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Carine Julcour-Lebigue, Jean-François Blanco, Laurie Barthe, Henri Delmas, Rinaldo Poli, et al..
Mass transfer assessment and kinetic investigation of biphasic catalytic systems. Congrès national de
la Société Chimique de France, Jul 2018, Montpellier, France. 2018. hal-04354189

HAL Id: hal-04354189

<https://hal.science/hal-04354189>

Submitted on 19 Dec 2023

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MASS TRANSFER ASSESSMENT AND KINETIC INVESTIGATION OF BIPHASIC CATALYTIC SYSTEMS

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Raj M. DESHPANDE,⁵ Ashutosh A. KELKAR,⁵*

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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)

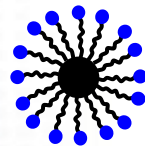
Industrial process: Ruhrchemie/Rhône Poulenc oxo process for the hydroformylation of propene into n-butanal, using **aqueous phase** and **hydrosoluble ligand** (TPPTS) – 800 000 tons aldehyde/year [Obrecht et al., 2013], Rh loss < 1 ppb

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

Strategies for biphasic catalysis:

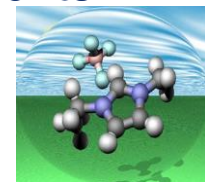
Water with additives

- * *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*
- * *scCO₂*



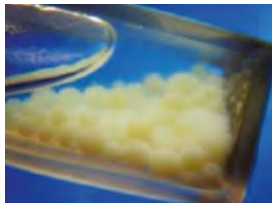
Main limitations: mass transfer, low reaction rate, and/or metal leaching

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 / μ environment?

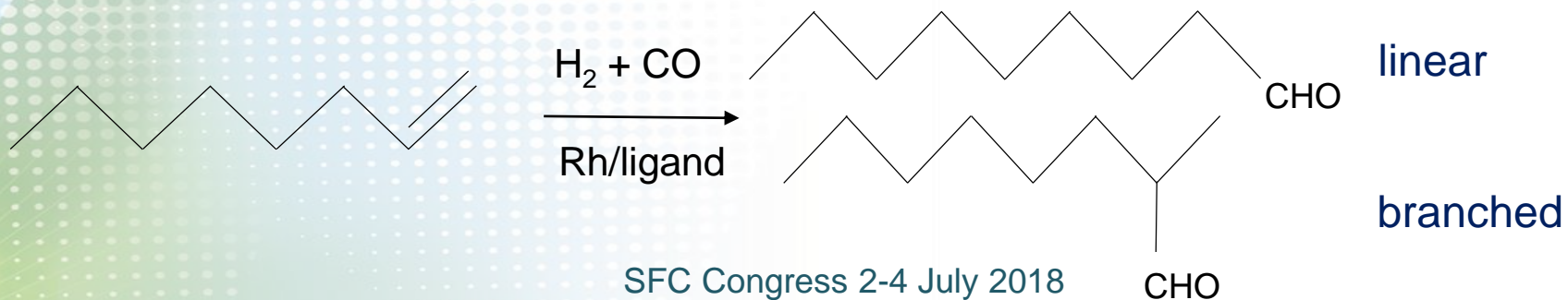


Mass transfer & kinetic study

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

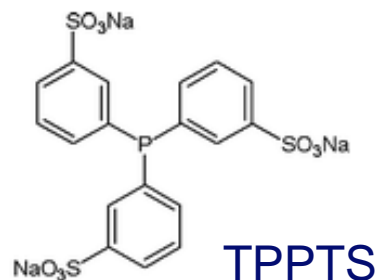


APPLICATION: Rh-catalyzed hydroformylation of oct-1-ene

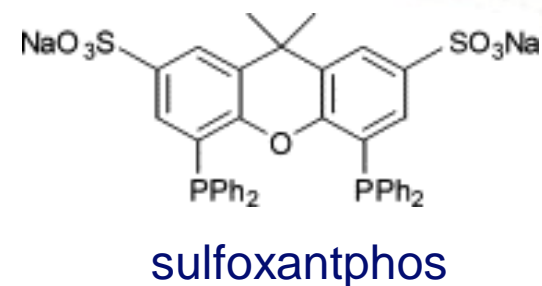


Ex.1: Ionic liquid biphasic catalysis

[Bmim][PF₆]/decane system



[BuPy][BF₄]/heptane system



PREVIOUS STUDIES (hydroformylation, ≤ 2004):

- **High activity & selectivity:** TOF > 1000 h⁻¹ (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 (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 H₂ and CO in [Bmim][PF₆]:

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

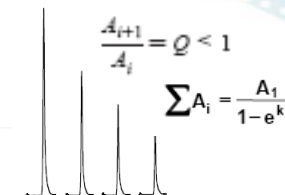
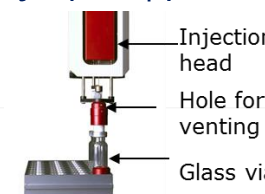
Similar, but slightly higher gas solubility in [BuPy][BF₄]

