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MASS TRANSFER ASSESSMENT AND KINETIC INVESTIGATION OF BIPHASIC CATALYTIC SYSTEMS

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Context

Homogeneous catalysis:

☺ high efficiency and selectivity towards desired product

☹ separation of the catalyst

Biphasic catalysis: confinement of the molecular catalyst in a solvent immiscible with the products (ex: water)

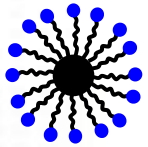
Industrial process: Ruhrchemie/Rhône Poulenc oxo process for the hydroformylation of propene into n-butanal, using **aqueous phase** and **hydrosoluble ligand** (TPPTS) – 800 000 tons aldehyde/year [Obrecht et al., 2013], Rh loss < 1 ppb

Pb: not applicable to higher olefins (> C4)!

Strategies for biphasic catalysis:

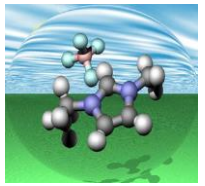
Water with additives

* *co-solvent in water*
* *ligand modification* → interfacial catalysis
* *phase transfer agents*
* *thermomorphic systems*
* *surfactants or amphiphilic polymers* → micellar(-like) catalysis



New solvents

* *fluorous solvents*
* *ionic liquids*
* *scCO$_2$*



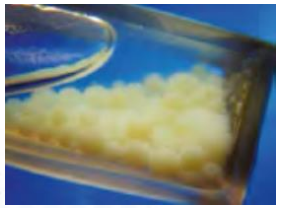
Main limitations: mass transfer, low reaction rate, and/or metal leaching

Objectives & strategy

OBJECTIVES: to reach a kinetic formulation including phase equilibria, to characterize interfacial mass transfer effects

HOW: Thermodynamic study

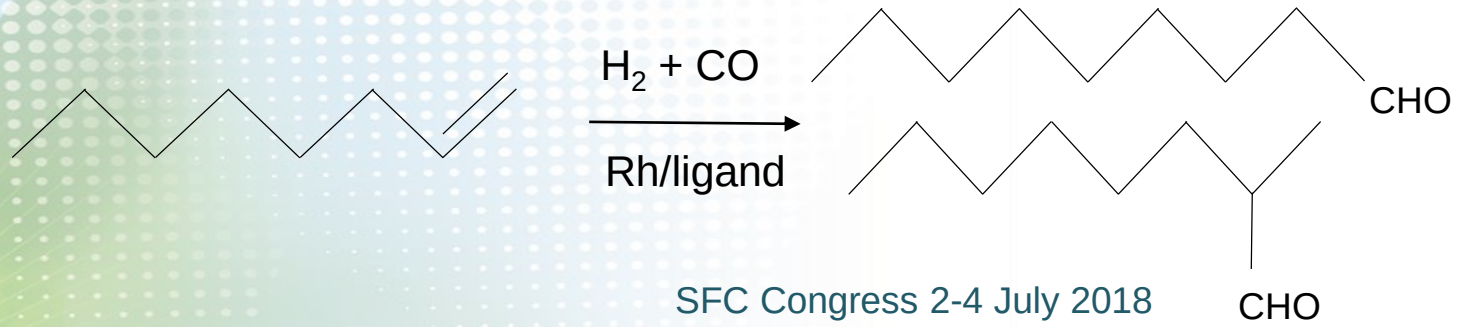
Concentration of the substrates
in the vicinity of the catalyst?
Effect of products / µenvironment?



Mass transfer & kinetic study

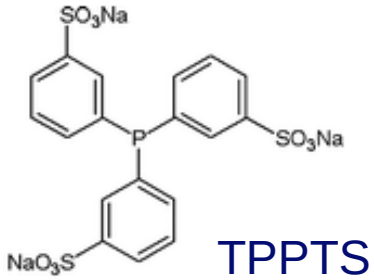
Relevant intrinsic rate laws (derived from reaction mechanism)?
Mass transfer performance?
Coupling of reaction & transfer ?

APPLICATION: Rh-catalyzed hydroformylation of oct-1-ene



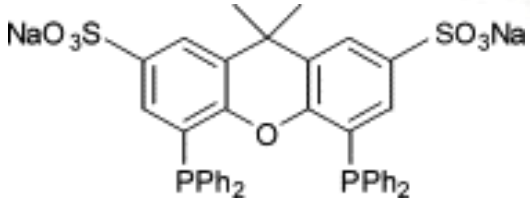
Ex.1: Ionic liquid biphasic catalysis

[Bmim][PF_6]/decane system



TPPTS

[BuPy][BF_4]/heptane system



sulfoxantphos

PREVIOUS STUDIES (hydroformylation, ≤ 2004):

- **High activity & selectivity**: TOF > 1000 h^{-1} (100ºC), l/b ratio > 40, rather low metal (Rh) loss (<0.1 %) [Chauvin et al. (1996), Bronger et al. (2004)]
- **Most of the studies dedicated to screening of ILs & ligands**

QUESTIONS:

- Thermodynamic *vs.* chemical effects?
- Relevant kinetic model?
- Viscosity effects on gas-liquid mass transfer?
- Coupling of reaction & transfer?

Thermodynamic study

Gas solubility in IL

Large discrepancies in the literature (by up to a factor 3)

- Dynamic gas absorption measurements in the reactor (ΔP_{reac})

Solvent	T (°C)	He, bar.m^3.kmol^{-1}	
		H_2	CO
[Bmim][PF_6]	20	898	449
	50	816	558
	100	869	663
[BuPy][BF_4]	60	470	419
	80	507	455
	100	724	487

Solubility of H_2 and CO in [Bmim][PF_6]:
data within the range of reported values (<20% dev. with Monte Carlo calculations [Urukova et al. (2005)])
($\Delta H_{solv,H2}$ = [-0.6, 3] kJ.mol^{-1}; $\Delta H_{solv,CO}$ = -3.8 kJ.mol^{-1})
~3 times lower than in decane, but ~2 times higher than in water

Similar, but slightly higher gas solubility in [BuPy][BF_4]

[Sharma et al. (2009)]

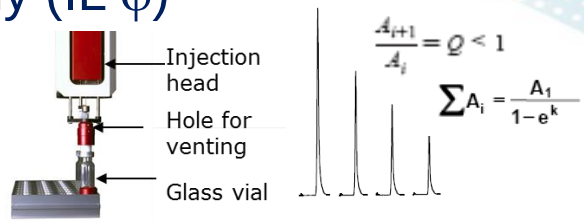
Thermodynamic study

Solubility & partition coef. of olefin (& aldehyde) in IL

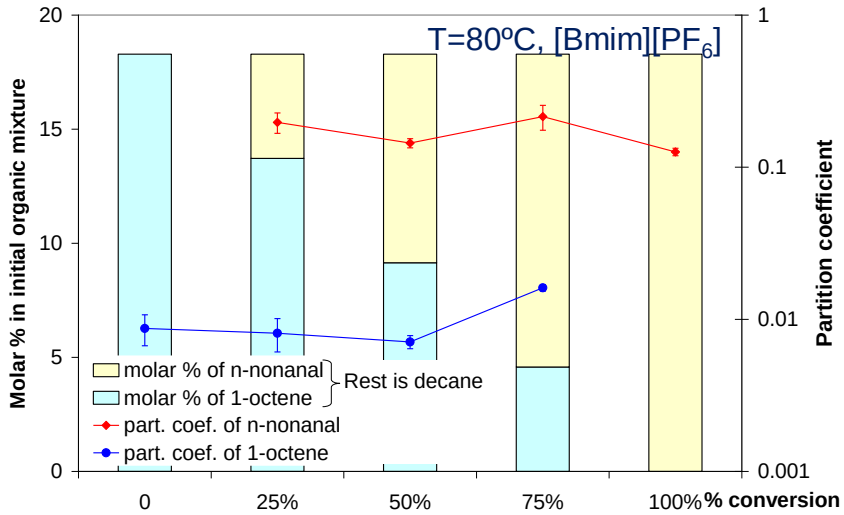
Very few values available

Routine chromatography or spectroscopy methods not suitable

- L-L equilibria measured at **reaction T**
- with the help of **Multiple HeadSpace** Gas Chromatography (IL φ)
- validation of solubility data by **thermogravimetry** (IL φ)



