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# MASS TRANSFER ASSESSMENT AND KINETIC INVESTIGATION OF BIPHASIC CATALYTIC SYSTEMS

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## 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)

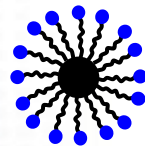
**Industrial process:** Ruhrchemie/Rhône Poulenc oxo process for the hydroformylation of propene into n-butanal, using **aqueous phase** and **hydrosoluble ligand** (TPPTS) – 800 000 tons aldehyde/year [Obrecht et al., 2013], Rh loss < 1 ppb

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

## Strategies for biphasic catalysis:

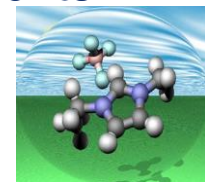
### Water with additives

- \* *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<sub>2</sub>*



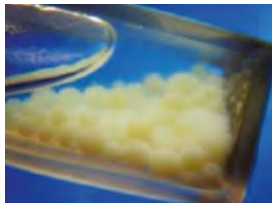
**Main limitations:** mass transfer, low reaction rate, and/or metal leaching

# 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 /  $\mu$ environment?

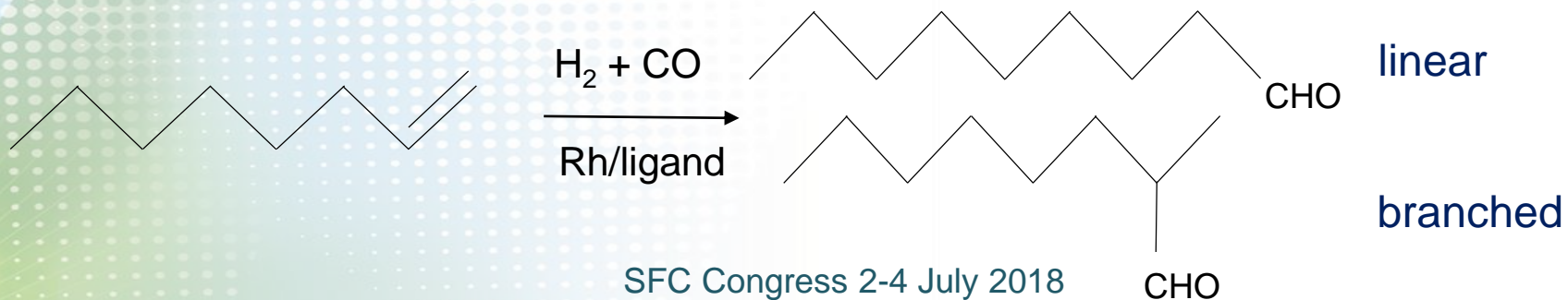


## Mass transfer & kinetic study

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

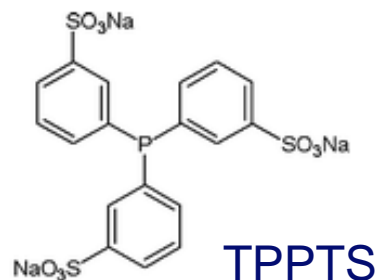


## APPLICATION: Rh-catalyzed hydroformylation of oct-1-ene

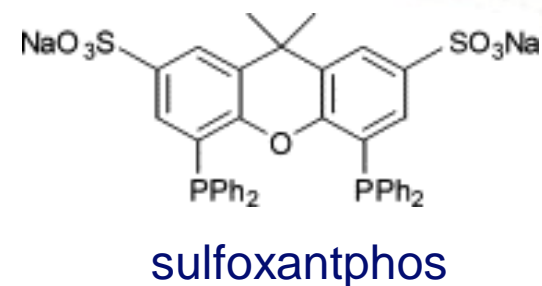


# Ex.1: Ionic liquid biphasic catalysis

[Bmim][PF<sub>6</sub>]/decane system



[BuPy][BF<sub>4</sub>]/heptane system



## PREVIOUS STUDIES (hydroformylation, ≤ 2004):

- **High activity & selectivity:** TOF > 1000 h<sup>-1</sup> (100°C), 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?

## Gas solubility in IL

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

- Dynamic gas absorption measurements in the reactor ( $\Delta P_{\text{reac}}$ )

Solvent	T (°C)	He, bar.m <sup>3</sup> .kmol <sup>-1</sup>	
		H <sub>2</sub>	CO
[Bmim][PF <sub>6</sub> ]	20	898	449
	50	816	558
	100	869	663
[BuPy][BF <sub>4</sub> ]	60	470	419
	80	507	455
	100	724	487

*Solubility of H<sub>2</sub> and CO in [Bmim][PF<sub>6</sub>]:*

*data within the range of reported values (<20% dev. with Monte Carlo calculations [Urukova et al. (2005)])*

*( $\Delta H_{\text{solv,H}_2} = [-0.6, 3] \text{ kJ.mol}^{-1}$ ;  $\Delta H_{\text{solv,CO}} = -3.8 \text{ kJ.mol}^{-1}$ )*

*~ 3 times lower than in decane, but ~ 2 times higher than in water*

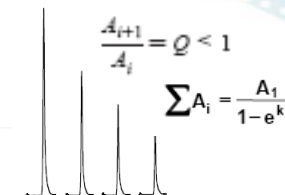
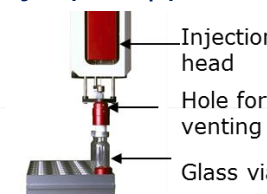
*Similar, but slightly higher gas solubility in [BuPy][BF<sub>4</sub>]*

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

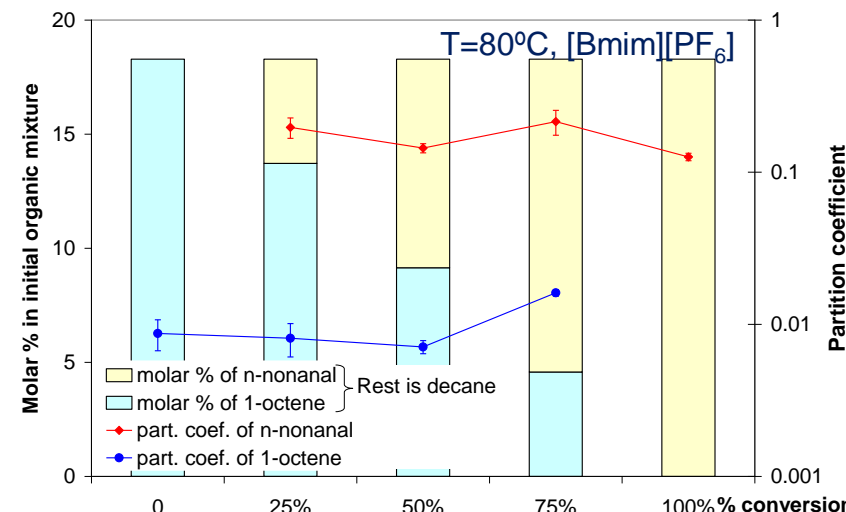
Very few values available

Routine chromatography or spectroscopy methods not suitable

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



System	T (°C)	TGA	MHS-GC/MS
oct-1-ene /[Bmim][PF <sub>6</sub> ]	25	0.6% ± 0.05%	0.64%
	80	0.85 ± 0.2	0.86 ± 0.15
/[BuPy][BF <sub>4</sub> ]	80	0.36%	
n-nonanal /[Bmim][PF <sub>6</sub> ]	25	11.6% ± 0.5%	15.5% ± 0.2%
	80	11.3 ± 0.3	12.9 ± 0.3%
/[BuPy][BF <sub>4</sub> ]	80	4.2%	