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

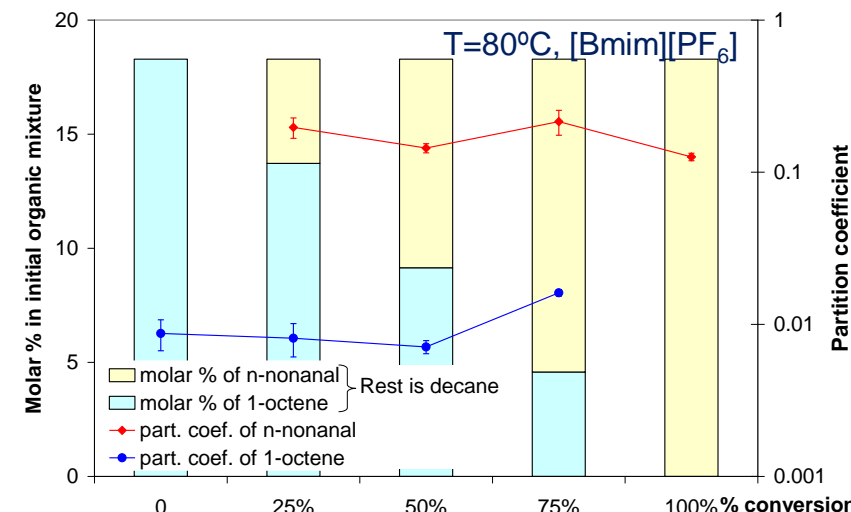
Very few values available

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

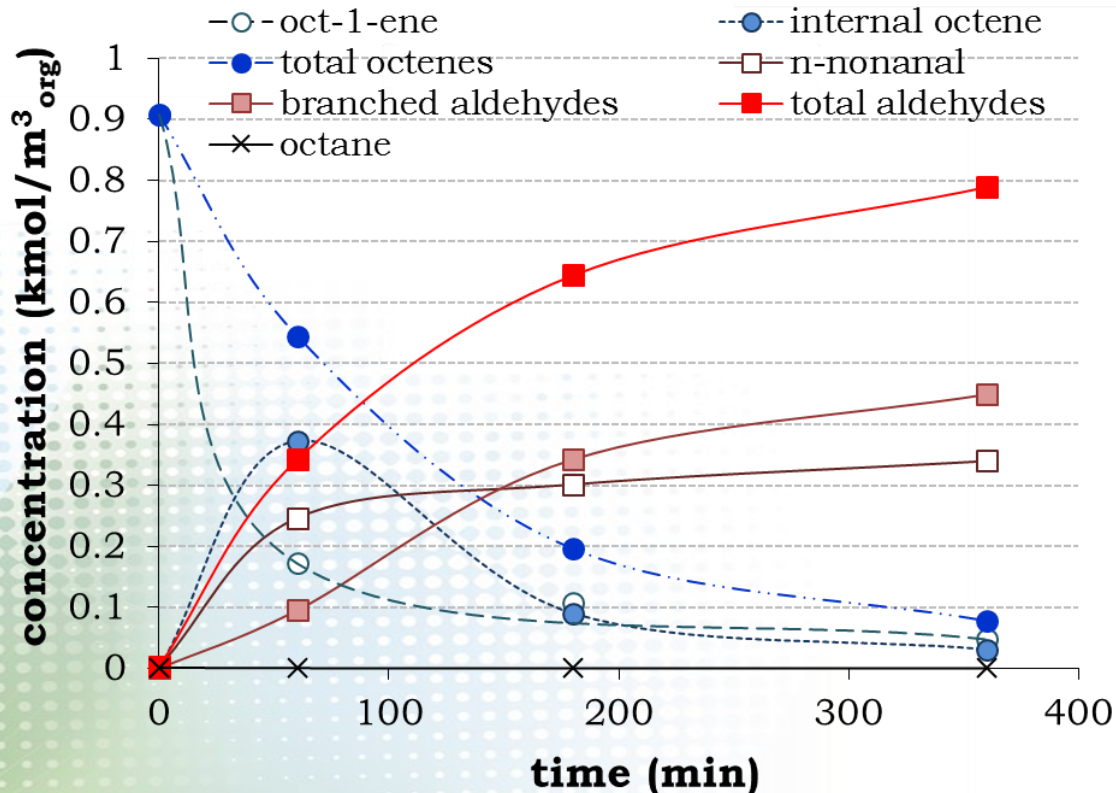
Solubility of octene in [Bmim][PF₆] (g / g):
 × 2000 with respect to water (25°C)
 Much higher solubility of n-nonanal
 Lower values in [BuPy][BF₄]

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][PF₆]/decane with TPPTS)



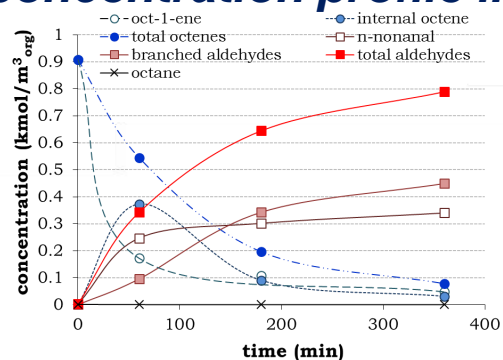
High isomerization of oct-1-ene
 → l/b ratio between 0.7 and 3
 TOF: 15-75 h⁻¹ after 1h (60-80°C)

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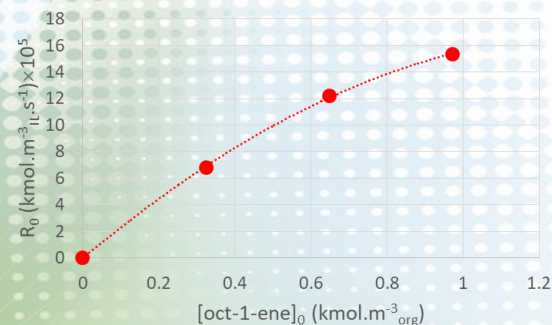


High isomerization of oct-1-ene
 → l/b ratio between 0.7 and 3
 TOF: 15-75 h⁻¹ after 1h (60-80°C)

