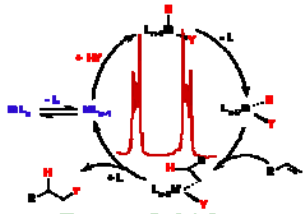
Continuous Homogeneous Catalysis
Membrane Separation & 2-Phase Approach



Dieter Vogt

Industrial Chemistry

University of Edinburgh

Materials Valley, Ludwigshafen , 23 January 2014

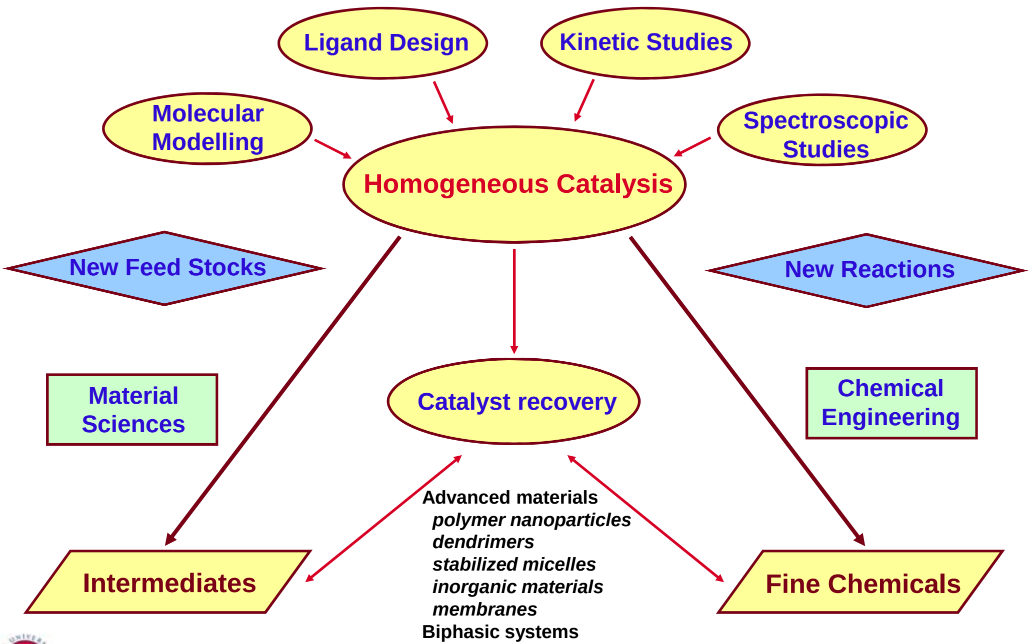
Industrial Homogeneous Catalysis

OXEA plant in Oberhausen

Outline

- Introduction
- MWE Catalysts and Membrane Filtration
- POSS-Enlarged Catalysts; Continuous Hydroformylation
- Latex-Enhanced Aqueous Phase Catalysis

The Homogeneous Catalysis Group



Homogeneous Catalysis Group

➢ Broad range of activities – from molecular base of homogeneous catalysis to applications & products

Mechanisms

- *kinetics*
- *stereoselection*
- *regioselection*
- *chemoselection*
- *…*

Processes

Methods

Applications

- *automated parallel synthesis*
- *automated parallel testing & analysis*
- *in situ spectroscopy*
- *DFT calculations & molecular modeling*
- *membrane technology*
- *immobilization & 2-phase catalysis*
- *combination of reaction engineering & catalysis*

- *enantiopure compounds for pharma, food, and agro*
- *specialty fine chemicals*
- *intermediates*
- *renewable feed stocks*

Immobilization of Homogeneous Catalysts

Immobilization

Supported Catalysis

Solid Support
inorganic
organic
→ *Filtration*

SLP
inorganic
organic
→ *Filtration*

Soluble Support
soluble polymer
dendrimers
→ *Ultra-Filtration*, *Nano-Filtration*, *Centrifugation*

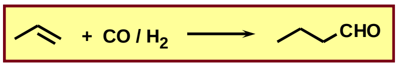
Multiphase Catalysis

Aqueous Phase
→ *Phase Separation*, *Extraction*

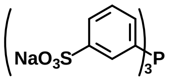
Nonaqueous Phase
organic two-phase
supercritical fluids
fluorous phase
ionic liquids
→ *Phase Separation*, *Extraction*

Catalyst-Recycling VII

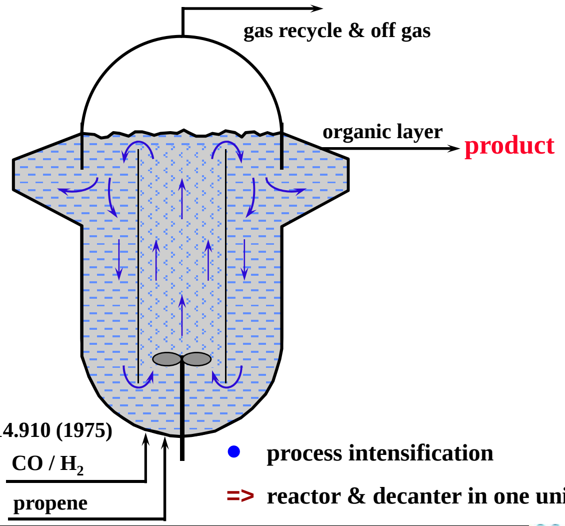
Ruhrchemie/Rhône Poulenc, two Phase Process