Partition coef. almost unchanged

Solubility of octene in [Bmim][PF<sub>6</sub>] (g / g):  
 × 2000 with respect to water (25°C)  
 Much higher solubility of n-nonanal  
 Lower values in [BuPy][BF<sub>4</sub>]

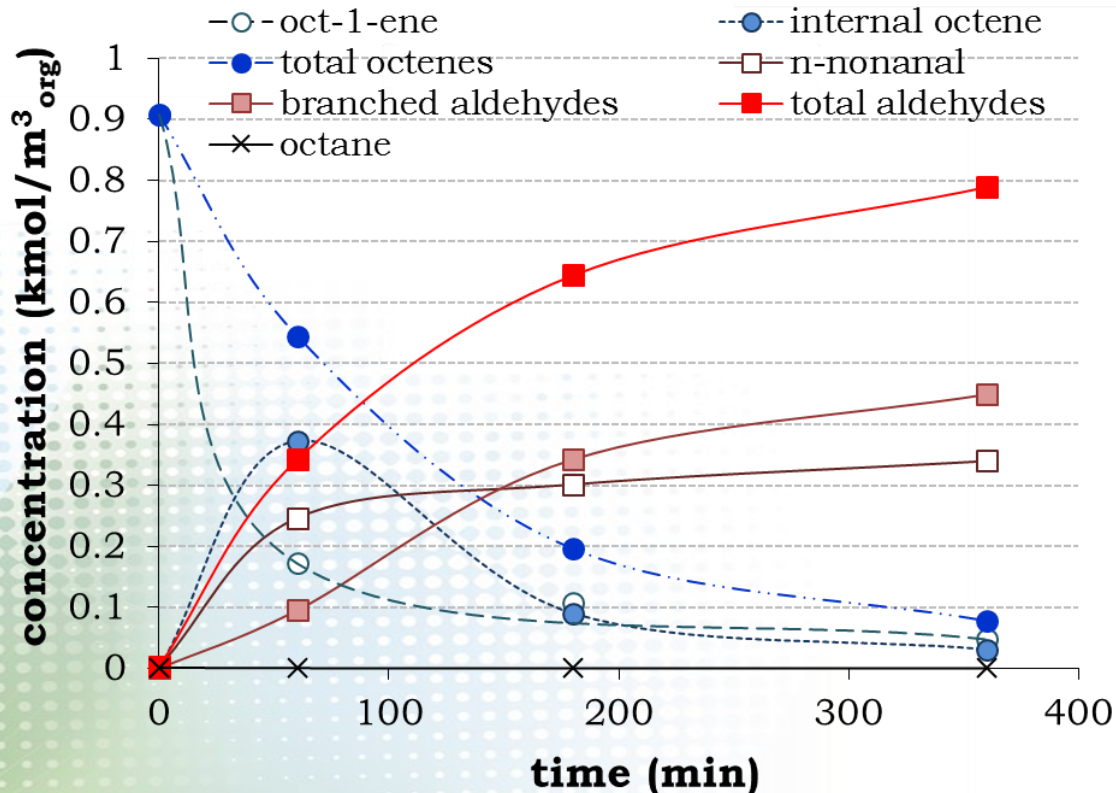


## Experimental study

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



### Typical time-concentration profile in solution ([Bmim][PF<sub>6</sub>]/decane with TPPTS)



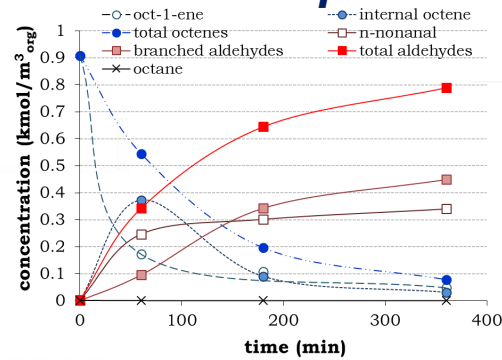
High isomerization of oct-1-ene  
 → l/b ratio between 0.7 and 3  
 TOF: 15-75 h<sup>-1</sup> after 1h (60-80°C)

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- instantaneous syngas consumption from  $P_{ballast}$  ( $R_0$ )
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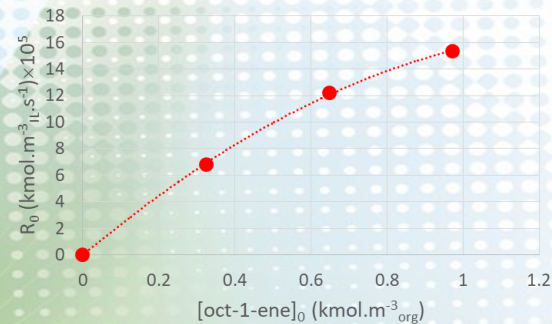


High isomerization of oct-1-ene  
 → l/b ratio between 0.7 and 3  
 TOF: 15-75 h<sup>-1</sup> after 1h (60-80°C)

## Parametric study

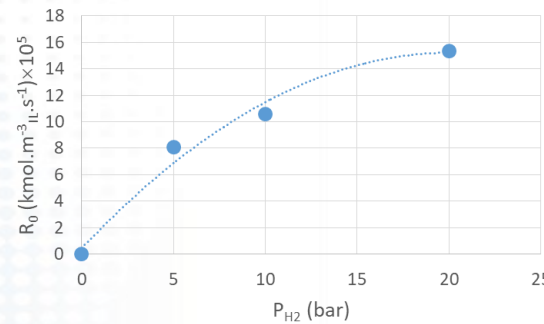
- Stirring speed & catalyst conc. (at given P/Rh) → to check for **chemical regime**