System	T (°C)	TGA	MHS-GC/MS
oct-1-ene			
/[Bmim][PF_6]	25	0.6% ± 0.05%	0.64%
	80	0.85 ± 0.2	0.86 ± 0.15
/[BuPy][BF_4]	80	0.36%	
n-nonanal			
/[Bmim][PF_6]	25	11.6% ± 0.5%	15.5% ± 0.2%
	80	11.3 ± 0.3	12.9 ± 0.3%
/[BuPy][BF_4]	80	4.2%	



Partition coef. almost unchanged

Solubility of octene in [Bmim][PF_6] (g / g):
*× **2000 with respect to water** (25°C)*
Much higher solubility of n-nonanal
Lower values in [BuPy][BF_4]

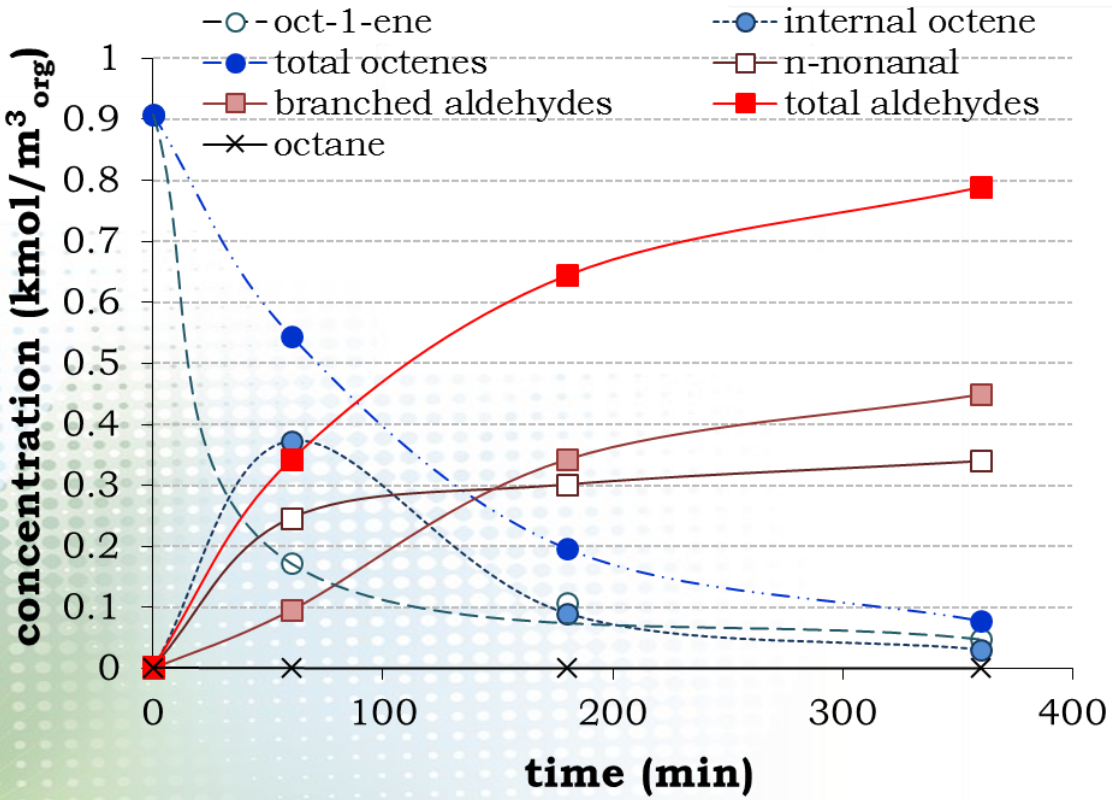
[Sharma et al. (2009)]

Kinetic study

Experimental study

- instantaneous syngas consumption from $P_{ballast}$ (R_0)
- speciation in organic φ by GC/FID (M balance, l/b ratio)

Typical time-concentration profile in solution ([Bmim][PF_6]/decane with TPPTS)



High isomerization of oct-1-ene
→ l/b ratio between 0.7 and 3
TOF: 15-75 h^{-1} after 1h (60-80ºC)

Kinetic study

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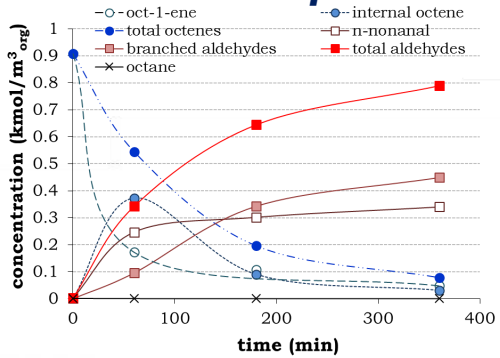
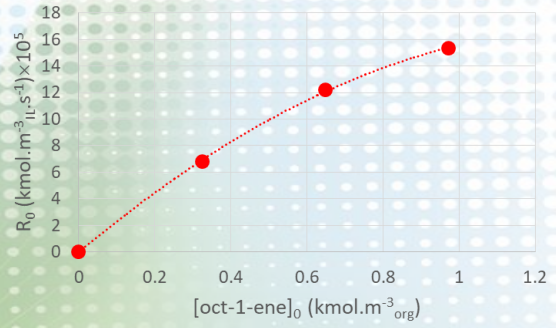


High isomerization of oct-1-ene
→ l/b ratio between 0.7 and 3
TOF: 15-75 h^{-1} after 1h (60-80ºC)

Parametric study

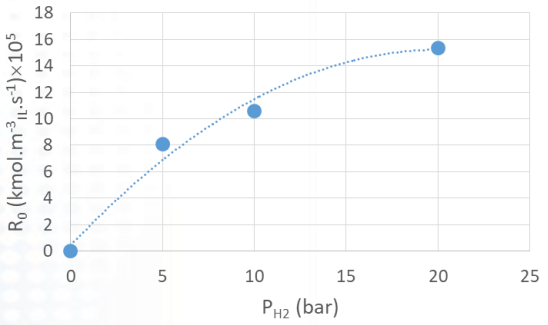
- Stirring speed & catalyst conc. (at given P/Rh) → to check for **chemical regime**

