aldehydes result in catalyst decomposition
- Higher aldehydes are produced using less efficient cobalt catalyst because there is no effective means to separate the catalyst from the reaction mixture

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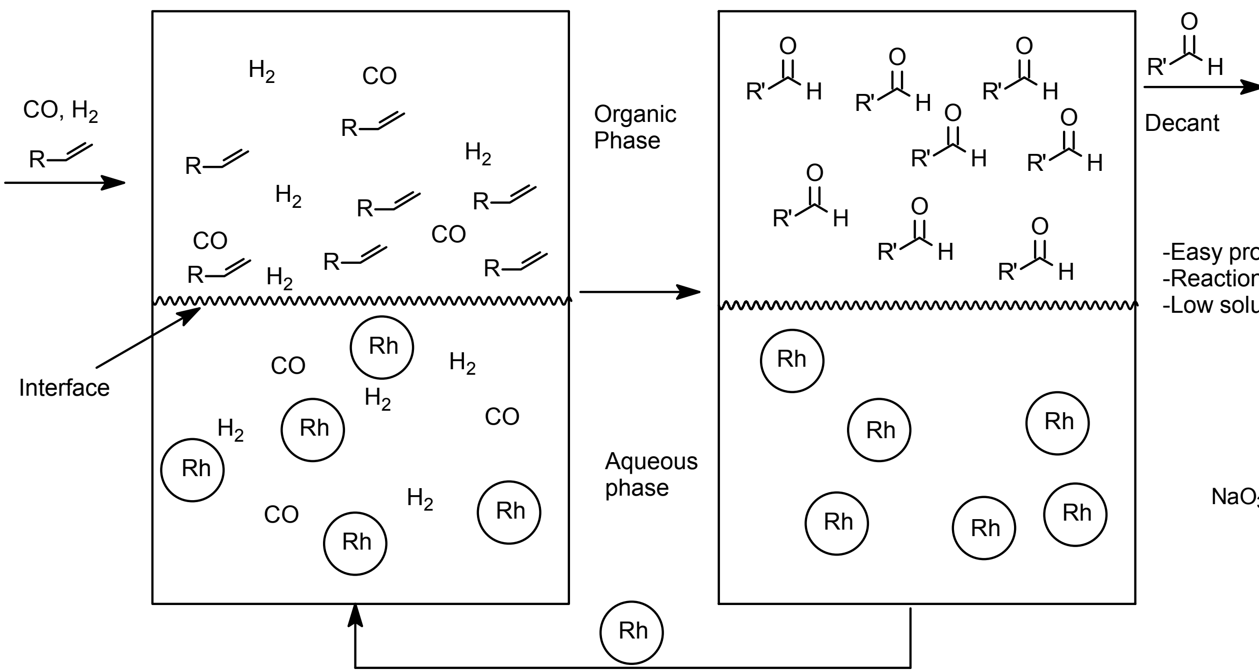
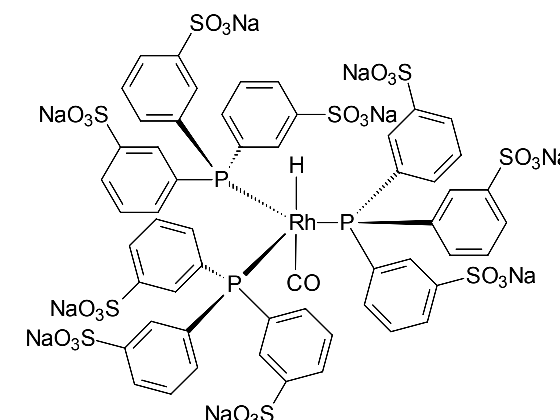
Biphasic Hydroformylation
(Ruhrchemie-Rhône Poulenc)