### Initial conc. of oct-1-ene

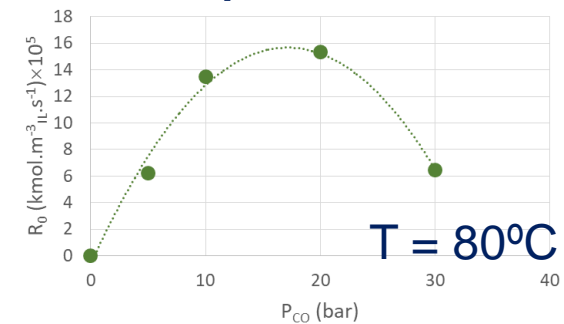


$E_a = 25.8 \text{ kcal.mol}^{-1}$

### Partial pressure of H<sub>2</sub>



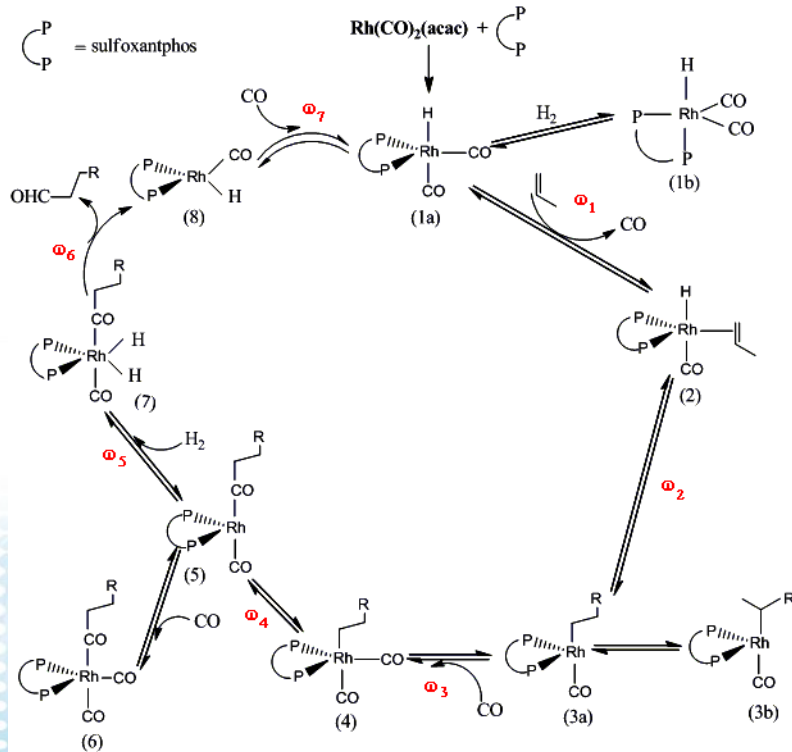
### Partial pressure of CO



$T = 80^\circ\text{C}$   
 $\omega = 1200 \text{ rpm}, V_{IL}/V_{org}: 40/60$

## Kinetic modeling

➤ Empirical rate models or derived from elementary reaction steps



[BuPy][BF<sub>4</sub>]/heptane with sulfoxantphos

« Christiansen matrix » approach

[Helferich, 2004; Murzin and Salmi, 2005]

$\omega_2 \omega_3 \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_3 \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_{-2} \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_{-2} \omega_{-3} \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_{-2} \omega_{-3} \omega_{-4} \omega_6 \omega_7$	$\omega_{-1} \omega_{-2} \omega_{-3} \omega_{-4} \omega_{-5} \omega_7$	$\omega_{-1} \omega_{-2} \omega_{-3} \omega_{-4} \omega_{-5} \omega_{-6}$
$\omega_1 \omega_3 \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_1 \omega_{-2} \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_1 \omega_{-2} \omega_{-3} \omega_5 \omega_6 \omega_7$	$\omega_1 \omega_{-2} \omega_{-3} \omega_{-4} \omega_6 \omega_7$	$\omega_1 \omega_{-2} \omega_{-3} \omega_{-4} \omega_{-5} \omega_7$	$\omega_1 \omega_{-2} \omega_{-3} \omega_{-4} \omega_{-5} \omega_{-6}$	$\omega_{-2} \omega_{-3} \omega_{-4} \omega_{-5} \omega_{-6} \omega_7$
$\omega_1 \omega_2 \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_1 \omega_2 \omega_{-3} \omega_5 \omega_6 \omega_7$	$\omega_1 \omega_2 \omega_{-3} \omega_{-4} \omega_6 \omega_7$	$\omega_1 \omega_2 \omega_{-3} \omega_{-4} \omega_{-5} \omega_7$	$\omega_1 \omega_2 \omega_{-3} \omega_{-4} \omega_{-5} \omega_{-6}$	$\omega_2 \omega_{-3} \omega_{-4} \omega_{-5} \omega_{-6} \omega_7$	$\omega_{-1} \omega_{-3} \omega_{-4} \omega_{-5} \omega_{-6} \omega_7$
$\omega_1 \omega_2 \omega_3 \omega_5 \omega_6 \omega_7$	$\omega_1 \omega_2 \omega_3 \omega_{-4} \omega_6 \omega_7$	$\omega_1 \omega_2 \omega_3 \omega_{-4} \omega_{-5} \omega_7$	$\omega_1 \omega_2 \omega_3 \omega_{-4} \omega_{-5} \omega_{-6}$	$\omega_2 \omega_3 \omega_4 \omega_{-5} \omega_{-6} \omega_7$	$\omega_{-1} \omega_3 \omega_4 \omega_{-5} \omega_{-6} \omega_7$	$\omega_{-1} \omega_{-2} \omega_4 \omega_{-5} \omega_{-6} \omega_7$
$\omega_1 \omega_2 \omega_3 \omega_4 \omega_6 \omega_7$	$\omega_1 \omega_2 \omega_3 \omega_4 \omega_{-5} \omega_7$	$\omega_1 \omega_2 \omega_3 \omega_4 \omega_{-5} \omega_{-6}$	$\omega_2 \omega_3 \omega_4 \omega_{-5} \omega_{-6} \omega_7$	$\omega_{-1} \omega_3 \omega_4 \omega_5 \omega_{-6} \omega_7$	$\omega_{-1} \omega_{-2} \omega_4 \omega_5 \omega_{-6} \omega_7$	$\omega_{-1} \omega_{-2} \omega_3 \omega_5 \omega_{-6} \omega_7$
$\omega_1 \omega_2 \omega_3 \omega_4 \omega_5 \omega_7$	$\omega_1 \omega_2 \omega_3 \omega_4 \omega_5 \omega_6$	$\omega_2 \omega_3 \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_3 \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_{-2} \omega_4 \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_{-2} \omega_3 \omega_5 \omega_6 \omega_7$	$\omega_{-1} \omega_{-2} \omega_3 \omega_4 \omega_6 \omega_7$