Initial conc. of oct-1-ene

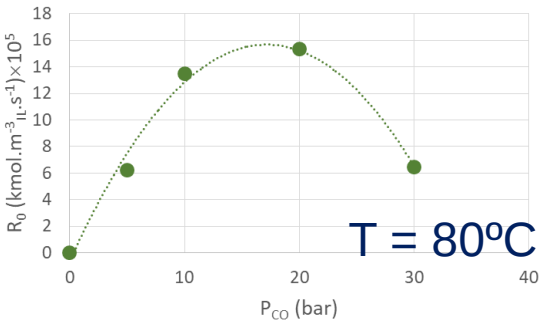


E_a = 25.8 kcal.mol^{-1}

Partial pressure of H_2



Partial pressure of CO

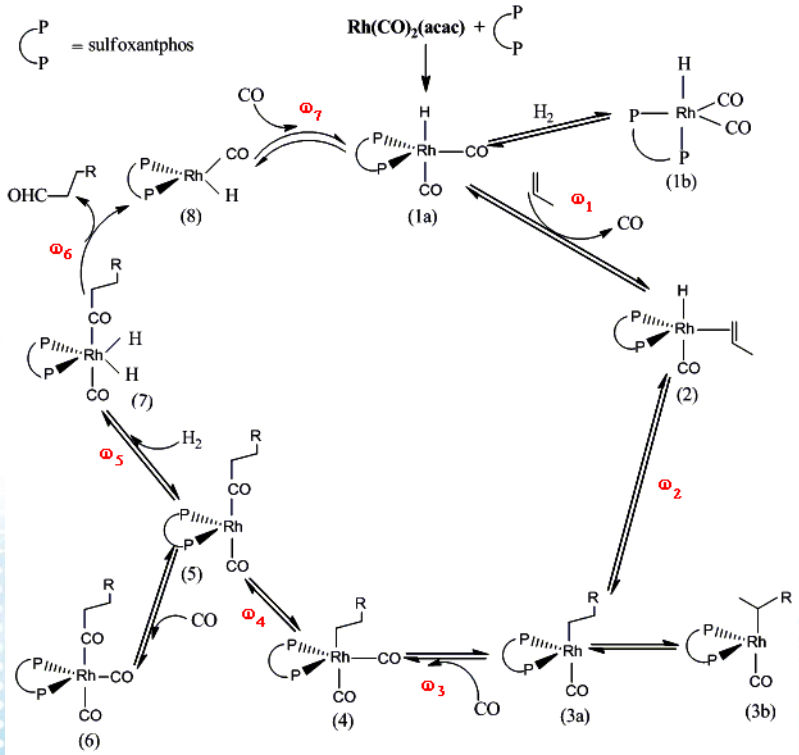


ω = 1200 rpm, V_{IL}/V_{org}:40/60

Kinetic study

Kinetic modeling

- Empirical rate models or **derived from elementary reaction steps**



[BuPy][BF_4]/heptane with sulfoxantphos

« Christiansen matrix » approach

[Helfferich, 2004; Murzin and Salmi, 2005]

$$\begin{pmatrix}
\omega_1\omega_2\omega_3\omega_4\omega_5\omega_6\omega_7 & \omega_{-1}\omega_3\omega_4\omega_5\omega_6\omega_7 & \omega_{-1}\omega_{-2}\omega_4\omega_5\omega_6\omega_7 & \omega_{-1}\omega_{-2}\omega_{-3}\omega_5\omega_6\omega_7 & \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-4}\omega_6\omega_7 & \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-4}\omega_{-5}\omega_7 & \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-4}\omega_{-5}\omega_{-6} \\
\omega_1\omega_3\omega_4\omega_5\omega_6\omega_7 & \omega_1\omega_{-2}\omega_4\omega_5\omega_6\omega_7 & \omega_1\omega_{-2}\omega_{-3}\omega_5\omega_6\omega_7 & \omega_1\omega_{-2}\omega_{-3}\omega_{-4}\omega_6\omega_7 & \omega_1\omega_{-2}\omega_{-3}\omega_{-4}\omega_{-5}\omega_7 & \omega_1\omega_{-2}\omega_{-3}\omega_{-4}\omega_{-5}\omega_{-6} & \omega_{-2}\omega_{-3}\omega_{-4}\omega_{-5}\omega_{-6}\omega_{-7} \\
\omega_1\omega_2\omega_4\omega_5\omega_6\omega_7 & \omega_1\omega_2\omega_{-3}\omega_5\omega_6\omega_7 & \omega_1\omega_2\omega_{-3}\omega_{-4}\omega_6\omega_7 & \omega_1\omega_2\omega_{-3}\omega_{-4}\omega_{-5}\omega_7 & \omega_1\omega_2\omega_{-3}\omega_{-4}\omega_{-5}\omega_{-6} & \omega_2\omega_{-3}\omega_{-4}\omega_{-5}\omega_{-6}\omega_{-7} & \omega_{-1}\omega_{-3}\omega_{-4}\omega_{-5}\omega_{-6}\omega_{-7} \\
\omega_1\omega_2\omega_3\omega_5\omega_6\omega_7 & \omega_1\omega_2\omega_3\omega_{-4}\omega_6\omega_7 & \omega_1\omega_2\omega_3\omega_{-4}\omega_{-5}\omega_7 & \omega_1\omega_2\omega_3\omega_{-4}\omega_{-5}\omega_{-6} & \omega_2\omega_3\omega_{-4}\omega_{-5}\omega_{-6}\omega_{-7} & \omega_{-1}\omega_3\omega_{-4}\omega_{-5}\omega_{-6}\omega_{-7} & \omega_{-1}\omega_{-2}\omega_{-4}\omega_{-5}\omega_{-6}\omega_{-7} \\
\omega_1\omega_2\omega_3\omega_4\omega_6\omega_7 & \omega_1\omega_2\omega_3\omega_4\omega_{-5}\omega_7 & \omega_1\omega_2\omega_3\omega_4\omega_{-5}\omega_{-6} & \omega_2\omega_3\omega_4\omega_{-5}\omega_{-6}\omega_{-7} & \omega_{-1}\omega_3\omega_4\omega_{-5}\omega_{-6}\omega_{-7} & \omega_{-1}\omega_{-2}\omega_4\omega_{-5}\omega_{-6}\omega_{-7} & \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-5}\omega_{-6}\omega_{-7} \\
\omega_1\omega_2\omega_3\omega_4\omega_5\omega_7 & \omega_1\omega_2\omega_3\omega_4\omega_5\omega_{-6}\omega_{-7} & \omega_2\omega_3\omega_4\omega_5\omega_{-6}\omega_{-7} & \omega_{-1}\omega_3\omega_4\omega_5\omega_{-6}\omega_{-7} & \omega_{-1}\omega_{-2}\omega_4\omega_5\omega_{-6}\omega_{-7} & \omega_{-1}\omega_{-2}\omega_{-3}\omega_5\omega_{-6}\omega_{-7} & \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-4}\omega_{-6}\omega_{-7} \\
\omega_1\omega_2\omega_3\omega_4\omega_5\omega_6 & \omega_2\omega_3\omega_4\omega_5\omega_6\omega_{-7} & \omega_{-1}\omega_3\omega_4\omega_5\omega_6\omega_{-7} & \omega_{-1}\omega_{-2}\omega_4\omega_5\omega_6\omega_{-7} & \omega_{-1}\omega_{-2}\omega_{-3}\omega_5\omega_6\omega_{-7} & \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-4}\omega_6\omega_{-7} & \omega_{-1}\omega_{-2}\omega_{-3}\omega_{-4}\omega_{-5}\omega_{-7}
\end{pmatrix}$$

$$R = \frac{\omega_1\omega_2\omega_3\omega_4\omega_5\omega_6\omega_7}{D_{Christiansen} + T_{inhibition}} C_{cat,IL}$$

Hypotheses on irreversibility of elementary steps & rate-determining steps

$$R = f([H_2]_{IL\,\varphi}, [CO]_{IL\,\varphi}, [cat]_{IL\,\varphi}, [octene]_{IL\,\varphi}, T)$$