Parametric study

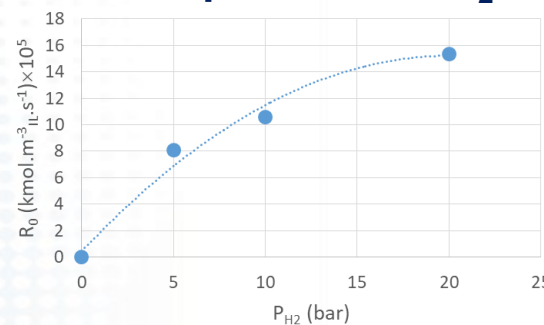
- Stirring speed & catalyst conc. (at given P/Rh) → to check for **chemical regime**

Initial conc. of oct-1-ene

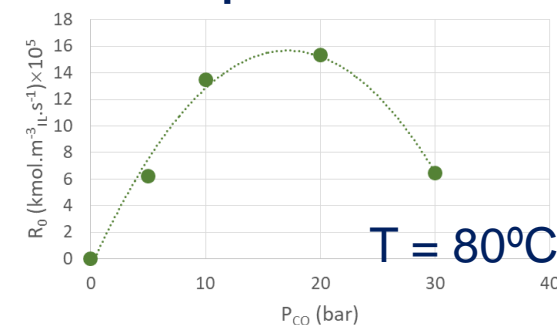


$$E_a = 25.8 \text{ kcal.mol}^{-1}$$

Partial pressure of H₂



Partial pressure of CO

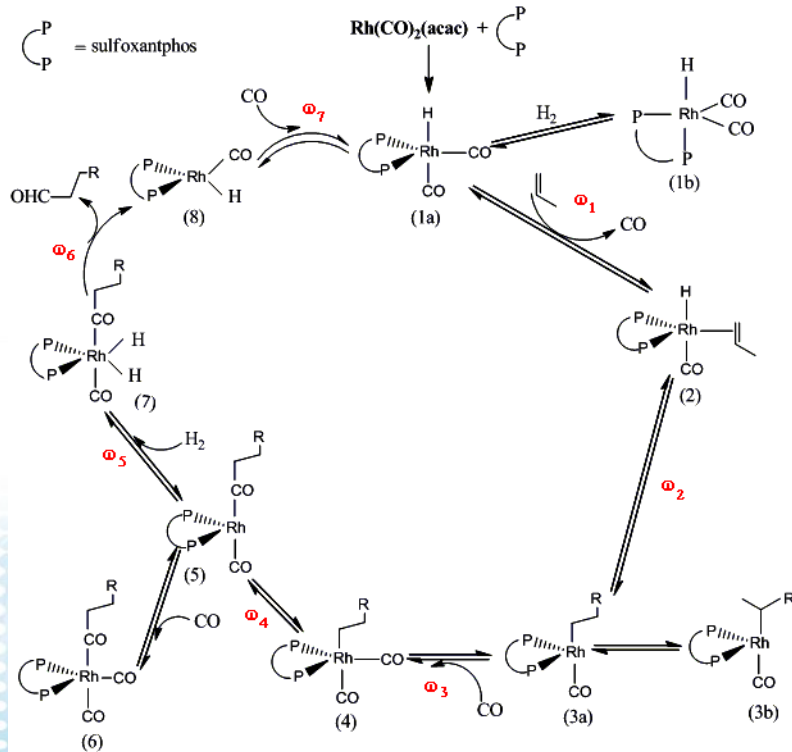


T = 80°C

$\omega = 1200 \text{ rpm}$, $V_{IL}/V_{org}: 40/60$

Kinetic modeling

➤ Empirical rate models or derived from elementary reaction steps



[BuPy][BF₄]/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

↓

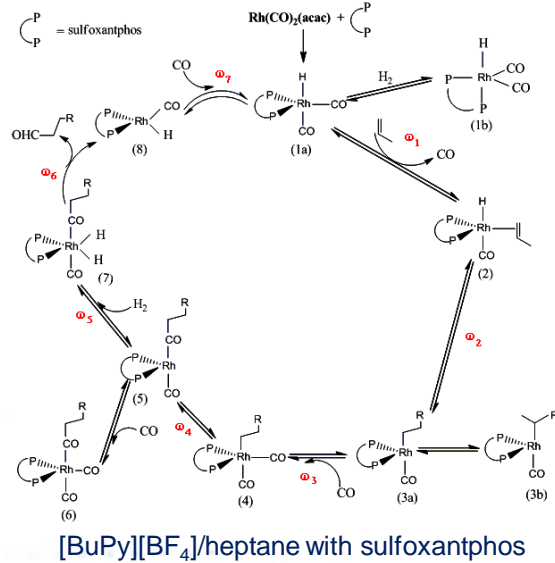
$$R = f ([H_2]_{\text{IL } \varphi}, [CO]_{\text{IL } \varphi}, [\text{cat}]_{\text{IL } \varphi}, [\text{octene}]_{\text{IL } \varphi}, T)$$

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

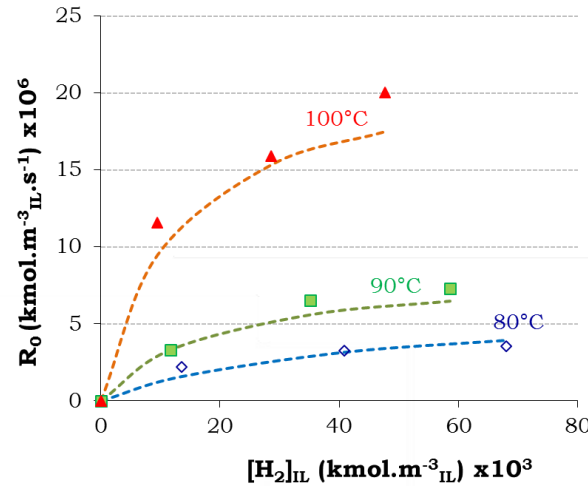
Ex: $R = \frac{kABCD}{(1 + K_a AB + K_b AD + K_c BD + K_d ABD + K_e DB^2 + K_f A + K_g AB^2 + K_h B + K_i D)}$