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

Hypotheses on irreversibility of elementary steps & rate-determining steps

↓

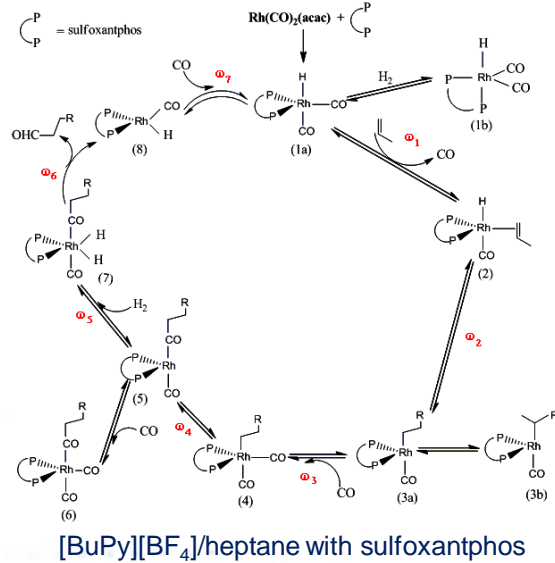
$$R = f ([H_2]_{\text{IL } \varphi}, [CO]_{\text{IL } \varphi}, [\text{cat}]_{\text{IL } \varphi}, [\text{octene}]_{\text{IL } \varphi}, T)$$

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

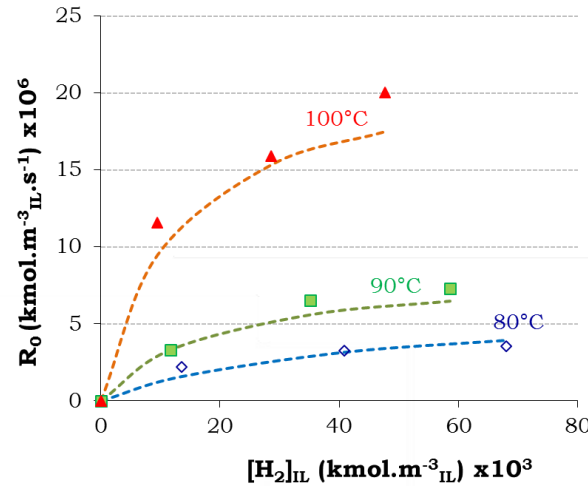
Ex: 
$$R = \frac{kABCD}{(1 + K_a AB + K_b AD + K_c BD + K_d ABD + K_e DB^2 + K_f A + K_g AB^2 + K_h B + K_i D)}$$

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

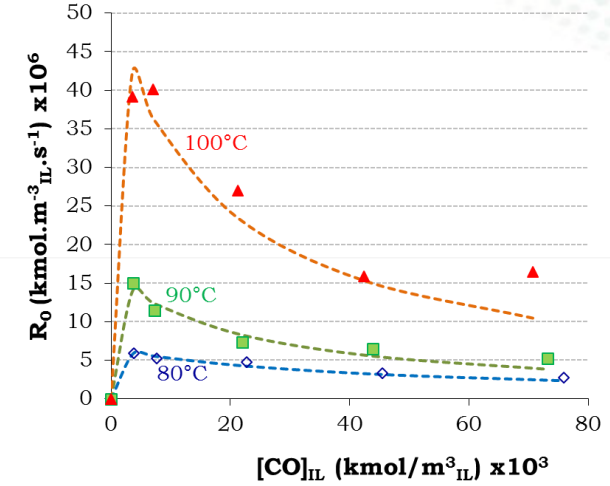
## Kinetic modeling



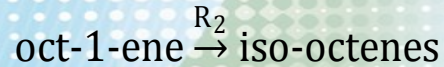
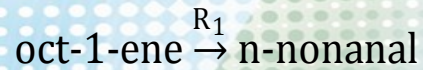
### Initial reaction rates



[Deshpande et al. (2011)]



### Accounting for isomerization



$$R_1 = \frac{k_1 C_{H_2,IL} C_{CO,IL} C_{cat,IL} C_{1oct,IL}}{(1 + K_{d1} C_{1oct,IL} C_{CO,IL}^3)}$$

addition of H<sub>2</sub> as rate determining step

### Time-concentration profiles

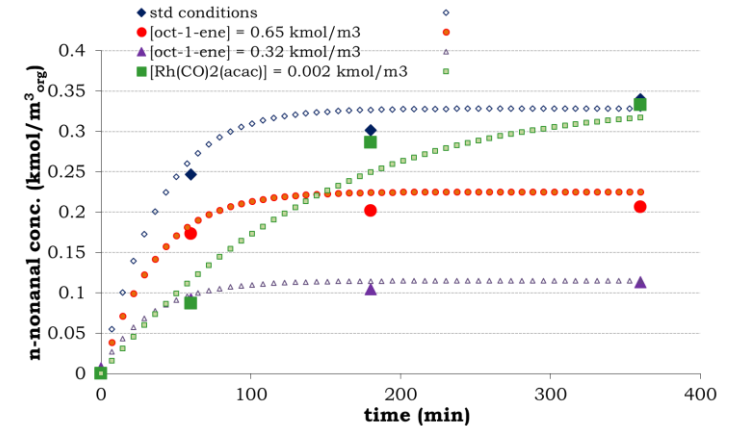
[Sharma et al. (2010)]

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

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

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

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



## G-L mass transfer evaluation without reaction ( $k_L a$ )

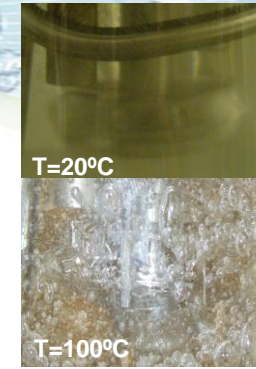
➤ Dynamic pressure step method:  $P_{\text{reac}} = f(t)$

➤ **In ionic liquids:**

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

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

(RSD +/- 20%)



1500 rpm

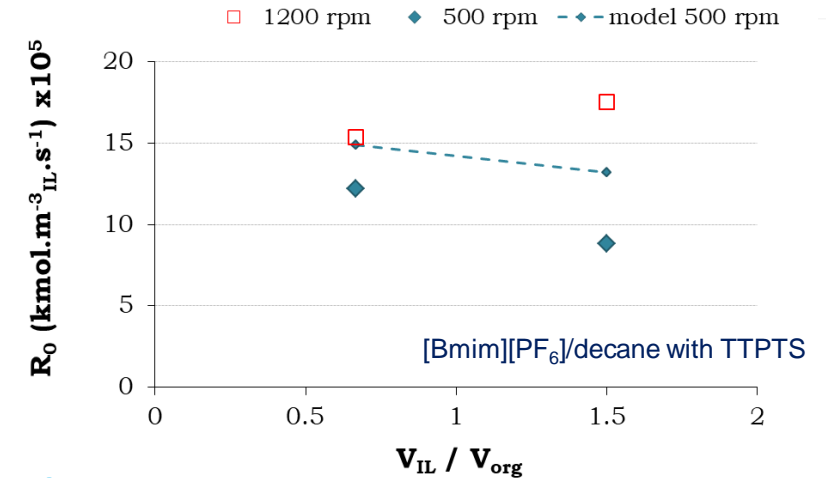
[Sharma et al. (2009)]