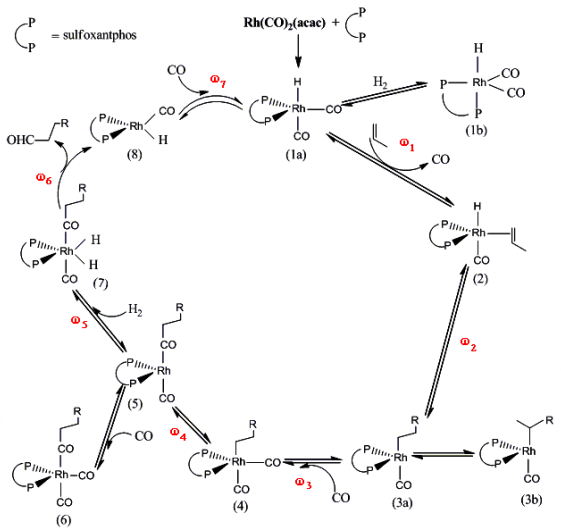
Selection of best model(s) & optimization of rate parameters based on initial rates (after sensitivity study)

Ex: $$R = \frac{kABCD}{(1 + K_aAB + K_bAD + K_cBD + K_dABD + K_eDB^2 + K_fA + K_gAB^2 + K_hB + K_iD)}$$

no limiting step, only the release of aldehyde product is an irreversible step

Kinetic study

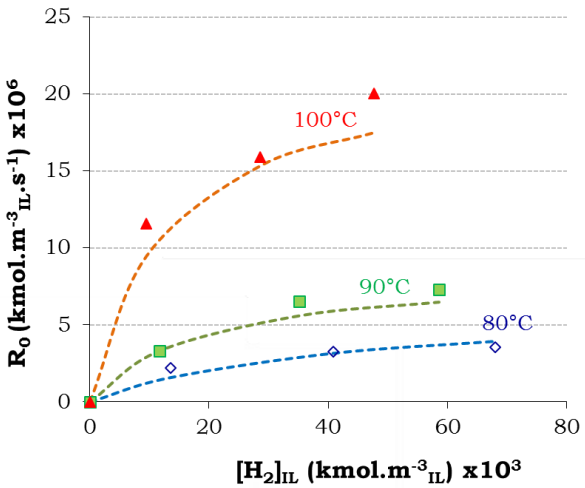
Kinetic modeling

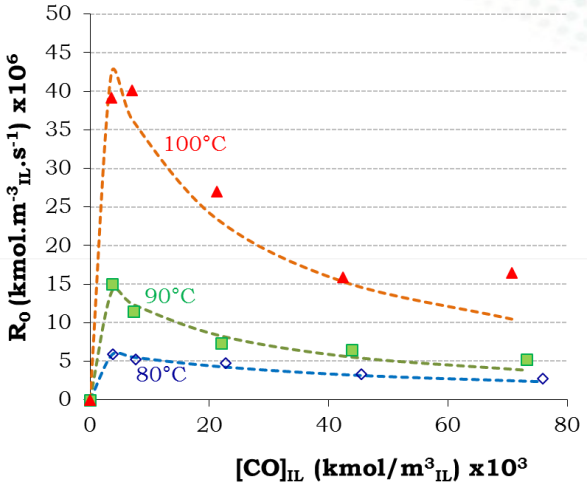


[BuPy][BF_4]/heptane with sulfoxantphos

Initial reaction rates

[Deshpande et al. (2011)]





Time-concentration profiles

[Sharma et al. (2010)]

Accounting for isomerization

$$\text{oct-1-ene} \xrightarrow{R_1} \text{n-nonanal}$$

$$\text{oct-1-ene} \xrightarrow{R_2} \text{iso-octenes}$$

$$\text{iso-octenes} \xrightarrow{R_3} \text{branched aldehydes}$$

$$R_1 = \frac{k_1 C_{H2,IL} C_{CO,IL} C_{cat,IL} C_{1oct,IL}}{\left(1 + K_{d1} C_{1oct,IL} C_{CO,IL}^3\right)}$$

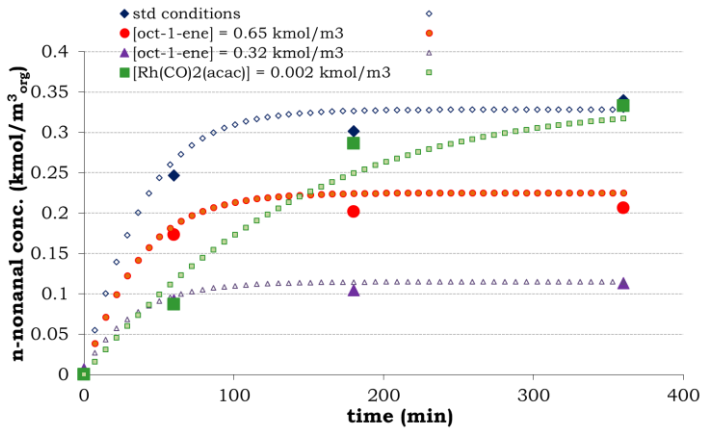
addition of H_2 as rate determining step

$$\left(V_{org} + V_{IL} K_{wnon} \frac{\rho_{IL}}{\rho_{org}}\right) \frac{dC_{nnon,org}}{dt} = R_1 V_{IL}$$

$$\left(V_{org} + V_{IL} K_{woct} \frac{\rho_{IL}}{\rho_{org}}\right) \frac{dC_{1oct,org}}{dt} = -(R_1 + R_2) V_{IL}$$

$$\left(V_{org} + V_{IL} K_{woct} \frac{\rho_{IL}}{\rho_{org}}\right) \frac{dC_{ioct,org}}{dt} = (R_2 - R_3) V_{IL}$$

$$\left(V_{org} + V_{IL} K_{wnon} \frac{\rho_{IL}}{\rho_{org}}\right) \frac{dC_{iald,org}}{dt} = R_3 V_{IL}$$

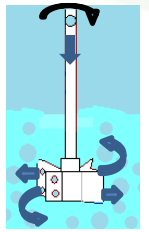


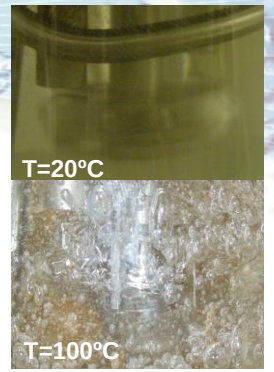
[Bmim][PF_6]/decane with TTPTS

G-L mass transfer effects

G-L mass transfer evaluation without reaction (k_La)

- Dynamic pressure step method: $P_{reac} = f(t)$





[Sharma et al. (2009)]

- ***In ionic liquids:***

  Correlation: $Sh_{GL} \propto Re_{st}^{\ b} \cdot (Fr_{st} - Fr_{st,cr})^{c} \cdot Sc_L^{\ 0,5}$

  or $Sh_{GL} \propto (Re_{st} - Re_{st,cr})^{b'} \cdot Fr_{st}^{\ c'} \cdot Sc_L^{\ 0,5}$

