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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)

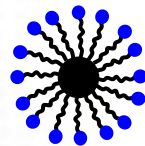
Industrial process: Ruhrchemie/Rhône Poulenc oxo process for the hydroformylation of propene into n-butanal, using **aqueous phase** and **hydrosoluble ligand** (TPPTS) – 800 000 tons aldehyde/year [Obrecht et al., 2013], Rh loss < 1 ppb

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

Strategies for biphasic catalysis:

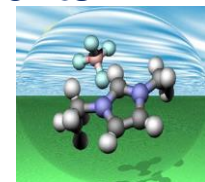
Water with additives

- * *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*



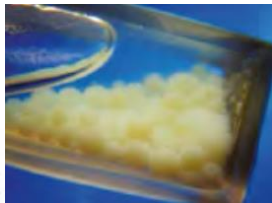
Main limitations: mass transfer, low reaction rate, and/or metal leaching

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?

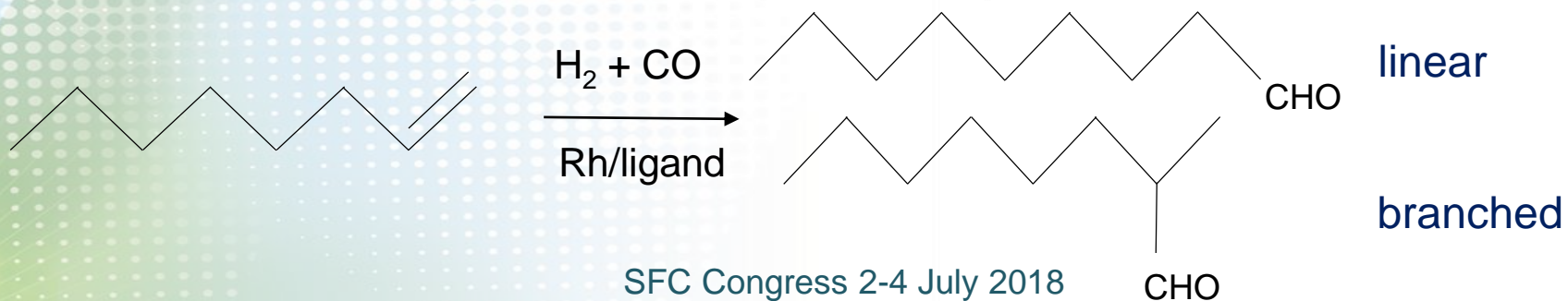


Mass transfer & kinetic study

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

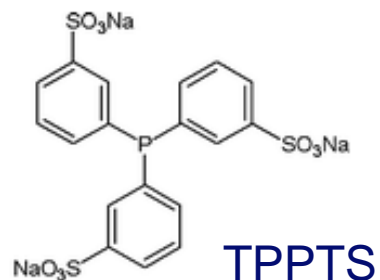


APPLICATION: Rh-catalyzed hydroformylation of oct-1-ene

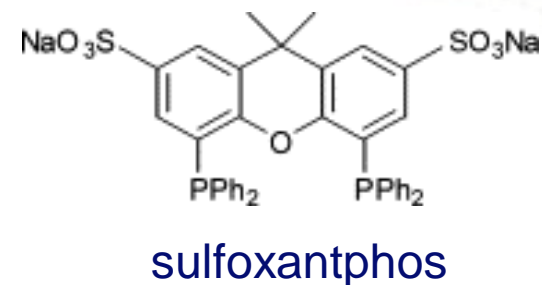


Ex.1: Ionic liquid biphasic catalysis

[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)])

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

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

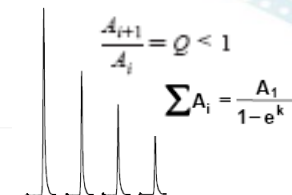
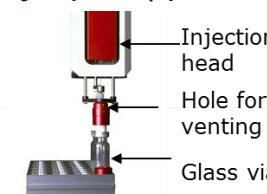
Similar, but slightly higher gas solubility in [BuPy][BF₄]