➤ **In emulsion:**

$k_L a \uparrow$  (by up to factor 10) when  $V_{IL}/V_{org} \downarrow$ ,  
marked variation around phase inversion

$$\frac{dC_{H2,IL}}{dt} - (k_L a)_{H2} (C_{H2,IL}^* - C_{H2,IL}) + \frac{k C_{H2,IL} C_{CO,IL} C_{cat,IL} C_{oct,IL}}{(1 + K_d C_{oct,IL} C_{CO,IL}^3)} \frac{\epsilon_{IL}}{(\epsilon_{IL} + (1 - \epsilon_{IL}) m_{H2})} = 0$$

$$\frac{dC_{CO,IL}}{dt} - (k_L a)_{CO} (C_{CO,IL}^* - C_{CO,IL}) + \frac{k C_{H2,IL} C_{CO,IL} C_{cat,IL} C_{oct,IL}}{(1 + K_d C_{oct,IL} C_{CO,IL}^3)} \frac{\epsilon_{IL}}{(\epsilon_{IL} + (1 - \epsilon_{IL}) m_{CO})} = 0$$

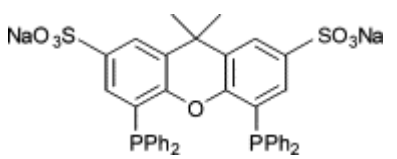


## Coupling of reaction and G-L mass transfer

- **Chemical regime** ( $\geq 1200$  rpm):  $R_0 \sim$  independent of  $V_{IL}/V_{org}$
- **Mass transfer regime** (500 rpm):  $R_0 \downarrow$  by 30% when  $V_{IL}/V_{org} \uparrow$  from 0.7 à 1.5
  - overestimation of  $R_0$  by the coupling model
  - supplementary resistance from L-L mass transfer?

[Bmim][PF<sub>6</sub>]/decane with TPPTS

## More selective ligand



sulfoxantphos

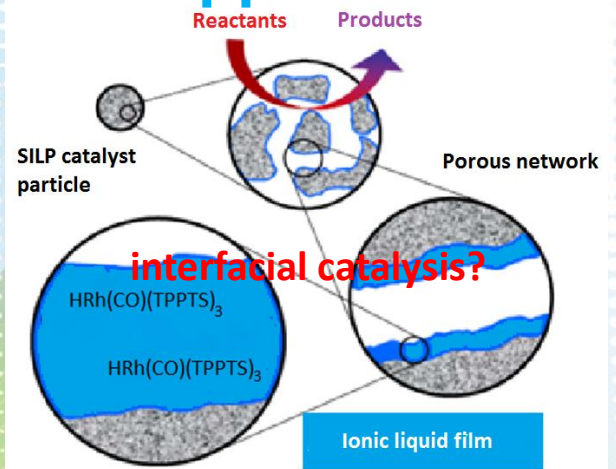
Conditions:  $[Rh(CO)_2(acac)] \sim 7.0 \cdot 10^{-3} \text{ kmol.m}^{-3}_{IL}$ ,  $SX:Rh = 5:1$ ,  
 $[oct-1-ene]_0 \sim 0.9 \text{ kmol.m}^{-3}_{org}$ ,  $p_{H_2} = p_{CO} \# 20 \text{ bar}$ ,  $IL:org = 40:60 \text{ v/v}$

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

Solvent	T (°C)	R <sub>0</sub> , kmol.m <sup>-3</sup> <sub>IL</sub> .s <sup>-1</sup>
[Bmim][PF <sub>6</sub> ]	80	13 · 10 <sup>-6</sup>
	100	46 · 10 <sup>-6</sup>
[BuPy][BF <sub>4</sub> ]	80	12 · 10 <sup>-6</sup>
	100	54 · 10 <sup>-6</sup>

➤ similar R<sub>0</sub> in both solvents (lower octene solubility in [BuPy][BF<sub>4</sub>], 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<sup>-1</sup> at 80°C  
 (conc. ratio of ~ 70 for olefin in between org. & IL φ)

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

# Ex.2: Biphasic catalysis with CCM

## From micellar catalyst ...

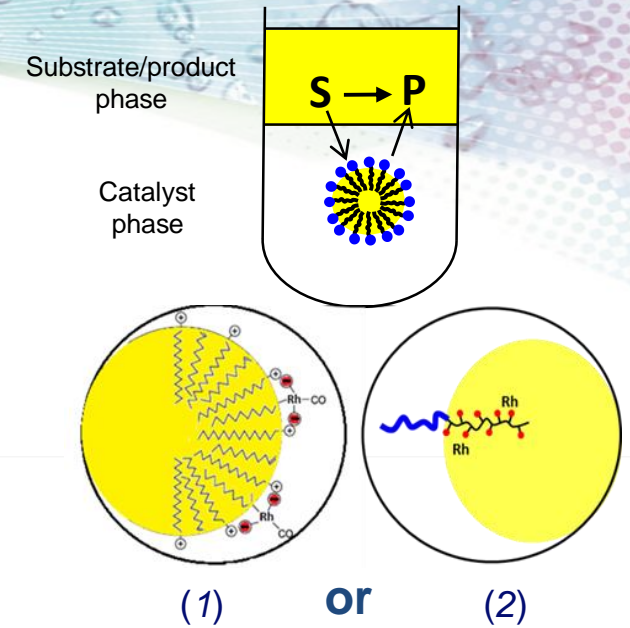
using *cationic surfactants* (1) or *amphiphilic ligands* (2)

☺ TOF up to 1000 h<sup>-1</sup> (1, 100°C) or 2500 h<sup>-1</sup> (2, 100°C)