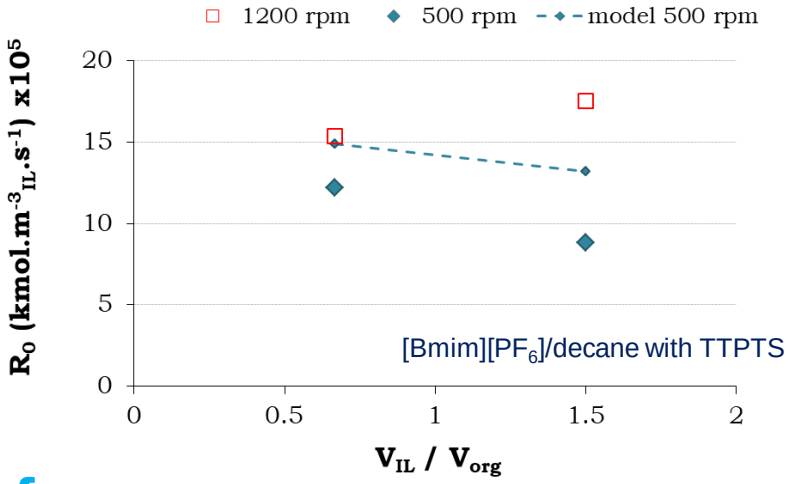
  (RSD +/- 20%)

- ***In emulsion:***

  k_La ↑ (by up to factor 10) when V_{IL}/V_{org} ↓, marked variation around phase inversion

$$\frac{dC_{H2,IL}}{dt} - (k_La)_{H2}\left(C^*_{H2,IL} - C_{H2,IL}\right) + \frac{kC_{H2,IL}C_{CO,IL}C_{cat,IL}C_{oct,IL}}{\left(1 + K_dC_{oct,IL}C^3_{CO,IL}\right)}\frac{\varepsilon_{IL}}{\left(\varepsilon_{IL} + (1-\varepsilon_{IL})m_{H2}\right)} = 0$$

$$\frac{dC_{CO,IL}}{dt} - (k_La)_{CO}\left(C^*_{CO,IL} - C_{CO,IL}\right) + \frac{kC_{H2,IL}C_{CO,IL}C_{cat,IL}C_{oct,IL}}{\left(1 + K_dC_{oct,IL}C^3_{CO,IL}\right)}\frac{\varepsilon_{IL}}{\left(\varepsilon_{IL} + (1-\varepsilon_{IL})m_{CO}\right)} = 0$$



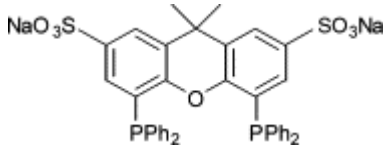
Coupling of reaction and G-L mass transfer

- *Chemical regime* (≥1200 rpm): R_0 ~ independent of V_{IL}/V_{org}
- *Mass transfer regime* (500 rpm): R_0 ↓ by 30% when V_{IL}/V_{org} ↑ from 0.7 à 1.5
  - → overestimation of R_0 by the coupling model
  - → supplementary resistance from L-L mass transfer?

Improvements of IL system

[Bmim][PF_6]/decane with TPPTS

More selective ligand



sulfoxantphos

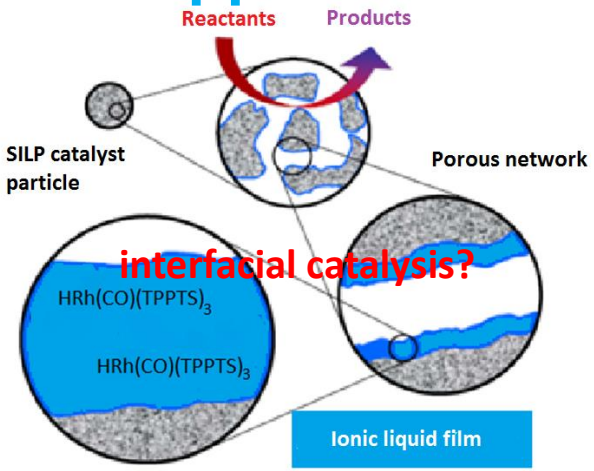
☺ **No isomerization**
☺ **Only n-nonanal detected as product**
☹ **But dramatic reduction of TOF** (by a factor 20)

Solvent	T (°C)	R_0, kmol.m^{-3}_{IL}.s^{-1}
[Bmim][PF_6]	80	$13 \cdot 10^{-6}$
	100	$46 \cdot 10^{-6}$
[BuPy][BF_4]	80	$12 \cdot 10^{-6}$
	100	$54 \cdot 10^{-6}$

Conditions: $[Rh(CO)_2(acac)] \sim 7.0 \cdot 10^{-3}$ kmol.m^{-3}_{IL}, SX:Rh = 5:1, $[oct\text{-}1\text{-}ene]_0 \sim 0.9$ kmol.m^{-3}_{org}, $p_{H2} = p_{CO}$ # 20 bar, IL:org = 40:60 v/v

➢ similar R_0 in both solvents (lower octene solubility in [BuPy][BF_4], partly offset by higher gas solubility)

Supported ionic liquid phase catalysis (SILPC)



➢ **Similar trend as biphasic catalysis**
…. but ☺ **lower amount of internal octenes** (with TPPTS)
no CO inhibition observed (?)

☺ **TOF increased by a factor 7** = up to 560 h^{-1} at 80ºC
(conc. ratio of ~ 70 for olefin in between org. & IL φ)

☺ **Stable activity under recycling** (Rh loss: 1-2 ppm)

[Sharma (2009)]

Ex.2: Biphasic catalysis with CCM

From micellar catalyst …

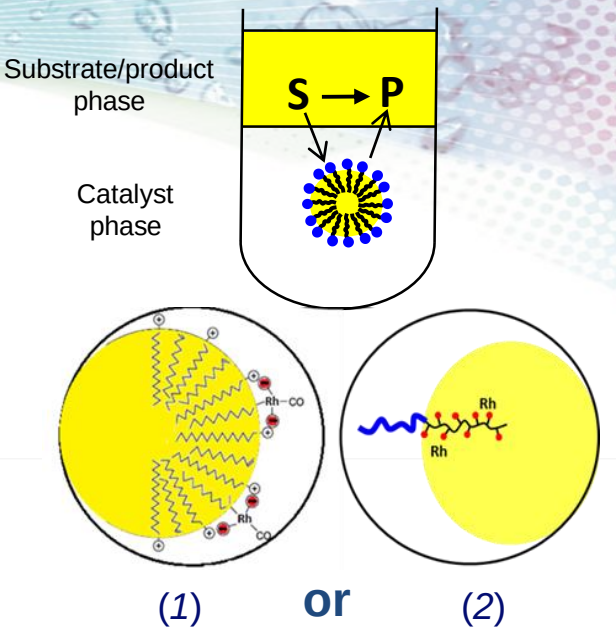
using *cationic surfactants* (*1*) or *amphiphilic ligands* (*2*)

☺ TOF up to 1000 h^{-1} (*1*, 100°C) or 2500 h^{-1} (*2*, 100°C)

☹ stable emulsions by excessive swelling of the micellar core

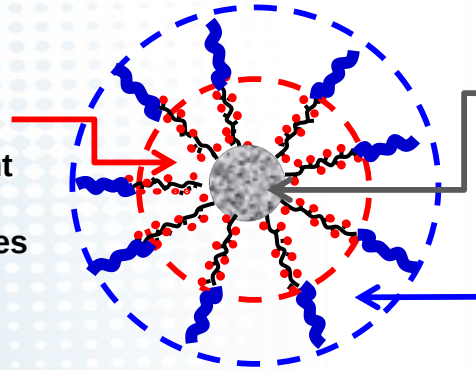
☹ Loss of catalytic objects at the interface

Loss of metal (Rh)



… to polymeric core-shell catalyst

by cross-linking the hydrophobic segments of self-assembled amphiphilic block copolymers synthesized by "controlled" radical polymerization