hydrophilic ligand: TPPTS



solubility: > 1 kg / l H_2O

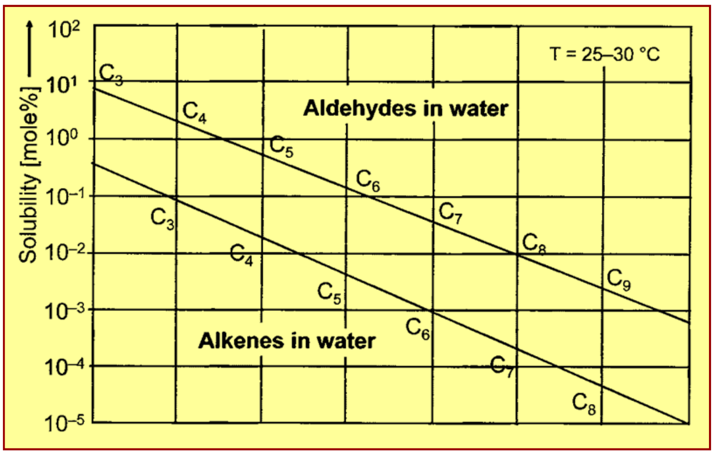


Rhône-Poulenc Recherche (E.G. Kuntz), FR 2.314.910 (1975)
E.G. Kuntz, *CHEMTECH* 1987, Sept., 570.

- process intensification

=> reactor & decanter in one unit

Solubility of Alkenes and Aldehydes in Water



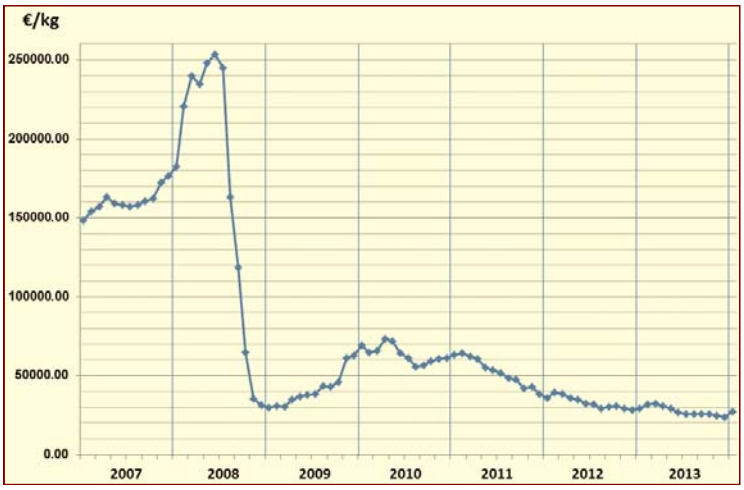
=> **Solubility of higher alkenes too low for efficient conversion in water !**

B. Cornils in *Multiphase Homogeneous Catalysis*, Wiley-VCH **2005**, 31.

Rhodium Price Past 7 Years

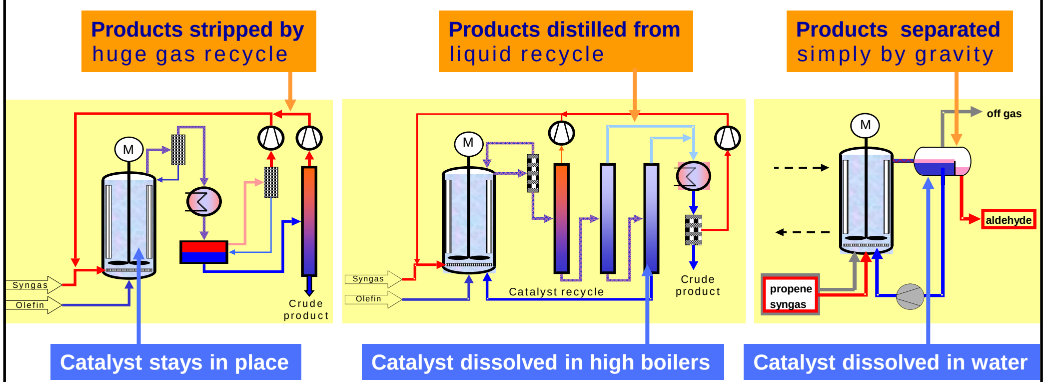
monthly values

Source: Johnson Matthey



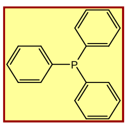
- **Price on 01-06-2011: 57 432 €/kg 16-01-2014: 27 066 €/kg**

Recycle Strategies for Propene-Oxo



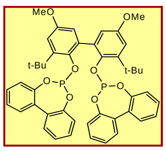
T 90 ... 100 °C
p 15 ... 18 bar
Sel ~ 98 %
linear 90 ... 93 %

Rh 250 w-ppm
ligand 7,5 %
STY 0,15 t/m³/h



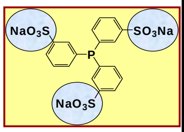
T 85 ... 90 °C
p 15 ... 18 bar
Sel 98 ... 99 %
linear 95 ... 98 %