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

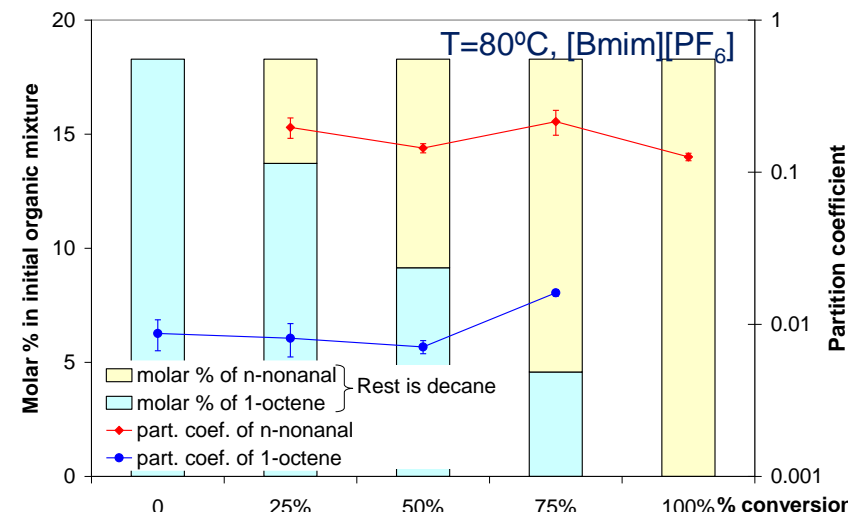
Very few values available

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

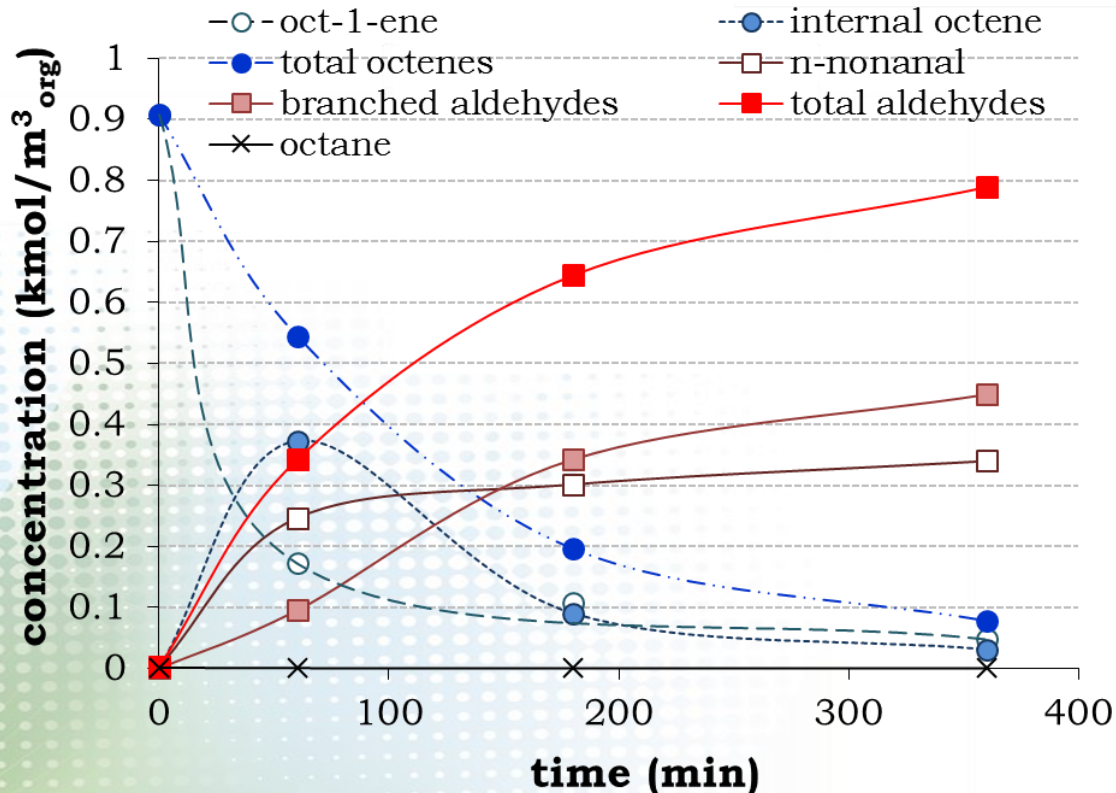
Solubility of octene in [Bmim][PF₆] (g / g):
 × 2000 with respect to water (25°C)
 Much higher solubility of n-nonanal
 Lower values in [BuPy][BF₄]