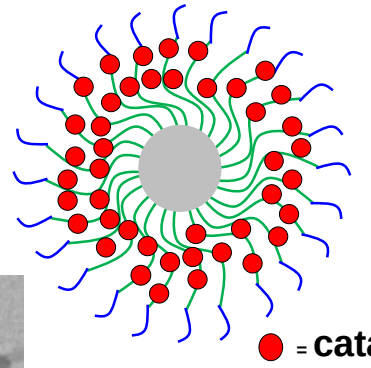
Hydrophobic functionalized layer
Favorable environment for the conversion of hydrophobic substrates
Immobilization of the catalyst

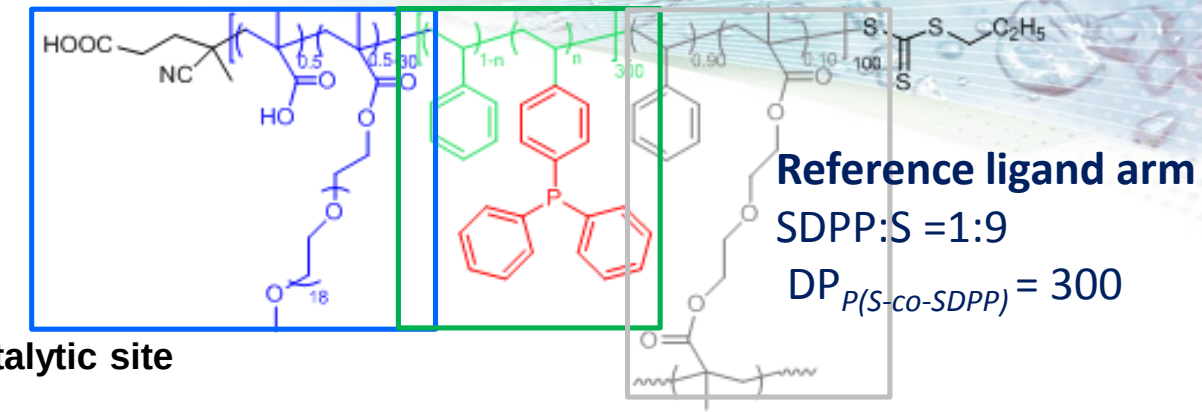
Cross-linked core
Limited swelling of the object
No free arms

Hydrophilic layer
Confinement in the aqueous phase

well-defined size and architecture

A closer look on CCM

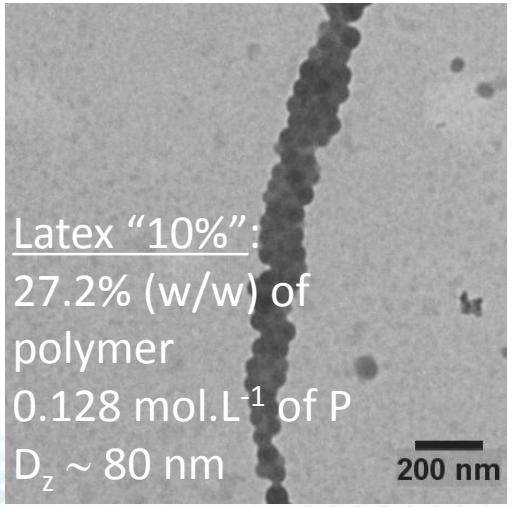




Reference ligand arm

SDPP:S =1:9

$DP_{P(S\text{-}co\text{-}SDPP)}$ = 300



- made by convergent synthesis in water (shell → core)
- reversible addition-fragmentation chain transfer (RAFT) as controlled polymerization method
- self-assembly of amphiphilic block copolymers
- addition of cross-linker together with additional styrene to form the core
- *in-situ* preparation of Rh-catalyst during heating period under a few bar of syngas (Rh precursor introduced after pre-swelling CCM with n-decanal (reaction solvent))

QUESTIONS:

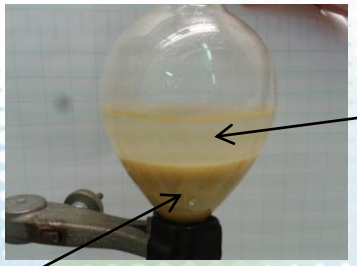
- Performance of CCM for aqueous biphasic catalysis?
- Driving mechanisms? Any limitation by mass transfer to/in the objects?
- How to optimize the objects?
- Content of the swelled CCM & phase separation dynamics?

Proof of concept (1/2)

Catalytic performance of CCM

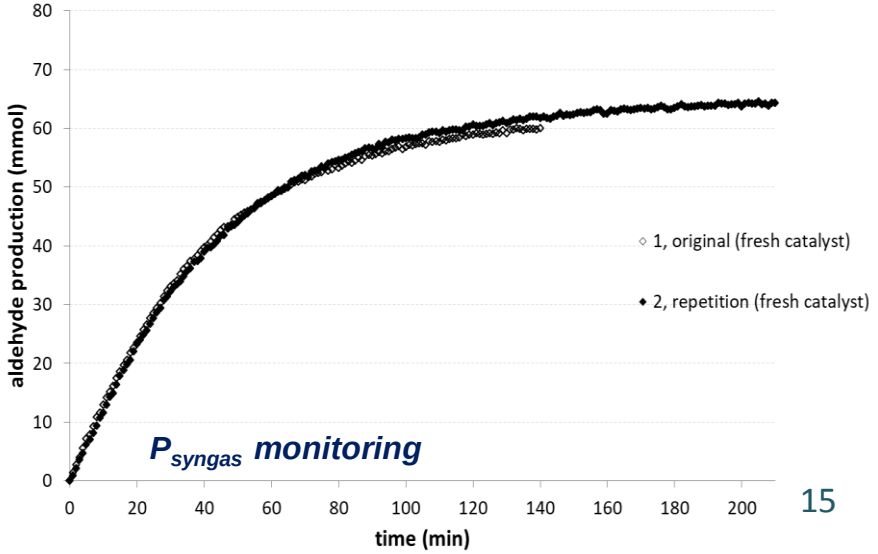
Std conditions: Ref. TTP@CCM, [Rh] = $6.5 \cdot 10^{-3}$ kmol·m$^{-3}_{aq}$, [oct-1-ene] = 1.1 kmol·m$^{-3}_{org}$ (solvent: n-decanal), P/Rh = 4, V_{org} = 75 mL, $V_{aq(ns)}$ = 25 mL, T = 363 K, P = 20 bar (CO/H_2 = 1), ω = 1200 rpm

- High catalytic activity (**TOF ~ 500 h^{-1}** *vs.* 1000 h^{-1} for homogeneous reaction with TPP functionalized star polymer), l/b ratio of ~ 5
- No hydrogenation and nearly no isomerization
- Low Rh leaching (~2 ppm measured by ICP/MS) and negligible activity of recovered organic phase
- **Excellent catalytic stability under recycling**, when kept under syngas or **without any caution**



Swelled TPP@CCM in aqueous phase

Organic phase (~90% aldehyde yield after 3 h)



[Zhang et al. (2014)]

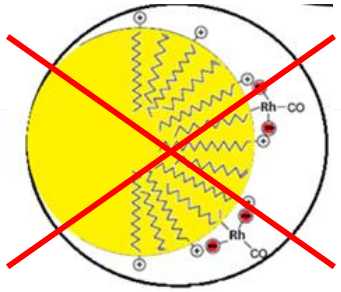
Proof of concept (2/2)

Driving mechanisms

➢ ~~**Interfacial catalysis?**~~

Addition of a stronger water-soluble ligand (sulfoXantphos, sX/Rh = 5)
→ inhibition of the reaction (TOF_{max} = 13 h^{-1})

No "surfactant effect"