☹ stable emulsions by excessive swelling of the micellar core

☹ Loss of catalytic objects at the interface

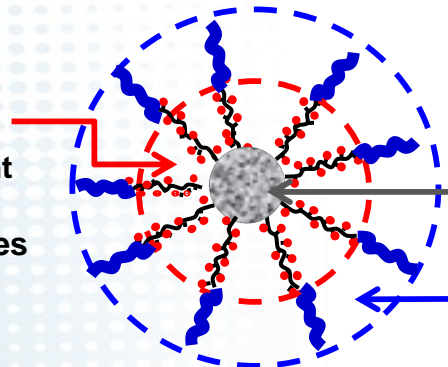
**Loss of metal (Rh)**



## ... 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

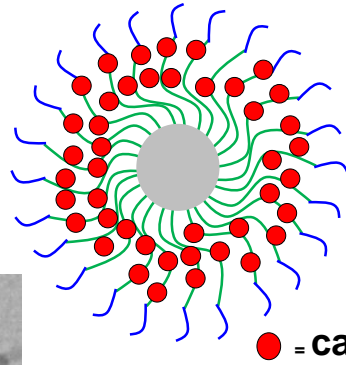


**Cross-linked core**  
Limited swelling of the object  
No free arms

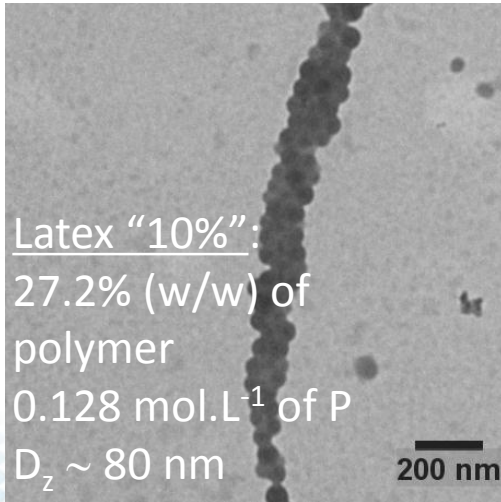
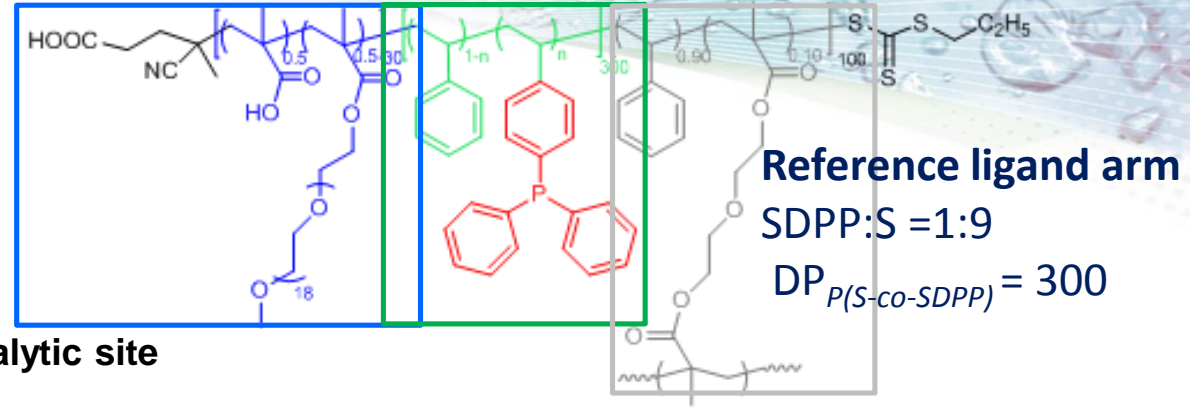
**Hydrophilic layer**  
Confinement in the aqueous phase

**well-defined size and architecture**

# A closer look on CCM



● = catalytic site



- 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?

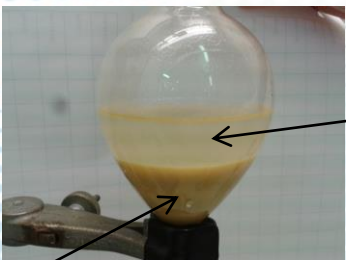


## Catalytic performance of CCM

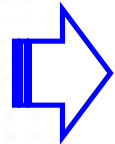
**Std conditions:** Ref. TTP@CCM,  $[Rh] = 6.5 \cdot 10^{-3} \text{ kmol} \cdot \text{m}^{-3}_{\text{aq}}$ ,  $[\text{oct-1-ene}] = 1.1 \text{ kmol} \cdot \text{m}^{-3}_{\text{org}}$  (solvent: n-decanal),  $P/Rh = 4$ ,  $V_{\text{org}} = 75 \text{ mL}$ ,  $V_{\text{aq(ns)}} = 25 \text{ mL}$ ,  $T = 363 \text{ K}$ ,  $P = 20 \text{ bar}$  ( $\text{CO}/\text{H}_2 = 1$ ),  $\omega = 1200 \text{ rpm}$



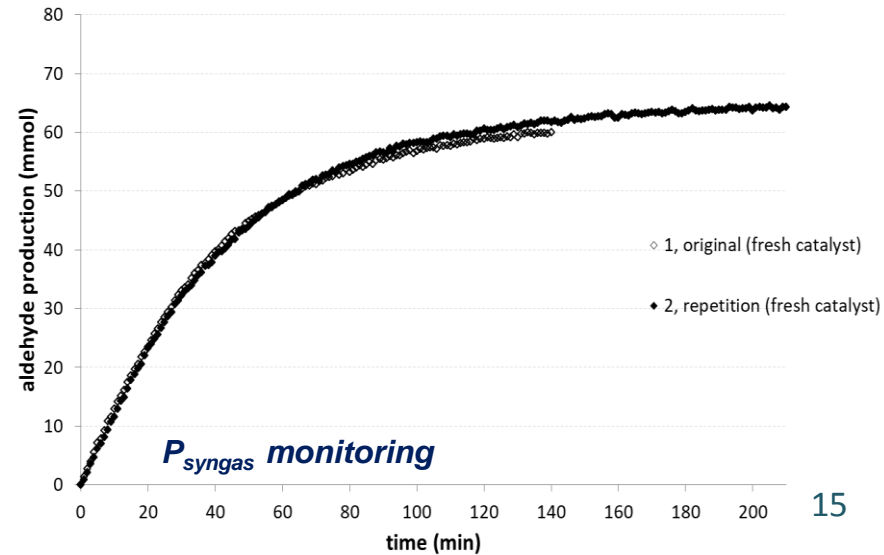
- High catalytic activity (**TOF ~ 500 h<sup>-1</sup>** vs. 1000 h<sup>-1</sup> for homogeneous reaction with TPP functionalized star polymer), l/b ratio of ~ 5
- No hydrogenation and nearly no isomerization
- Low Rh leaching (~2 ppm measured by ICP/MS) and negligible activity of recovered organic phase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



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



Swelled  
TPP@CCM in  
aqueous phase



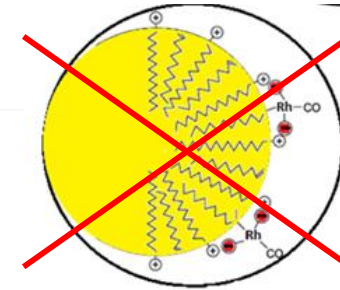
## Driving mechanisms

➤ ~~Interfacial catalysis?~~

Addition of a stronger water-soluble ligand (sulfoXantphos,  $sX/Rh = 5$ )

→ inhibition of the reaction ( $TOF_{max} = 13 \text{ h}^{-1}$ )