Rh 80 w-ppm
ligand 2 %
STY 0,20 t/m³/h

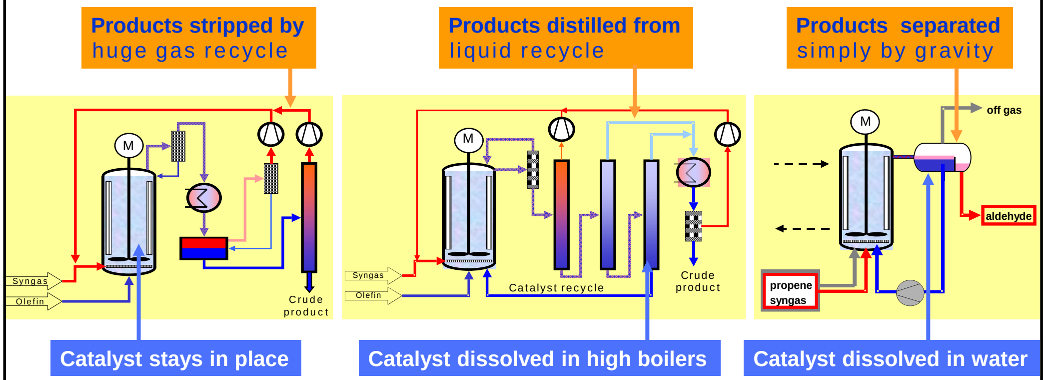


T ~ 120 °C
p ~ 50 bar
Sel 98 ... 99 %
linear 93 ... 97 %

Rh 800 w-ppm
ligand 30 w-% (H_2O)
STY 0,15 t/m³/h



Recycle Strategies for Propene-Oxo



- Propene hydroformylation, 400 kt/a

400 m³ reactor volume	300 m³ reactor volume	400 m³ reactor volume
50 kg Rh inventory (2.87 M€)	15 kg Rh inventory (0.86 M€)	200 kg Rh inventory (11.46 M€)
15 t ligand inventory	4 t ligand inventory	100 t ligand inventory

Metal and Ligand Losses

- Rh losses
  - Rh-cluster formation & precipitation

    at 1 ppm loss of Rh *=> 200 €/t product*
    => 20 M€/a at 100 kt/a scale
- Ligand losses
  - Traces of water by aldol-reaction
  - Saponification of phosphite catalyzed by acids
  - Product of hydrolysis are phosphoric acids
  - Autocatalytic process !!!!!!
    - *Ligand : ~ 10-fold mol-mass compared to Rh*
    - *Typical L/Rh = 10*
    - *Ligand price magnitude: ~ 0,5 M€/t*

    => 100 ppm ligand loss / 1 ppm Rh
    => 50 €/t product => ~ 5 M€/a at 100 kt/a scale

for deactivation pathways see e.g. P. W. N. M. van Leeuwen, *Appl. Catal. A: General* **2001**, *212*, 61.

Industrial Homogeneous Catalysis

Shell plants in Stanlow

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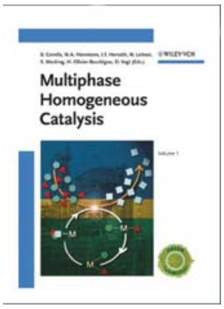
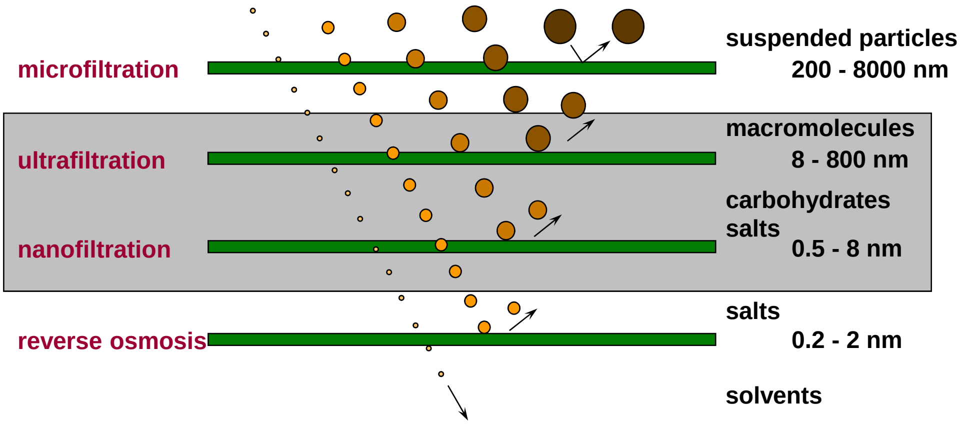
Continuous Homogeneous Catalysis
Catalyst Recycling

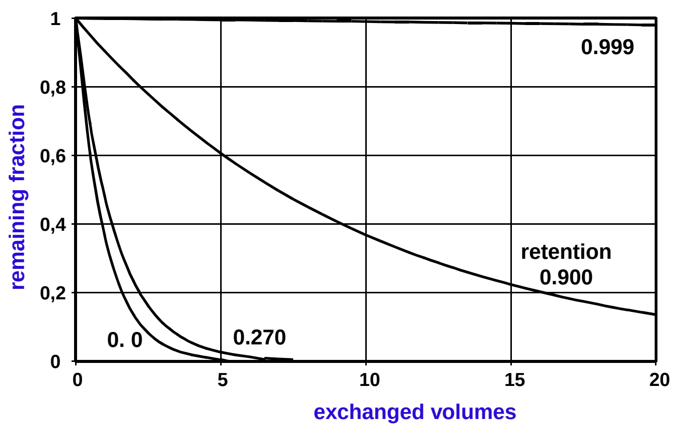


- C. Müller, D. Vogt, “Immobilization and Compartmentalization of Homogeneous Catalysts” in Green Catalysis (Eds. P. T. Anastas, R. H. Crabtee), Wiley-VCH **2009**, Vol. 1, pp 127-152.
- N. J. Ronde, D. Vogt, *"Separation by Size-Exclusion Filtration - Homogeneous Catalysts Applied in Membrane Reactors"* in *Recovery and Recycling of Homogeneous Catalysts* (Eds. D. Cole-Hamilton, R.P. Tooze), Springer 2006, pp 73-104.
- D. Vogt,*"Organic-Organic Biphasic Catalysis"* in *Multiphase Homogeneous Catalysis* (Eds.: B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, Wiley-VCH **2005**, pp 309-337. M. Janssen, J. Wilting, C. Müller, D. Vogt, *Angew. Chem. Int. Ed.* **2010**, *49*, 7738-7741.
- M. Janssen, C. Müller, D. Vogt, *Dalton Trans.* **2010**, *39*, 8403-8411.
- M. Janssen, C. Müller, D. Vogt, *Green Chem.* **2011**, *13*, 2247-2257.