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

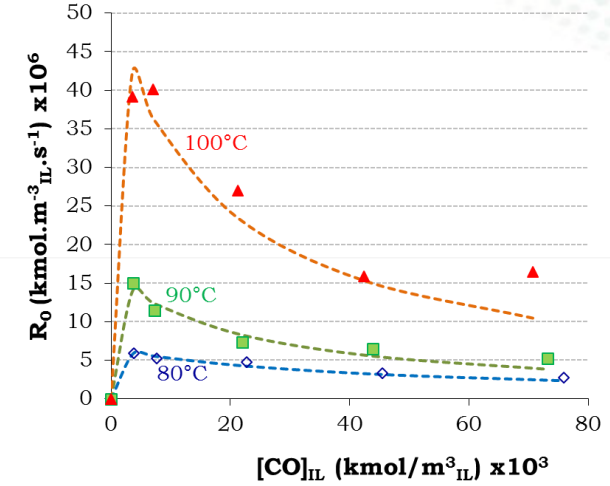
Kinetic modeling



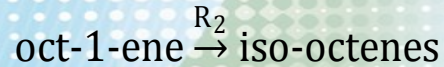
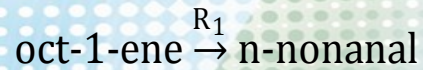
Initial reaction rates



[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 H₂ as rate determining step

Time-concentration profiles

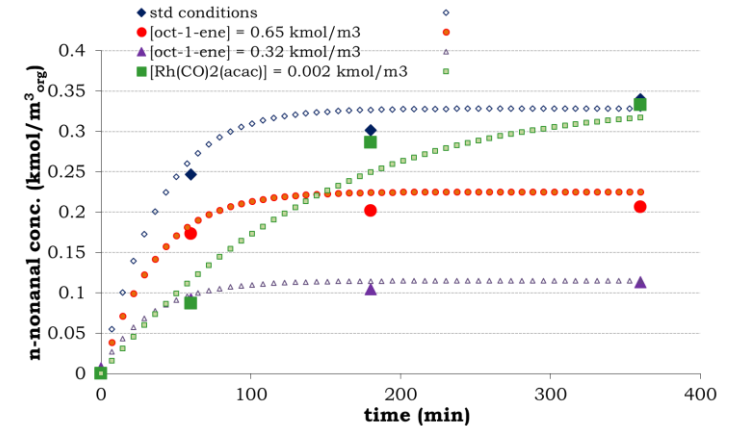
[Sharma et al. (2010)]

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

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

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

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



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

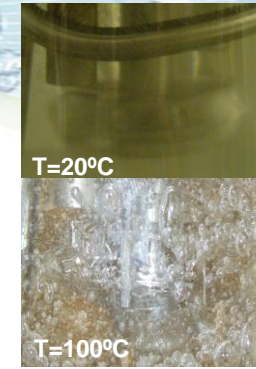
➤ Dynamic pressure step method: $P_{\text{reac}} = f(t)$

➤ **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

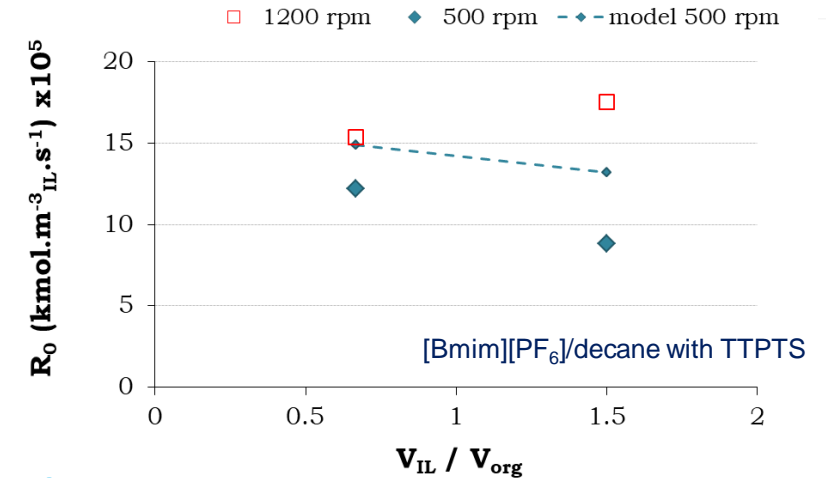
[Sharma et al. (2009)]

➤ **In emulsion:**

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

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

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

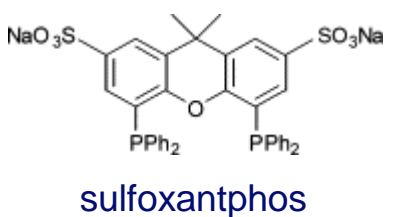


Coupling of reaction and G-L mass transfer

- **Chemical regime** (≥ 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][PF₆]/decane with TPPTS