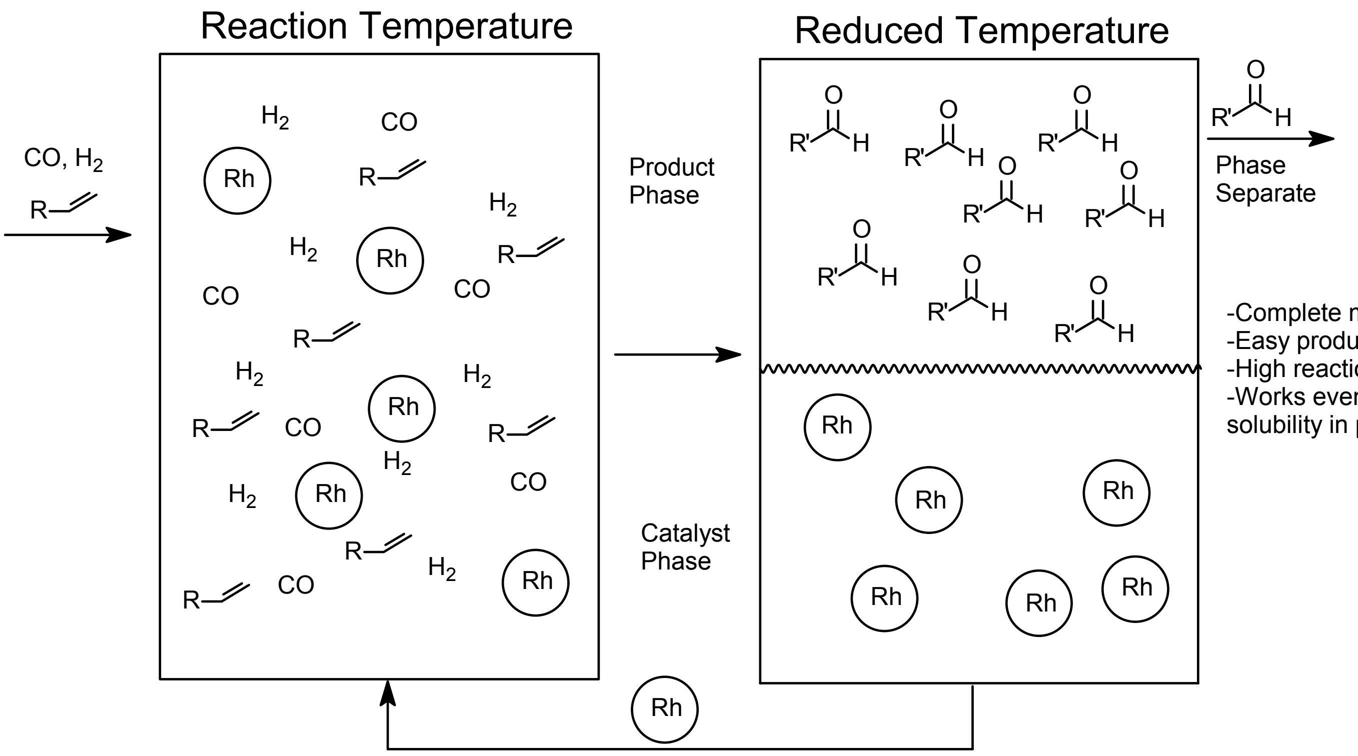


- Easy product and catalyst separation
- Reaction only at the interface
- Low solubility of sustrate reduces reaction rate



Wiebus, E., and B. Cornils (1996). "Water-soluble catalysts improve hydroformylation of olefins," *Organic Processing*, March 63-66.

Thermomorphic Hydroformylation



- -Complete mixing
- -Easy product and catalyst separation
- -High reaction rates
- -Works even if olefin has low solubility in polar phase

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Fluorous Thermomorphic Hydroformylation

- **Hydroformylation has be done using perfluoromethylcyclohexane/toluene thermomorphic solution with fluorinated phosphine ligands**
- **Catalyst: $HRh(CO)\text{-}(P(CH_2CH_2(CF_2)_5CF_3)_3))_3$**
- **Problem is that fluorinated solvents and ligands are very expensive**

Horváth, I.T., and J. Rábai (1994). "Facile Catalyst Separation Without Water: Fluorous Biphase Hydroformylation of Olefins," Science 266, 72-75