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 »**

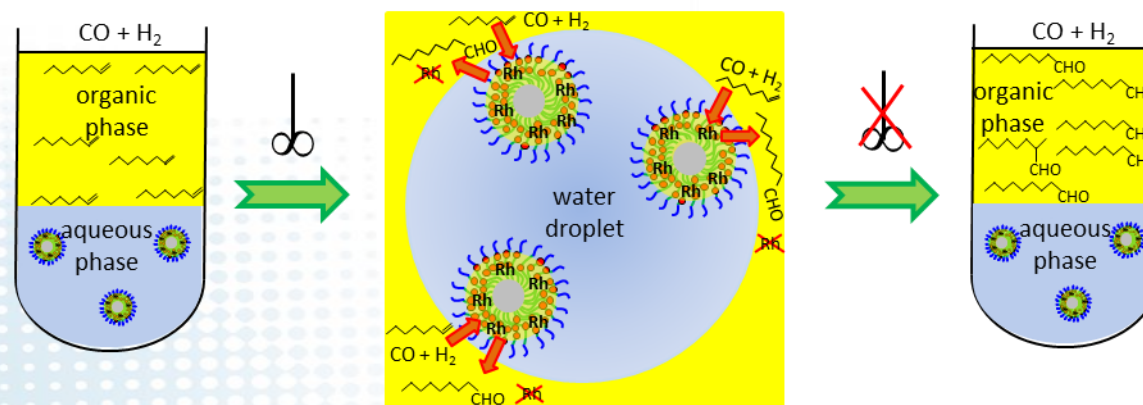
*Catalysis within the hydrophobic microenvironment gathering catalyst and substrate*

# Mass transfer effects

## External mass transfer limitation?

- Variation of  $\omega$  [1200-1600 rpm]  $\rightarrow$   $< 25\%$  variation of  $R_0$
  - Increase of [Rh] by a factor 4
    - \* at given P/Rh
    - \* at given [TPP@CCM] $\rightarrow$  **threefold increase in  $R_0$**
  - Variation of [TPP@CCM] at given [Rh]
- $\rightarrow$  no significant effect of P/Rh [4-12] on TOF nor on regioselectivity

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



## External mass transfer limitation?

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  - $\rightarrow$  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 *chemical effect for SDPP/S (Rh dimeric species?)*
  - $\rightarrow$  reduction of  $R_0$  by a factor  $> 3$
- Increase of DP: from 300 to 500  $\rightarrow R_0$  & l/b ratio unchanged
- Variation of T [70-90°C]  $\rightarrow E_A \sim 22 \text{ kcal.mol}^{-1}$ 
  - $\rightarrow$  value close to those reported in chemical regime in homogeneous / biphasic system with TPP(TS)

Internal diffusion within the objects is not rate-limiting

# 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 +



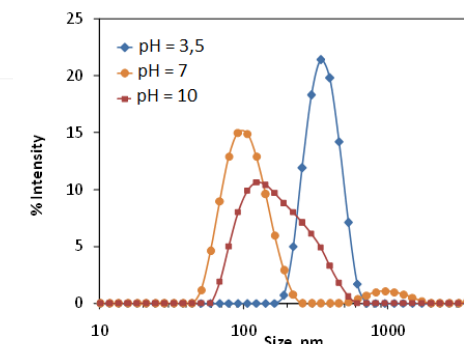
→ Accessibility to the catalytic complexes not significantly reduced by cross-linking ( $R_0 \downarrow$  by 30%), but **dramatic reduction of Rh loss** from 7.2 to 0.6 ppm

→ Rh loss sensible to  $\omega$  for CCM, but no effect for nanogel

## Shell properties

→ stability  $\uparrow$  when pH  $\uparrow$  from 3.5 to 7 → effect of methacrylic acid moieties

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

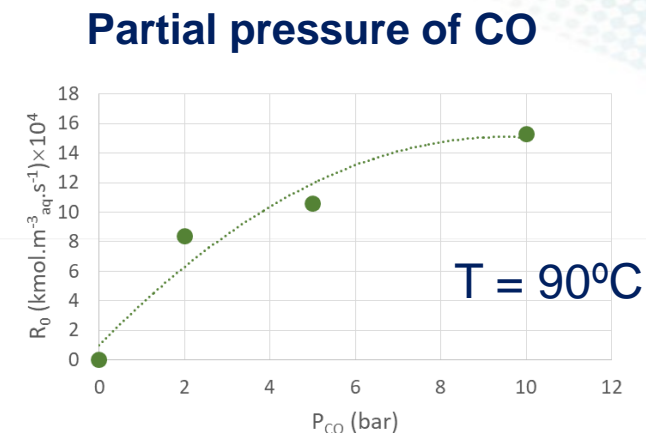
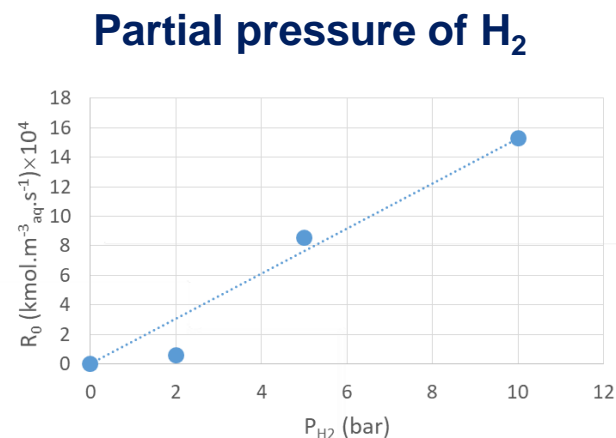
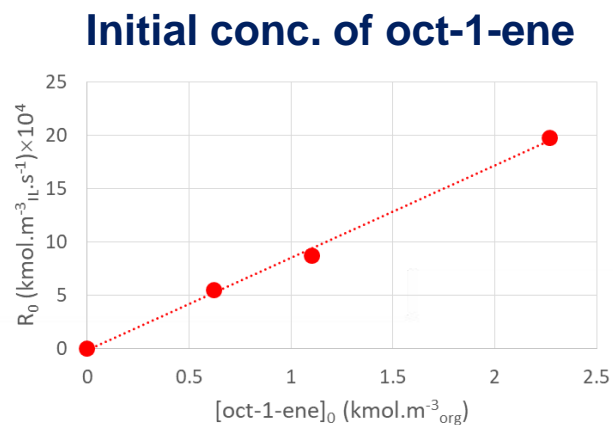