More selective ligand



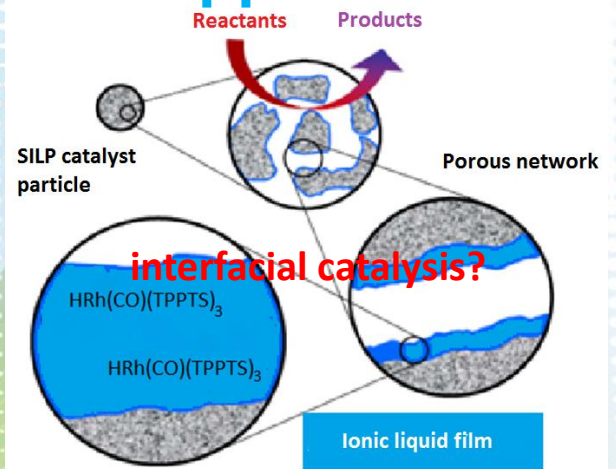
Conditions: $[Rh(CO)_2(acac)] \sim 7.0 \cdot 10^{-3} \text{ kmol.m}^{-3}_{IL}$, $SX:Rh = 5:1$,
 $[oct-1-ene]_0 \sim 0.9 \text{ kmol.m}^{-3}_{org}$, $p_{H_2} = p_{CO} \# 20 \text{ bar}$, $IL:org = 40:60 \text{ v/v}$

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

Solvent	T (°C)	R ₀ , kmol.m ⁻³ _{IL} .s ⁻¹
[Bmim][PF ₆]	80	13 · 10 ⁻⁶
	100	46 · 10 ⁻⁶
[BuPy][BF ₄]	80	12 · 10 ⁻⁶
	100	54 · 10 ⁻⁶

➤ similar R₀ in both solvents (lower octene solubility in [BuPy][BF₄], 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 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 ...

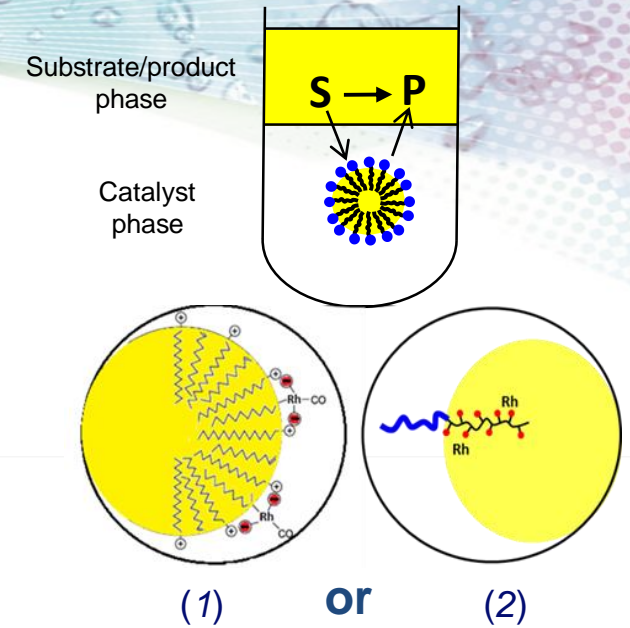
using *cationic surfactants* (1) or *amphiphilic ligands* (2)

☺ TOF up to 1000 h⁻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

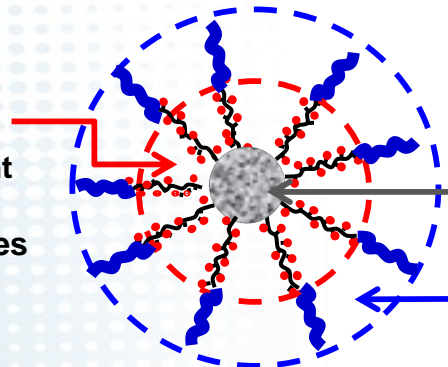
Loss of metal (Rh)



... 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

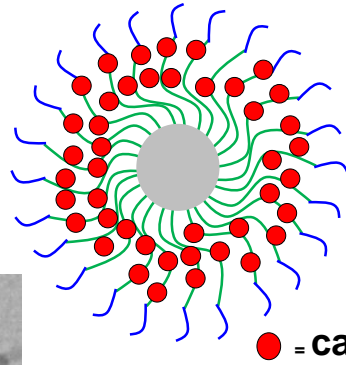


Cross-linked core
Limited swelling of the object
No free arms

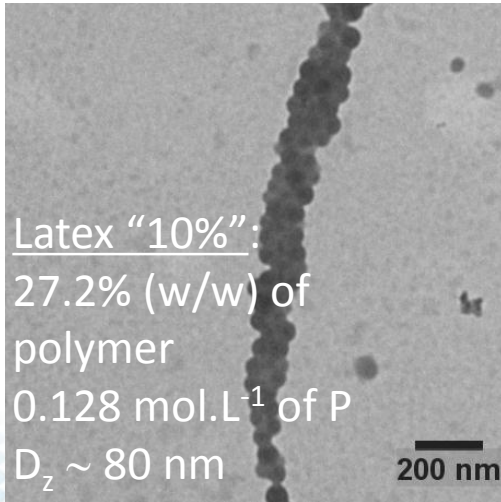
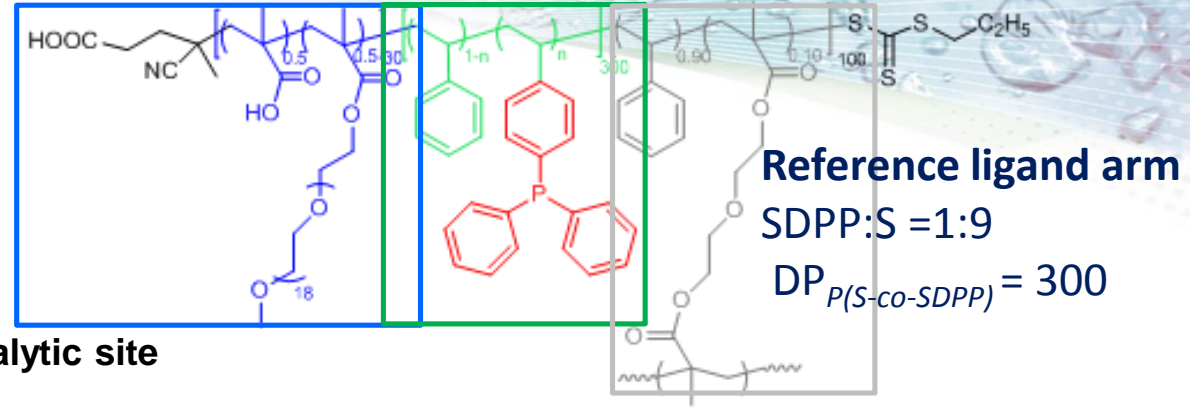
Hydrophilic layer
Confinement in the aqueous phase