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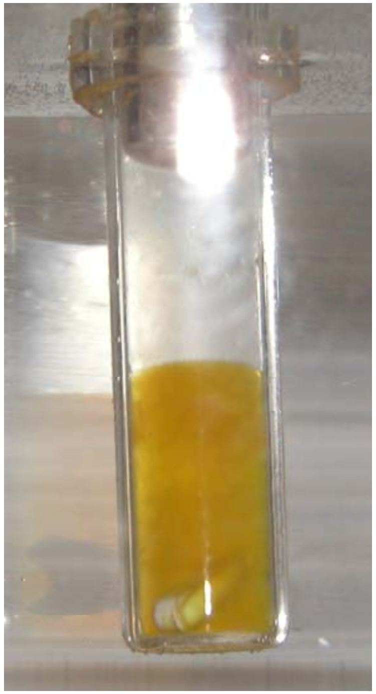
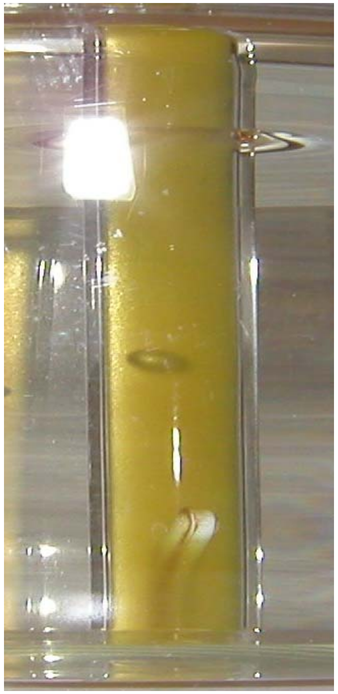
Non-Fluorous Thermomorphic Solutions

- **Common solvent pairs that reversibly change from being biphasic to monophasic as a function of temperature**
  - Methanol/cyclohexane (125°C)
  - *n*-butanol/water (49°C)
- **TDA's approach is to use conventional solvents and ligands for thermomorphic hydroformylation**

Thermomorphic Catalyst Solution



25°C



70°C

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Thermomorphic Hydroformylation Results (Batch)

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/H_2 (molar ratio) = 1, $P(CO/H_2)$ = 500 psi, T = 100°C. Reaction time = 2h.

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Reuse of Catalyst (Batch)

Cycle	Olefin Conversion (mol. %)	Linear (mol %)	Branched (mol %)	L/B Aldehyde Ratio	Rh Loss (μg/g)*
1	36.6	25.6	11.0	2.3	3
2	25.8	25.4	0.4	64	<1
3	27.9	27.9	0.0	-	<1
4	29.9	29.7	0.2	148	6
5	19.4	17.7	1.7	10	1

Reaction conditions: Alkene = 1-octene, CO/H_2 (molar ratio) = 1, $P(CO/H_2)$ = 500 psi, T = 100°C, reaction time = 4h, *Rh loss (μg) per gram of organic phase solution.

Technical Barriers

- **Show that our catalyst system can produce higher aldehydes in a continuous reactor with:**
  - High selectivity (linear/branched ratio)
  - Reasonable rates
  - Long catalyst lifetime
  - Low rhodium loss
- **How issue will be addressed**
  - Built a bench-scale continuous reactor
  - Do process optimization and long-term testing

Bench-Scale Continuous Reactor

- Reactor body manufactured by Autoclave Engineers
- 300 ml volume
- Fitted with Magnedrive stirrer and Dispersimax™ impeller for improved gas dispersion in liquid
- Rated up to 4700 psig at 200ºC, 3800 psig at 538ºC
- Computer controlled (OptoControl software)