Membrane Processes and Related Particle Sizes

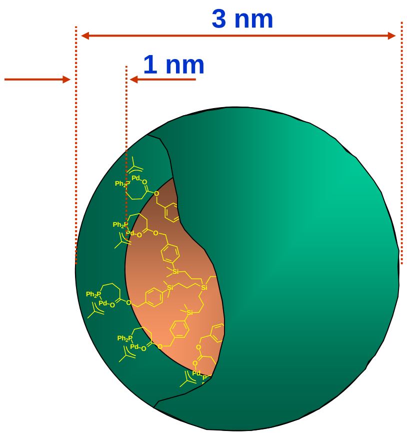


Wash-Out Depending on the Retention



➡ **In practice > 99.9% retention required, for larger scale applications even > 99.99%**

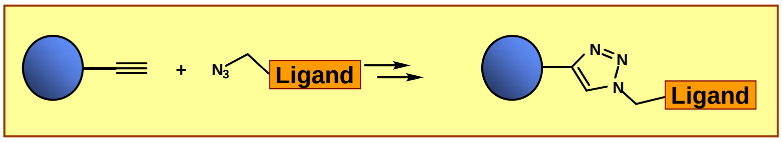
Dendritic Effects



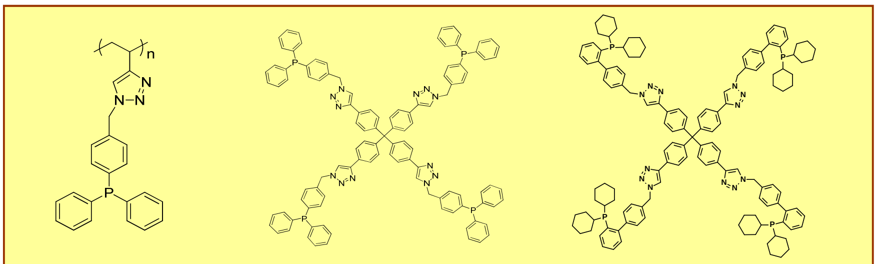
- 12 Pd complexes concentrated within a shell of 9.95 nm^3 => [Pd] = 2 mol/l !
- in normal catalytic run [Pd] = 5 mmol/l

- **High local concentration of active sites**
  => site isolation to overcome catalyst deactivation

'Clicked' Supported Catalysts



1) 5 mol % $CuSO_4.5H_2O$, 10 mol % Na-ascorbate, THF/Water, r.t., >95%
2) $HSiCl_3$, toluene, D



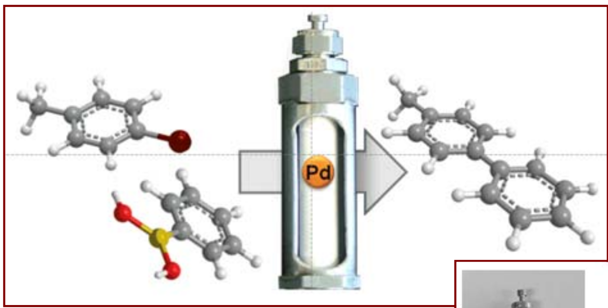
PPh$_3$ on support I

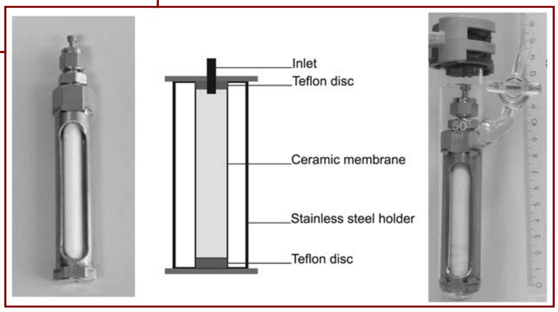
PPh$_3$ on support II

Buchwald lig. on support II

M. Janssen, C. Müller, D. Vogt, *Adv. Synth. Catal.* **2009,** *351*, 313-318.

‘Click’ Dendritic Phosphines

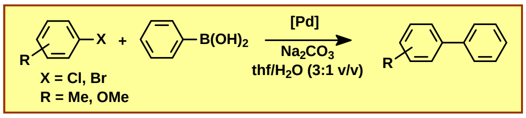


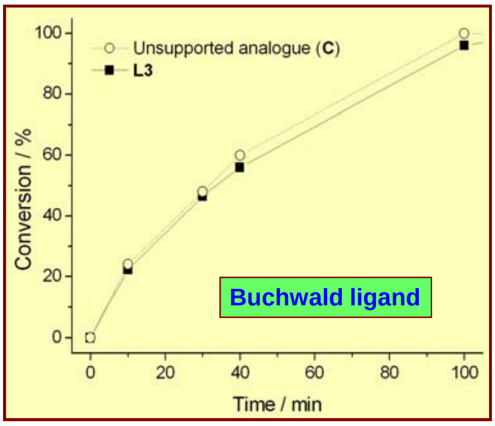


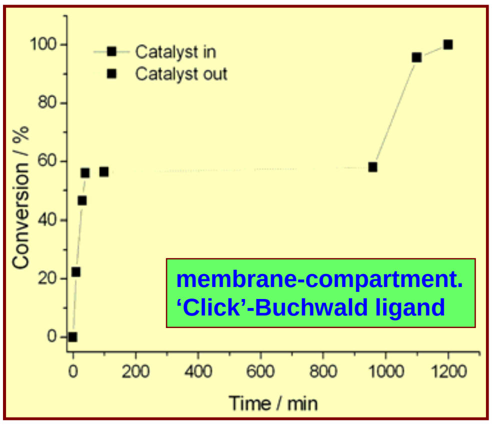
M. Janssen, C. Müller, D. Vogt, *Adv. Synth. Catal.* **2009,** *351*, 313-318.