well-defined size and architecture

A closer look on CCM



● = 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:

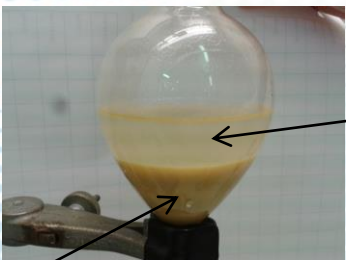
- Performance of CCM for aqueous biphasic catalysis?
- Driving mechanisms? Any limitation by mass transfer to/in the objects?
- How to optimize the objects?
- Content of the swelled CCM & phase separation dynamics?

Catalytic performance of CCM

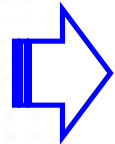
Std conditions: Ref. TTP@CCM, $[Rh] = 6.5 \cdot 10^{-3} \text{ kmol} \cdot \text{m}^{-3}_{\text{aq}}$, $[\text{oct-1-ene}] = 1.1 \text{ kmol} \cdot \text{m}^{-3}_{\text{org}}$ (solvent: n-decanal), $P/Rh = 4$, $V_{\text{org}} = 75 \text{ mL}$, $V_{\text{aq(ns)}} = 25 \text{ mL}$, $T = 363 \text{ K}$,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



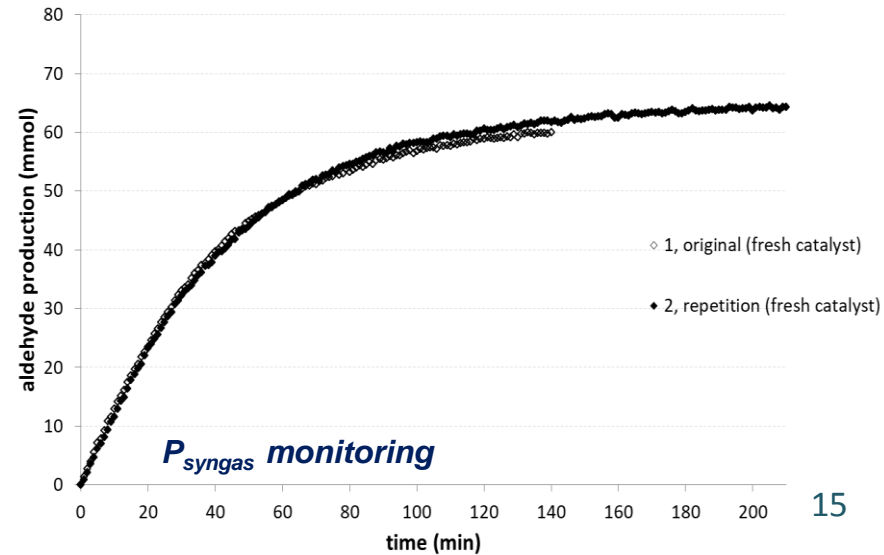
- High catalytic activity (**TOF ~ 500 h⁻¹** vs. 1000 h⁻¹ for homogeneous reaction with TPP functionalized star polymer), l/b ratio of ~ 5
- No hydrogenation and nearly no isomerization
- Low Rh leaching (~2 ppm measured by ICP/MS) and negligible activity of recovered organic phase
- **Excellent catalytic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



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



Swelled
TPP@CCM in
aqueous phase



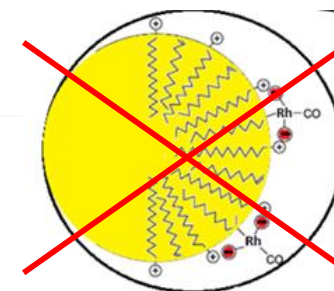
Driving mechanisms

➤ ~~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 »**

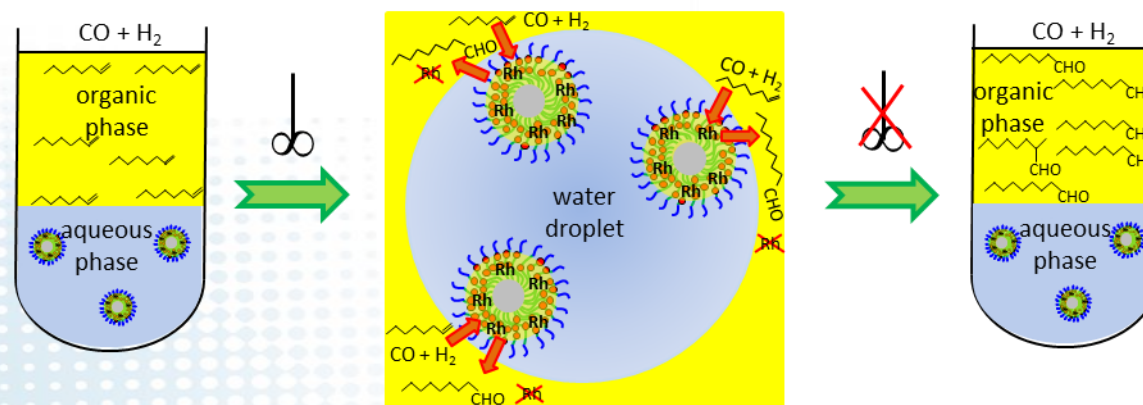
Catalysis within the hydrophobic microenvironment gathering catalyst and substrate

Mass transfer effects

External mass transfer limitation?