DLS aq  $\phi$  with CCM 1

# Towards a kinetic model

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

### Parametric study



$$E_a = 20.2 \text{ kcal.mol}^{-1}$$

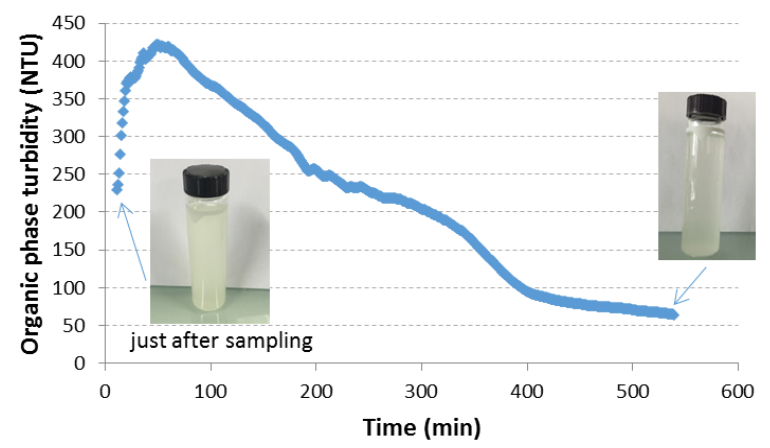
### Evaluation of the nanogel composition

- 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 $\phi$ separation

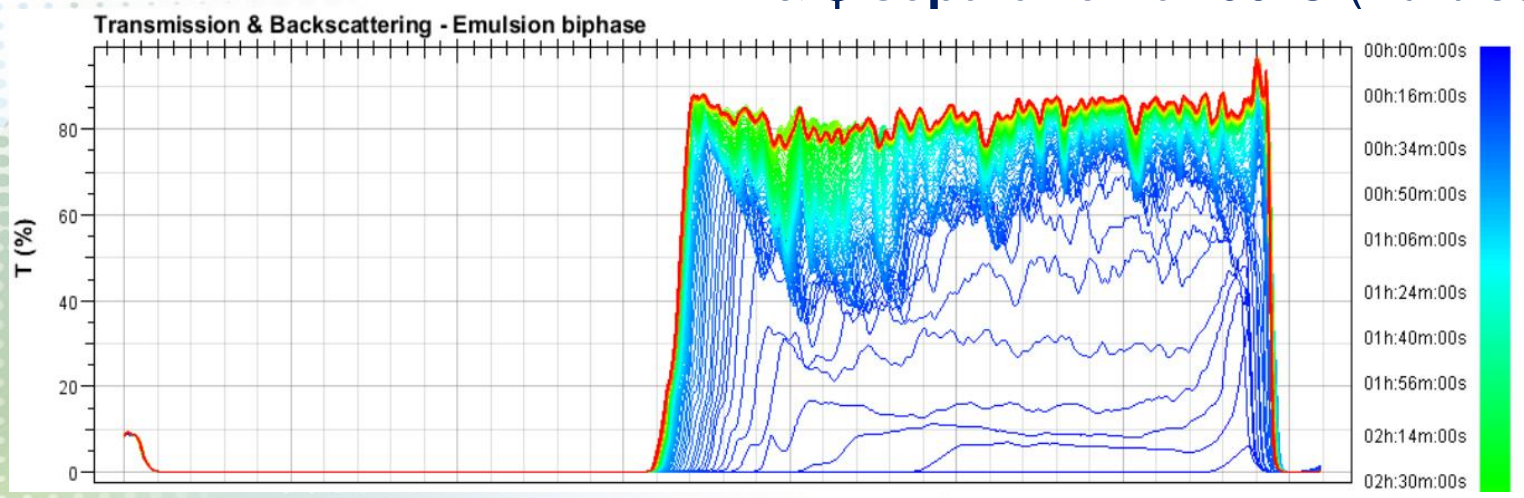
## Turbidity evolution



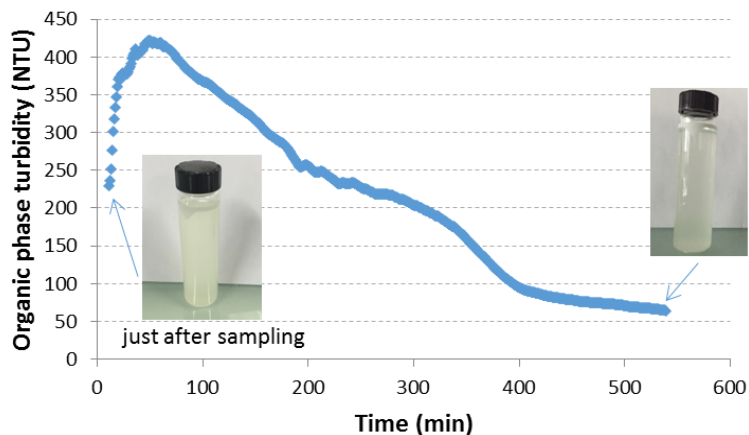
Sampling (30 mL) close to the W/O interface,  
10 min after stopping the stirring  
→ **translucent organic phase**  
**Separation at ambient T**  
→ NTU obtained after 8h ~ value of samples  
analyzed by ICP / AES for Rh leaching

## Stability evolution

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



## Turbidity evolution



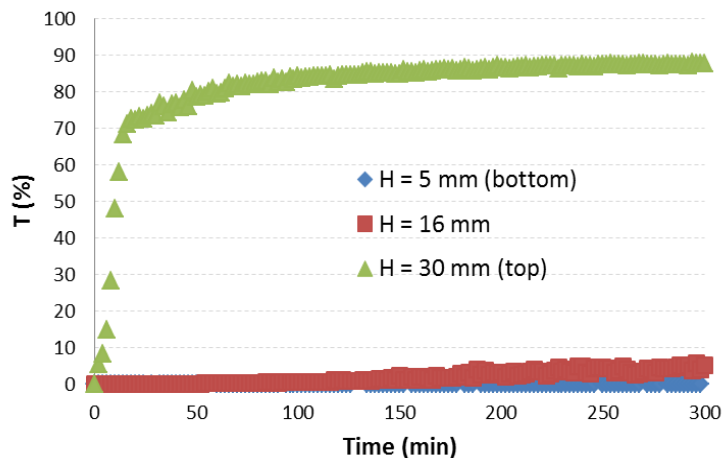
Sampling (30 mL) close to the W/O interface,  
10 min after stopping the stirring

→ **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)**  
&  $\phi$  separation at 60°C (Turbiscan)

showing **2 successive steps**:

→ a rapid disengagement (formation of two distinct  $\phi$ ) in 20 minutes

→ a much slower  $\phi$  evolution tending towards a plateau after 3 hours

$T = 83\% \leftrightarrow 0.02\%$  of solid content  
 $\leftrightarrow [Rh] \sim 1 \text{ ppm} (P/Rh = 4)$



# 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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Pr. Henri Delmas



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Jean-Louis Labat



Pr. Rinaldo Poli



Dr. Eric Manoury



Dr. Carine Julcour



Dr. Laurie Barthe



Marie Morere



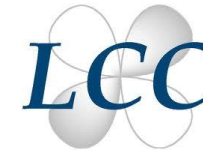
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