‘Clicked’ Supported Catalysts

in Suzuki Coupling Reactions







M. Janssen, C. Müller, D. Vogt, *Adv. Synth. Catal.* **2009,** *351*, 313-318.

Industrial Homogeneous Catalysis

DOW site in Tarragona, Spain

Outline

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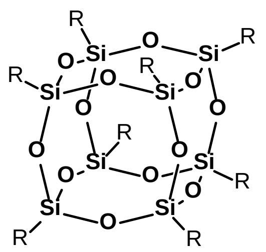
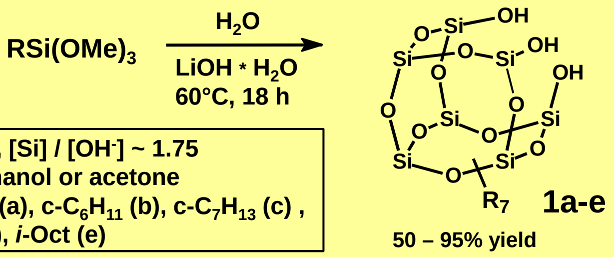
Polyhedral Oligosilsesquioxanes (POSS)



- ➢ Rigid Si-O cages
- ➢ Well defined three-dimensional structure
- ➢ High solubility in apolar and certain polar solvents
- ➢ Generally thermodynamically and kinetically stable

→ Molecular Weight Enlarged Ligands for homogeneous catalysis

Improved POSS Trisilanol Synthesis

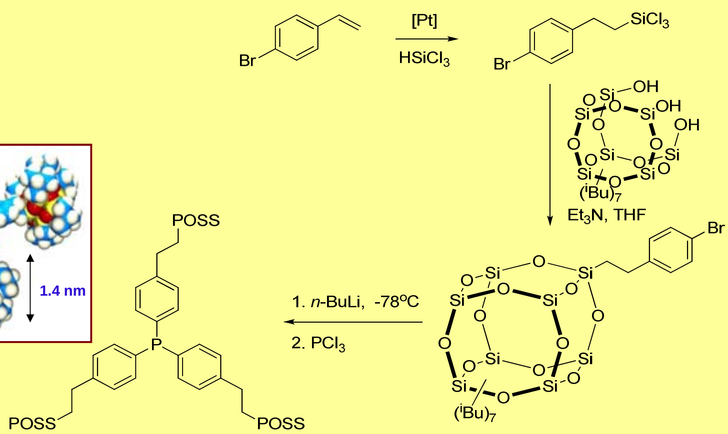


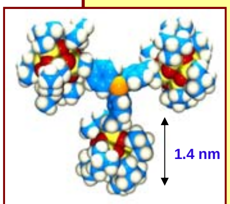
[Si] ~ 1-2 M, [Si] / [OH$^-$] ~ 1.75
solvent: ethanol or acetone
R = c-C_5H_9 (a), c-C_6H_{11} (b), c-C_7H_{13} (c), *i*-Bu (d), *i*-Oct (e)

- **Base catalyzed routes for POSS trisilanols**
- **Cheap starting materials**
- **TU/e pilot plant: 1.1 kg of 1d per day (10 L batch reactor)**

- F.J. Feher, *Chem. Commun.* **1999**, 2153
- J.D. Lichtenhan, F. J. Feher *et al.*, *Pat. Appl.*, **2001**, PCT/WO01/10871
- H.C.L. Abbenhuis *et al.*, *Pat. Appl.*, **2003**, PCT/WO03/95547

Synthesis of PPh_3-POSS

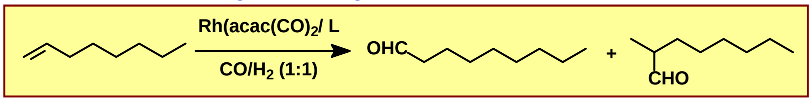


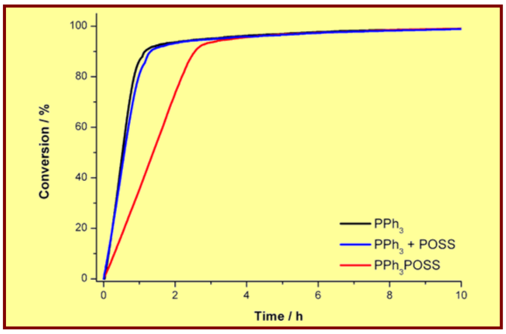


M. Janssen, J. Wilting, C. Müller, D. Vogt, *Angew. Chem. Int. Ed.* **2010**, *49*, 7738-7741.

Batch Experiments

Hydroformylation of 1-octene





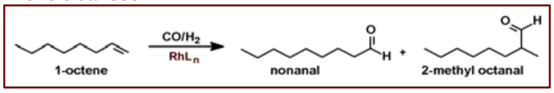
T = 80ºC, p = 20 bar, solvent = toluene, V_{tot} = 22 mL,
$Rh(acac)(CO)_2$, [Rh] = 0.53 mM, Rh:L = 1:5

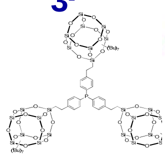
- **POSS has no significant influence on activity**

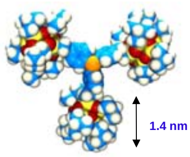
M. Janssen, J. Wilting, C. Müller, D. Vogt, *Angew. Chem. Int. Ed.* **2010**, *49*, 7738-7741.