- Variation of ω [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



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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

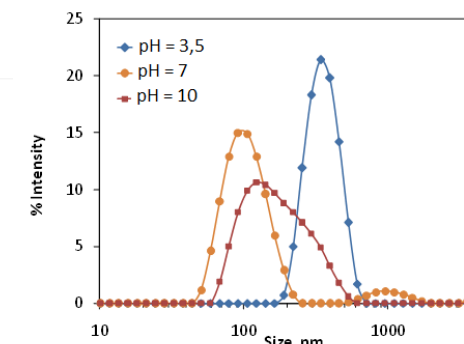
Length of hydrophobic segment /

→ 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 +



DLS aq ϕ with CCM 1

→ 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 ω for CCM, but no effect for nanogel

Shell properties

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

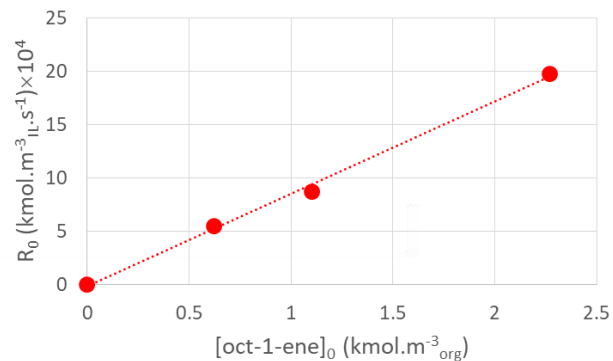
→ $[Rh]_{org}$ reduced to 0.1 ppm at 60°C → effect of thermosensitive PEG

Towards a kinetic model

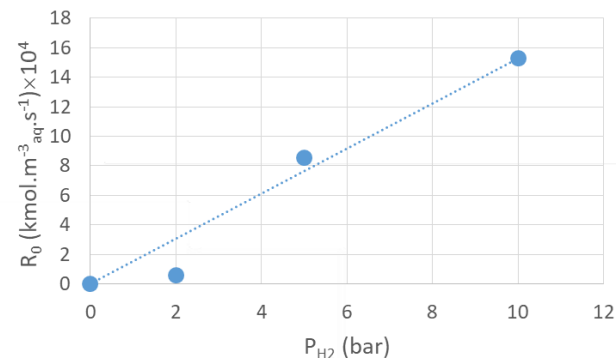
Selection of nanogel with 5% SDPP (pH=7)

Parametric study

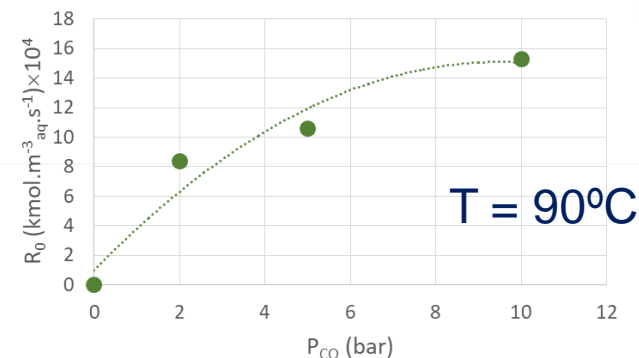
Initial conc. of oct-1-ene



Partial pressure of H₂



Partial pressure of CO



T = 90°C

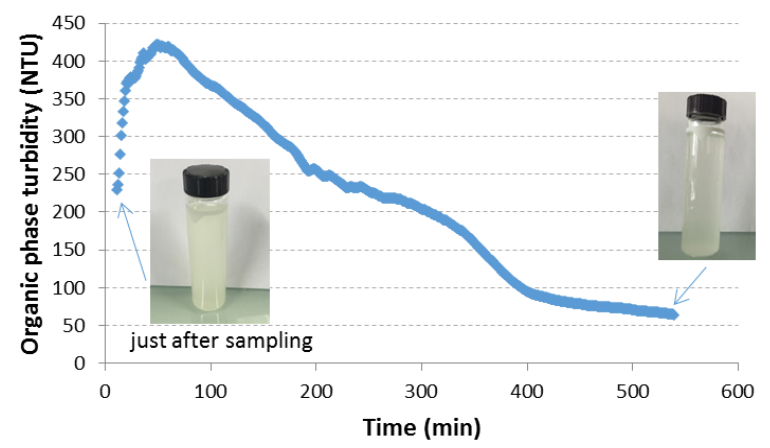
$$E_a = 20.2 \text{ kcal.mol}^{-1}$$

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)