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)



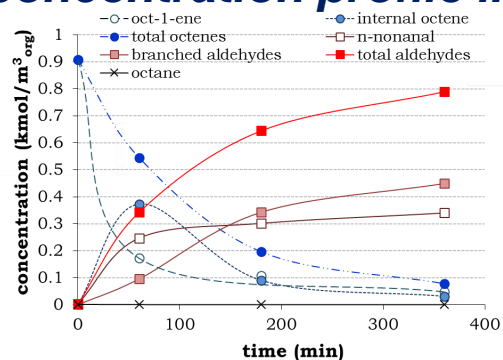
High isomerization of oct-1-ene
 → l/b ratio between 0.7 and 3
 TOF: 15-75 h⁻¹ after 1h (60-80°C)

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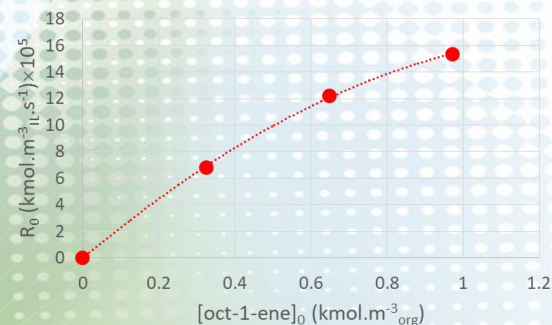


High isomerization of oct-1-ene
 → l/b ratio between 0.7 and 3
 TOF: 15-75 h⁻¹ after 1h (60-80°C)

Parametric study

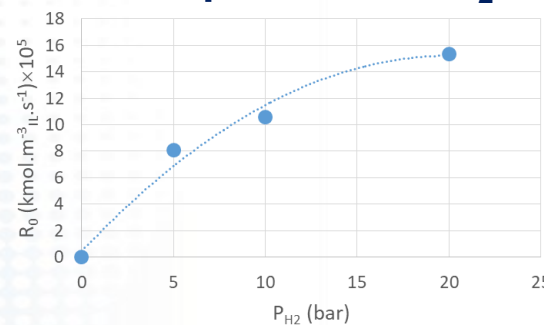
- Stirring speed & catalyst conc. (at given P/Rh) → to check for **chemical regime**