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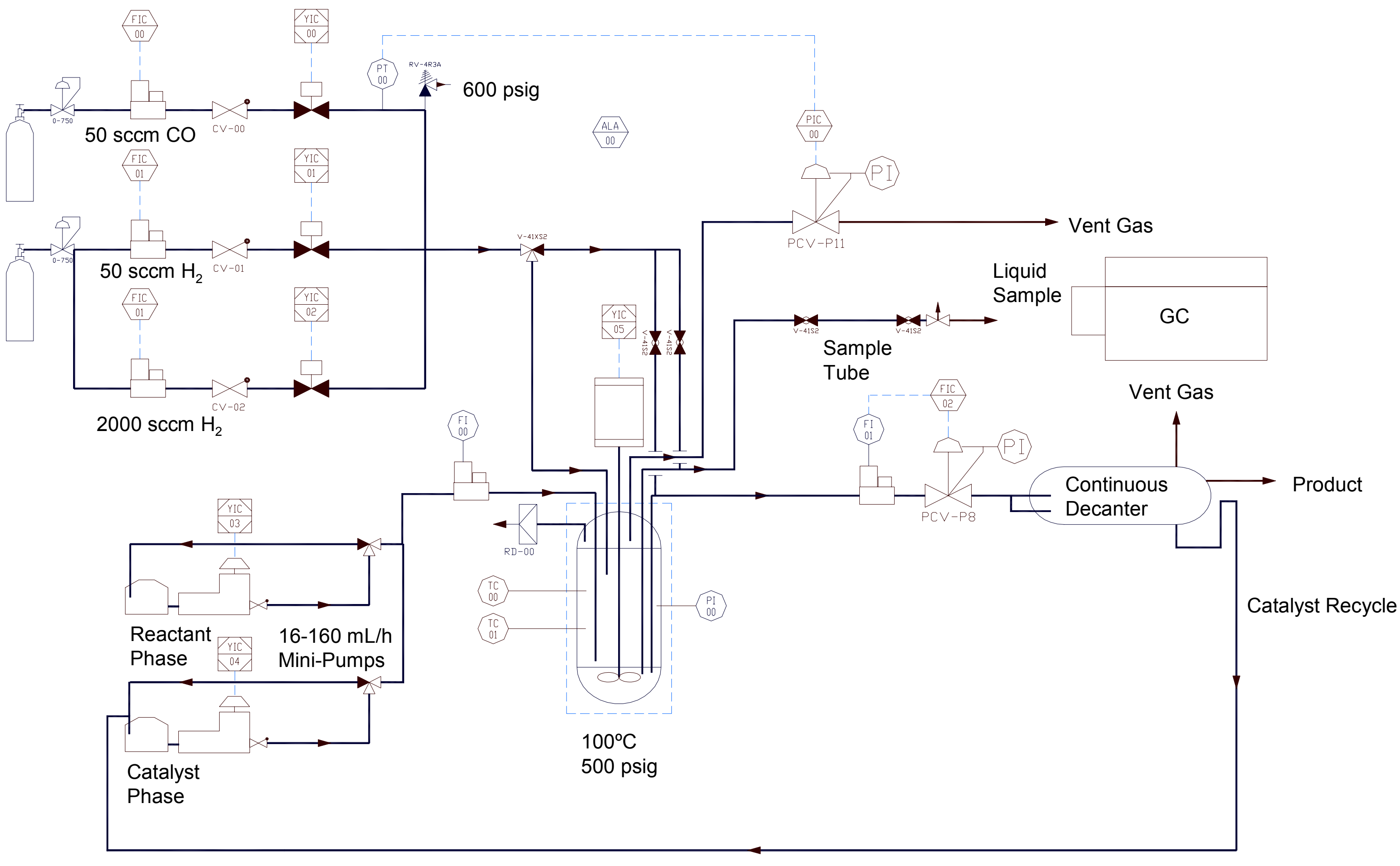
P&ID of Bench-Scale Continuous Reactor



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Summary

- Successfully developed thermomorphic catalyst system for hydroformylation in batch mode
- Built a continuous bench-scale reactor
- In the process of optimizing catalyst system in a continuous system to be followed by long-term catalyst durability testing
- From the results of our work we expect to convince our commercial partner to license the technology

Acknowledgement

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