Continuous Hydroformylation with POSS-Enlarged PPh_3/Rh

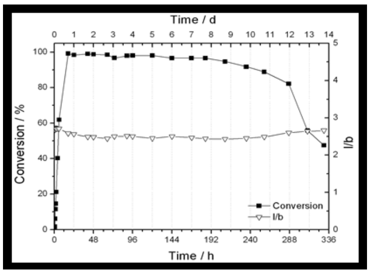
Michèle Janssen

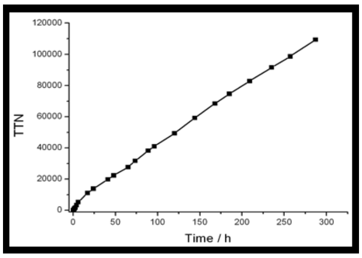






Unprecedented Example



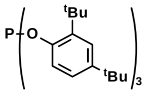


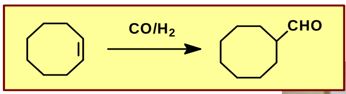
- **Conversion is constant for 10 days**
- **Regioselectivity is constant: l/b = 2.5**

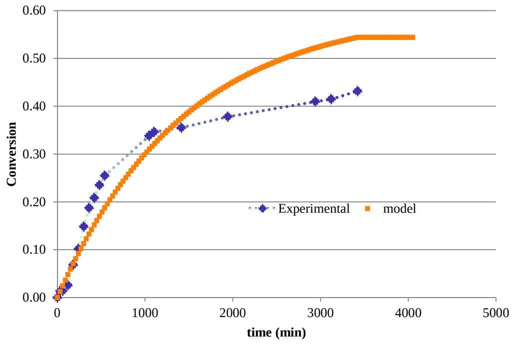
M. Janssen, C. Müller, D. Vogt, *Dalton Trans.* **2010**, *39, 8403.*
M. Janssen, J. Wilting, C. Müller, D. Vogt, *Angew. Chem., Int. Ed.* **2010**, *49*, 7738.

- **tTON after 14 days > 110,000**
- **very low leaching (Rh: 0.045% & P: 0.74%) of total initial amount**
- **> 99% retention after 2 weeks!**

Continuous Hydroformylation







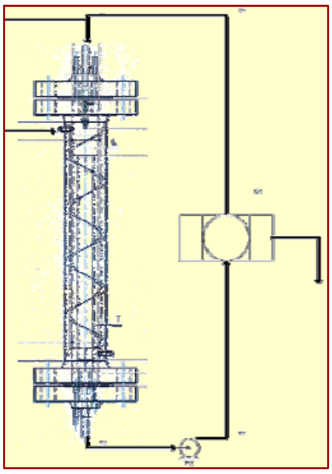
2.8 M **cyclooctene**, 0.71 M cyclooctane, **6.14**x10^{-5} M Rh and 1.84 x10^{-3} M Ligand and 50 (vol) % toluene as solvent, under 20 bar syngas pressure (CO/H_2=1) , 70 °C

In-house built membrane reactor

Hydroformylation in Jet-Loop Reactor

- **Design and construction of jet-loop reactor with integrated membrane separation**
- **Jet-loop reactors: circulation and fluid dispersion achieved by liquid jet drive**
  - ✓ **high mass transfer performance**
  - ✓ **better dispersing effects**
  - ✓ **relatively low power input**

➡ **Thorough kinetic investigation by experimental design approach**



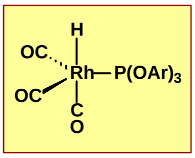
Hydroformylation in Jet-Loop Reactor

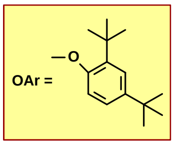
Model Systems

Catalyst: Rh/P(OAr)$_3$; [Rh] = 40ppm ; toluene as solvent

- very bulky, monodentate phosphite
- strong π-acceptor ligand

- very active catalyst (TOF up to 10^5 h^{-1})
- only one ligand coordinated
- excess of L needed (L/Rh = 30)

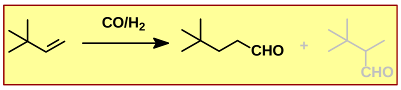




Model substrates:

- 3,3-dimethyl-1-butene (neohexene)
- no isomerization possible

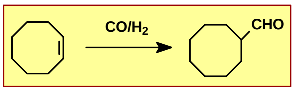
T = 80°C, p = 40 bar



typical l/b ~ 15 (92% linear)

- cyclooctene
- only branched
- isomerization not observable

T = 120°C, p = 40 bar



S. Güven, B. Hamers, R. Franke, M. Priske, M. Becker, D. Vogt, *Catal. Sci. Technol.* **2014**, *4*, 524.
S. Güven, M. M. L. Nieuwenhuizen, B. Hamers, R. Franke, M. Priske, M. Becker, D. Vogt, *ChemCatChem* **2014**, DOI: 10.1002/cctc.201300818

Hydroformylation in Jet-Loop Reactor

Hydroformylation Kinetics

$$HRhP(CO)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRhP(CO)_2 + CO \quad (1)$$

$$HRhP(CO)_2 + \text{olefin} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HRhP(CO)_2(\text{olefin}) \quad (2)$$

$$HRhP(CO)_2(\text{olefin}) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RRhP(CO)_2 \quad (3)$$

$$RRhP(CO)_2 + CO \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} RRhP(CO)_3 \quad (4)$$

$$RRhP(CO)_3 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} RC(O)RhP(CO)_2 \quad (5)$$