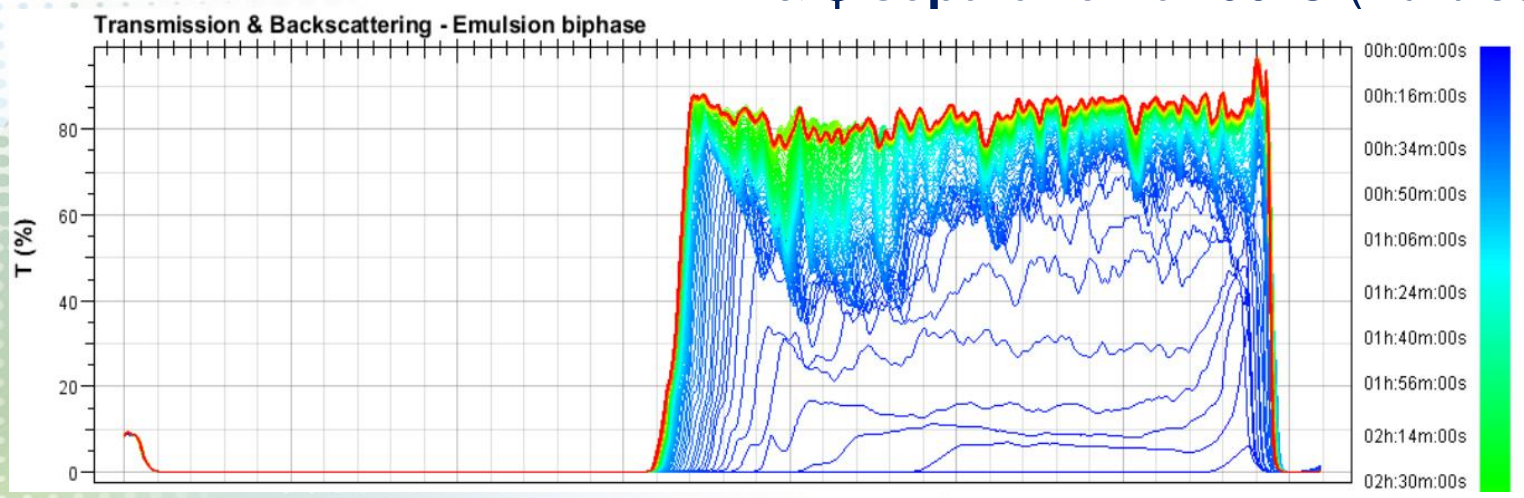
Turbidity evolution



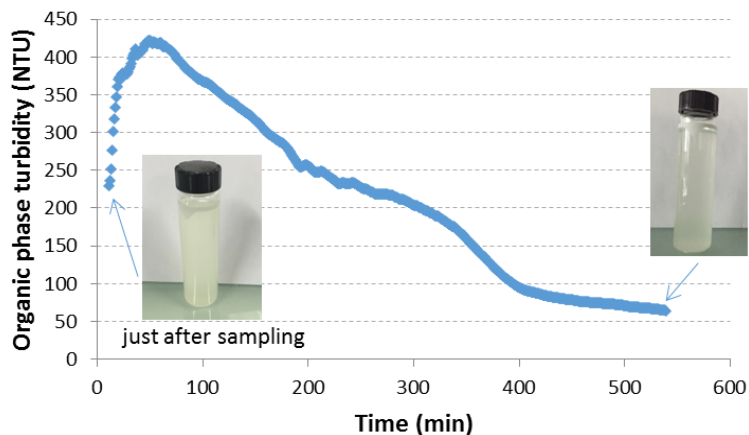
Sampling (30 mL) close to the W/O interface, 10 min after stopping the stirring
→ **translucent organic phase**
Separation at ambient T
→ NTU obtained after 8h ~ value of samples analyzed by ICP / AES for Rh leaching

Stability evolution

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



Turbidity evolution



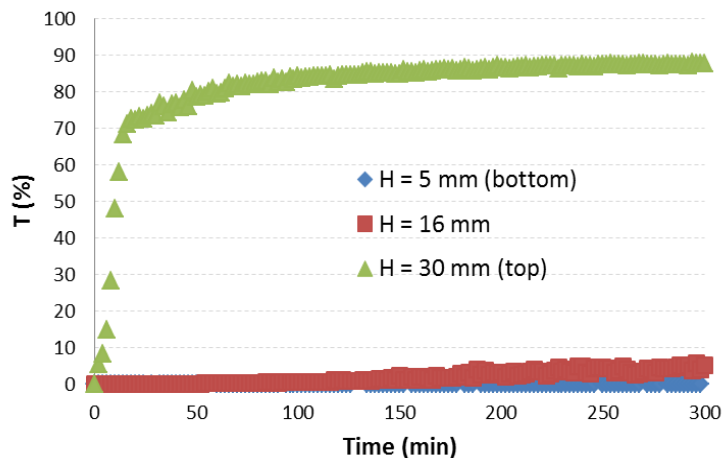
Sampling (30 mL) close to the W/O interface,
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→ **translucent organic phase**

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)

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

$T = 83\% \leftrightarrow 0.02\%$ 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



Indo-French Center For the Promotion of Advanced Research
for funding the project 3305-2 “Reaction Engineering in Ionic Liquids”



Agence Nationale de la Recherche
for funding the Biphasnanocat Project (ANR-11-BS07-025-01),

Our PhD & post-doc students: A. Sharma, A. Cardozo, E. Lobry

Our technical staff: J.L. Labat, M. Morere I. Coghe, L. Farhi, M.L. Pern (LGC),
for their support on the reactor pilot and the analyses

Our project partners at NCL, LCC & C2P2

Thank you for your kind attention!



Pr. Henri Delmas



Dr. Jean-François Blanco



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Pr. Rinaldo Poli



Dr. Eric Manoury



Dr. Carine Julcour



Dr. Laurie Barthe



Marie Morere



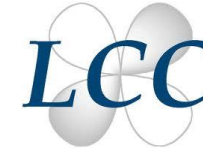
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