Phosphine-free CCM
→ very similar results as the homogeneous reaction without any ligand:
aldehyde yield = 13% after 4 h (internal octenes = 35% of the substrate charge)

Rh coordination within the objects

➢ **Concept of « nano-reactors »**

Catalysis within the hydrophobic microenvironment gathering catalyst and substrate

[Zhang et al. (2014)]

Mass transfer effects

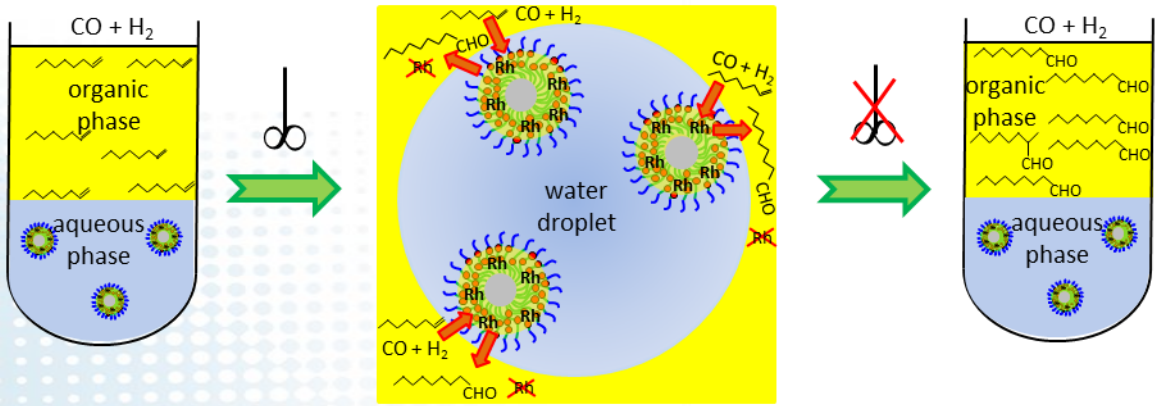
External mass transfer limitation?

- **Variation of ω** [1200-1600 rpm] → < 25% variation of R_0
- **Increase of [Rh]** by a **factor 4**
  - * at given P/Rh
  - * at given [TPP@CCM]

  → **threefold increase in R_0**
- Variation of [TPP@CCM] at given [Rh]

→ no significant effect of P/Rh [4-12] on TOF nor on regioselectivity

Weak external mass transfer resistance, probably at gas-emulsion interface



[Cardozo et al. (2015)]

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→ no significant effect of P/Rh [4-12] on TOF nor on regioselectivity

Weak external mass transfer resistance, probably at gas-emulsion interface

Internal mass transfer limitation?

- **Increase of SDPP:S**: from 1:19 to 1:3 → reduction of R_0 by a factor > 3

chemical effect for SDPP/S (Rh dimeric species?)

- **Increase of DP**: from 300 to 500 → R_0 & l/b ratio unchanged
- Variation of T [70-90°C] → E_A ~22 kcal.mol^{-1}

→ value close to those reported in chemical regime in homogeneous / biphasic system with TPP(TS)

Internal diffusion within the objects is not rate-limiting

[Cardozo et al. (2015)]

Optimization of CCM architecture

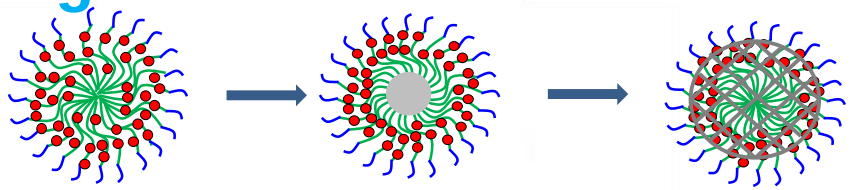
Length of hydrophobic segment /

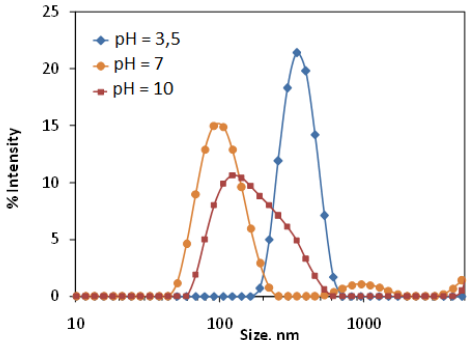
→ no significant effect of increasing DP on R_0 or regioselectivity, slight reduction of Rh loss

Functionalization degree (SDDP:S) -

→ Significant decrease of activity for higher SDPP:S, low effect on l/b ratio or metal leaching (CCM or nanogel)

Cross-linking extent +





DLS aq φ with CCM ↿

→ Accessibility to the catalytic complexes not significantly reduced by cross-linking (R_0 ↓ by 30%), but **dramatic reduction of Rh loss** from 7.2 to 0.6 ppm

→ Rh loss sensible to ω for CCM, but no effect for nanogel

Shell properties

→ stability ↑ when pH ↑ from 3.5 to 7 → effect of methacrylic acid moieties

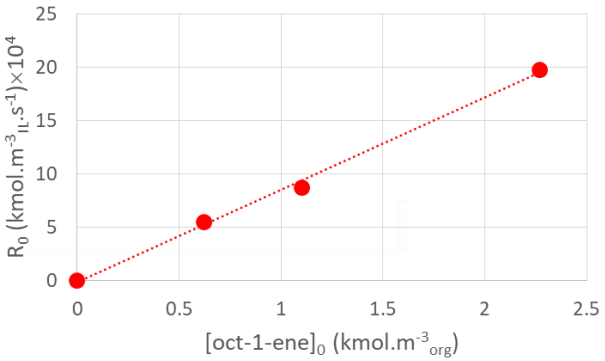
→ $[Rh]_{org}$ reduced to 0.1 ppm at 60ºC → effect of thermosensitive PEG

Towards a kinetic model

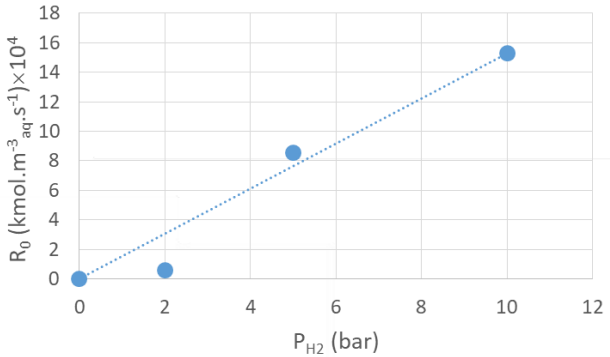
Selection of nanogel with 5% SDPP (pH=7)