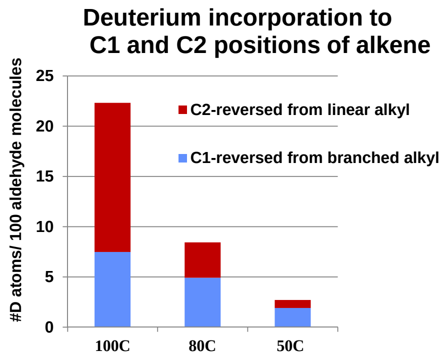
$$RC(O)RhP(CO)_2 + CO \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} RC(O)RhP(CO)_3 \quad (6)$$

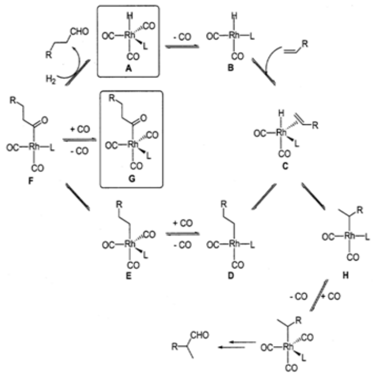
$$RC(O)RhP(CO)_2 + H_2 \xrightarrow{k_7} HRhP(CO)_2 + RC(O)H \quad (7)$$

- rate law for Rh/bulky P(OAr)$_3$ from literature*: $r = \dfrac{Kk[Rh][alkene]}{[CO] + K}$

*)A. van Rooy, E. N. Orij, P.C. J. Kamer and P. van Leeuwen, *Organometallics*, **1995**, *14*, 34.
S. Güven, B. Hamers, R. Franke, M. Priske, M. Becker, D. Vogt, *Catal. Sci. Technol.* **2014**, *4*, 524.

^{2}H-NMR to Study Reversibility





Unexpected result:

- with increasing T, the linear Rh-alkyl becomes much more reversible than the branched one !

S. Güven, B. Hamers, R. Franke, M. Priske, M. Becker, D. Vogt, *Catal. Sci. Technol.* **2014**, *4*, 524.

Jet-loop Reactor

- **Model studies in glass-walled reactor using reaction mixture**

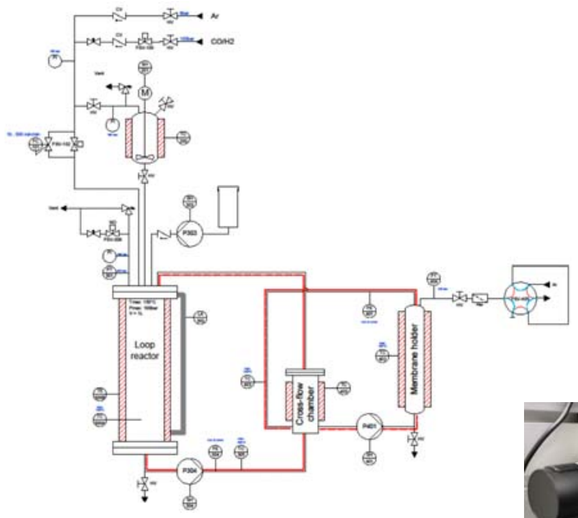
water

toluene

toluene+aldehyde

reaction mixture

Jet-Loop Reactor Set-Up



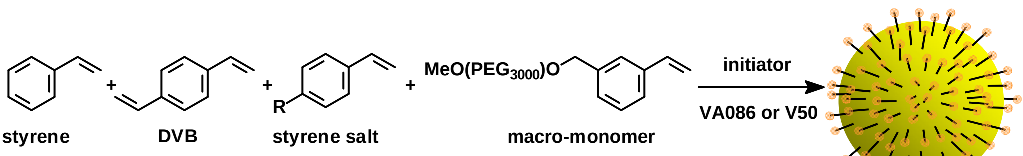
Industrial Homogeneous Catalysis

Evonik Oxeno pilot plant

Outline

- Introduction
- MWE Catalysts and Membrane Filtration
- POSS-Enlarged Catalysts; Continuous Hydroformylation
- **Latex-Enhanced Aqueous Phase Catalysis**

Latices as Phase-Transfer Agents

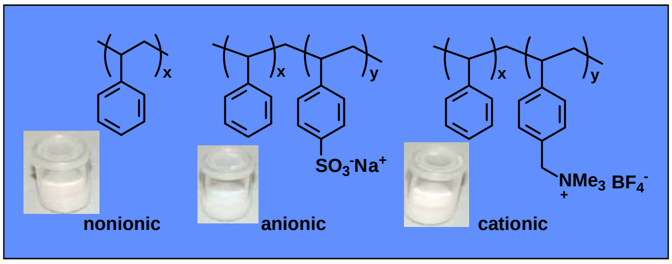


R= H ; $SO_3^{\ominus}Na^{\oplus}$; $CH_2N(Me)_3^{\oplus}BF_4^{\ominus}$; $BPh_3^{\ominus}Na^{\oplus}$

Typical latex composition

styrene	73%
styrene salt	20%
DVB	4%
PEG_{3000}	2%
initiator V50	1%

V50 = 2,2'-Azobis(2-methyl-propionamide) dihydrochloride



K. Kunna, C. Müller, J. Loos, D. Vogt, *Angew. Chem. Int. Ed.* **2006**, 45, 7289-7292.

Latices as Phase-Transfer Agents

Organic Phase
1-octene

before

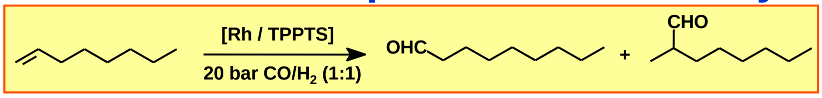
Aqueous Phase
Latex, $Rh(acac)(CO)_2/(TPPTS)$