Parametric study

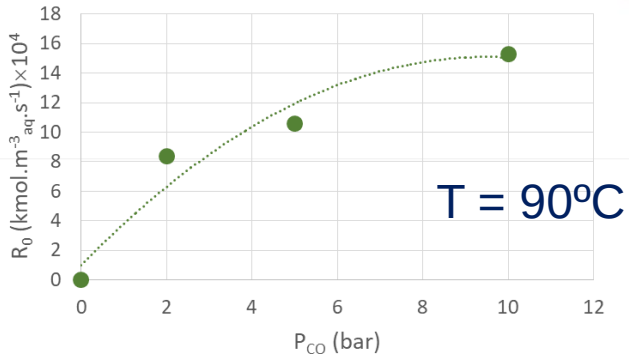
Initial conc. of oct-1-ene



Partial pressure of H_2



Partial pressure of CO

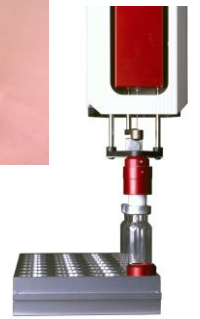


E_a = 20.2 kcal.mol^{-1}

Evaluation of the nanogel composition

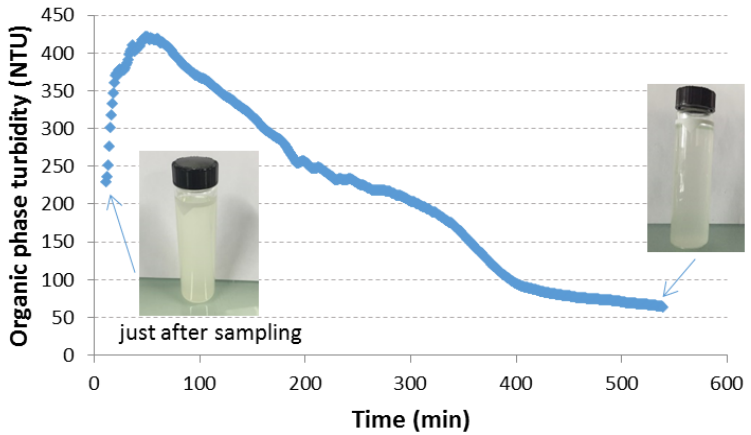
- Concentration of the latex by centrifugal ultrafiltration
- Extraction of the object content by MHS & GC-MS analysis

→ up to now only qualitative information (difficulty in standardizing the method)



Dynamics of φ separation

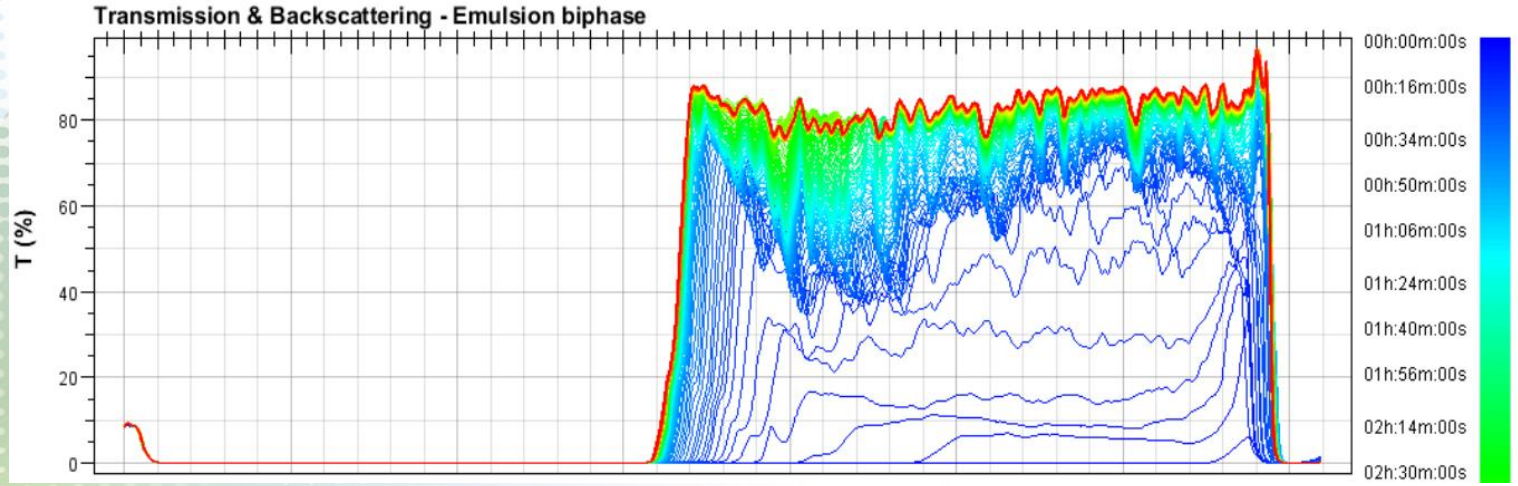
Turbidity evolution



Sampling (30 mL) close to the W/O interface, 10 min after stopping the stirring
→ **translucent organic phase**
Separation at ambient T
→ NTU obtained after 8h ~ value of samples analyzed by ICP / AES for Rh leaching

Stability evolution

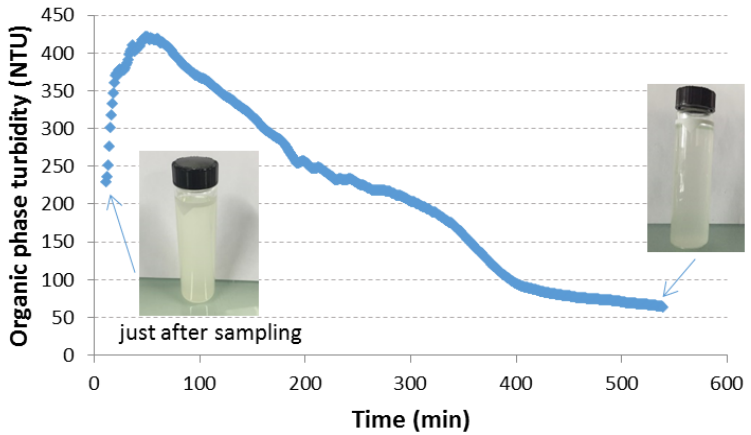
Sampling of the whole emulsion (20 mL) & **φ separation at 60°C** (Turbiscan)



[Lobry et al. (2016)]

Dynamics of φ separation

Turbidity evolution



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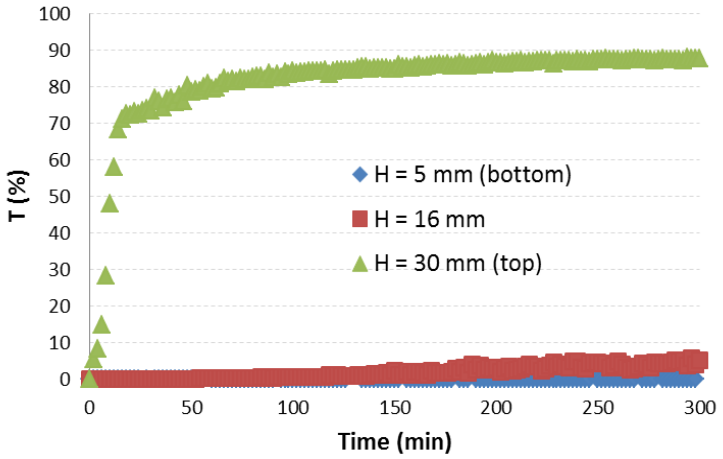

Sampling of the whole emulsion (20 mL) & **φ separation at 60ºC** (Turbiscan)

showing **2 successive steps**:
→ a rapid disengagement (formation of two distinct φ) in 20 minutes
→ a much slower φ evolution tending towards a plateau after 3 hours

T = 83% ↔ 0.02% of solid content
↔ [Rh] ~ 1 ppm (P/Rh = 4)

[Lobry et al. (2016)]

Conclusions & perspectives

- **High Turn Over Frequency** was obtained for the Rh-catalyzed hydroformylation of oct-1-ene in multiphase systems, using either ionic liquids or nanogel-based catalysts in water

- **Successful collaboration between chemistry and chemical engineering teams** allowed **understanding several features** of these complex systems, as well as providing **clues for their optimization**

- Kinetic, mass transfer & separation studies paved the **way for the design & scale-up of continuous process** with these systems, but still Rh leaching needs to be further reduced

- Further developments would be also required to better describe the **coupling between mass transfer & catalytic reaction**

Acknowledgements

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