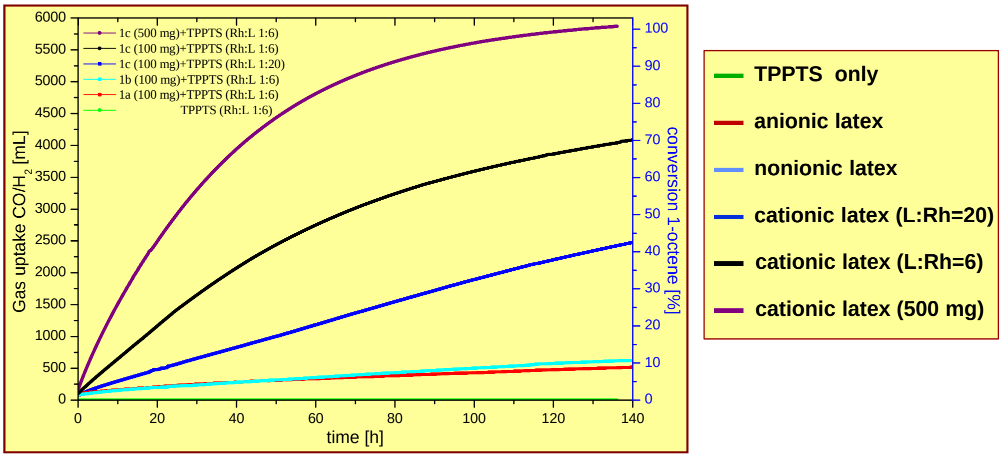
hydroformylation

analysis

after

Latex Enhanced Aqueous Phase Catalysis

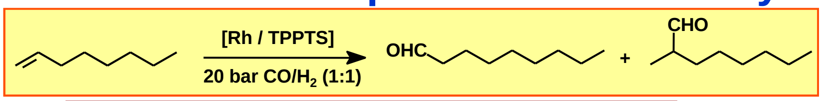


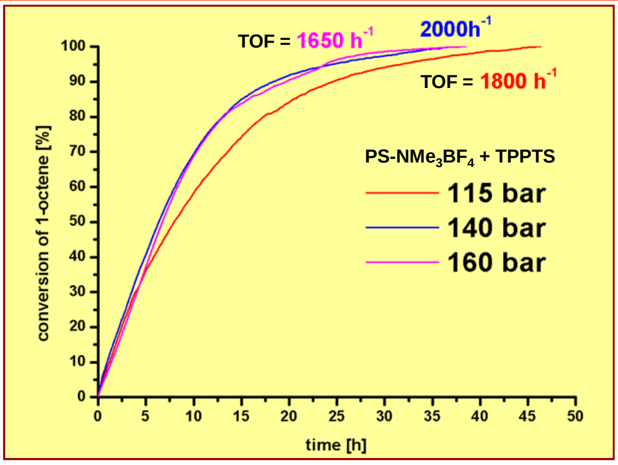


1-octene (150 mmol); ligand (0.21 mmol); $[Rh(acac)(CO)_2]$ (0.035 mmol); latex: 100 mg solid content;
S:P:Rh 5000:6:1; water phase : org. phase 1:2.3; CO/H_2 1:1; p = 20 bar; T = 80° C; stirring: 600 rpm.

K. Kunna, C. Müller, J. Loos, D. Vogt, *Angew. Chem. Int. Ed.* **2006**, 45, 7289-7292.

Latex Enhanced Aqueous Phase Catalysis

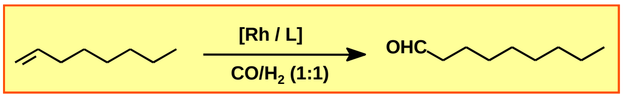


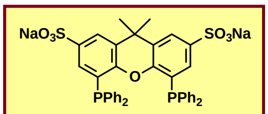


1-octene (150 mmol); ligand (0.21 mmol); $[Rh(acac)(CO)_2]$ (0.035 mmol); latex: 500 mg solid content;
S:P:Rh 5000:6:1; water phase : org. phase 1:2.3; CO/H_2 1:1; T = 80° C; stirring: 600 rpm.

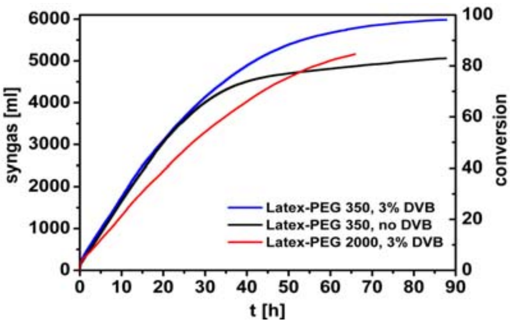
K. Kunna, *unpublished results*

Latex Enhanced Aqueous Phase Catalysis





Sulfoxantphos



- $X_{1\text{-octene}}$ = 99%, l/b=28, TOF: 109 h^{-1}
- $X_{1\text{-octene}}$ = 99%, l/b=9
- $X_{1\text{-octene}}$ = 84%, l/b=45

1-octene (150 mmol), $[Rh(acac)(CO)_2]$, SulfoXantphos
S:L:Rh 3500:2:1, 1.8 wt.% latex, T= 110 ºC, p=40 bar, rpm= 600

H. Nowothnick, A. Rost, T. Hamerla, R. Schomäcker, C. Müller, D. Vogt, *Catal. Sci. Technol.* **2013**, *3*, 600.

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