Initial conc. of oct-1-ene

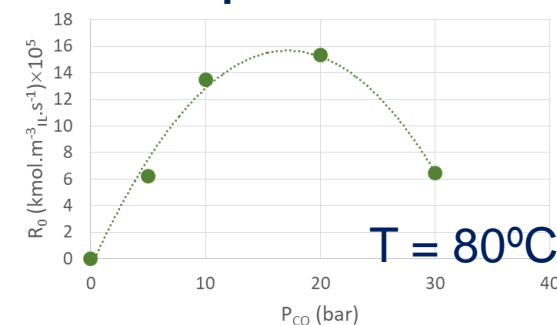


$$E_a = 25.8 \text{ kcal.mol}^{-1}$$

Partial pressure of H₂



Partial pressure of CO

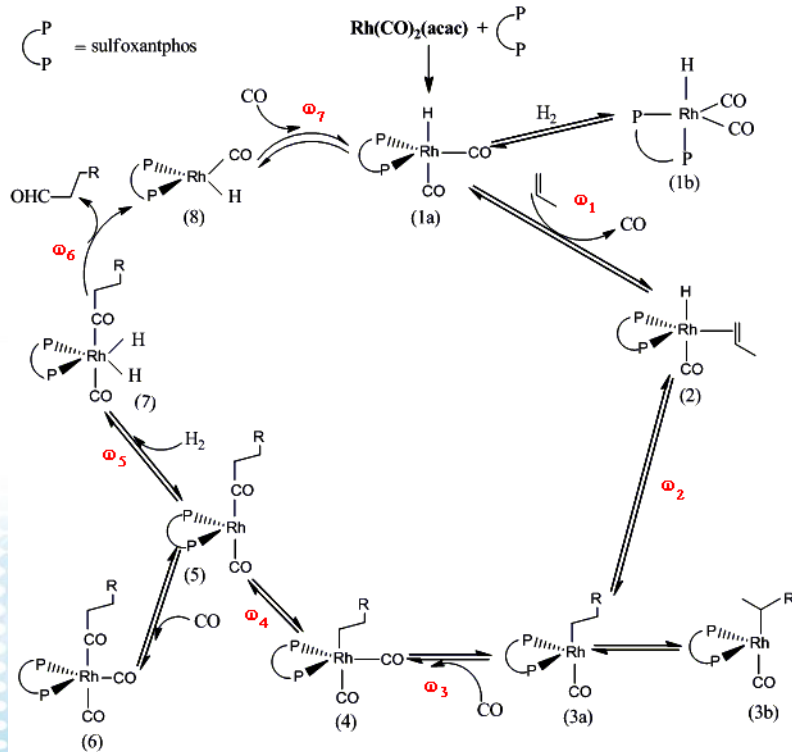


T = 80°C

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

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

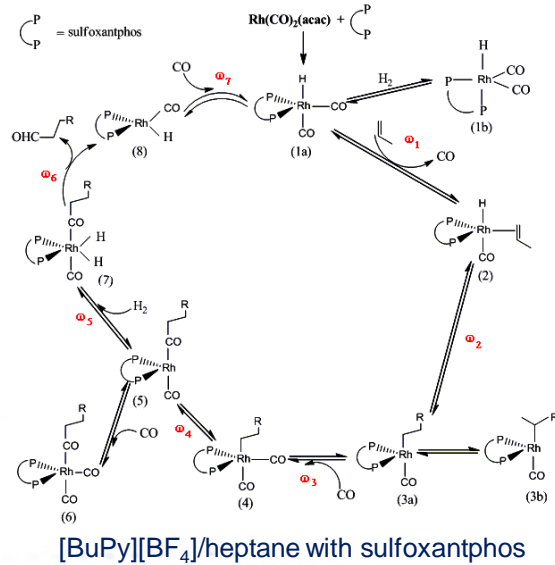
$$R = f ([H_2]_{\text{IL } \varphi}, [CO]_{\text{IL } \varphi}, [\text{cat}]_{\text{IL } \varphi}, [\text{octene}]_{\text{IL } \varphi}, T)$$

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

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

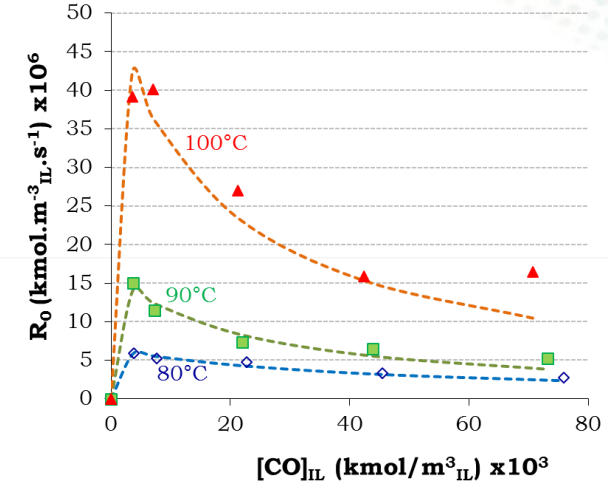
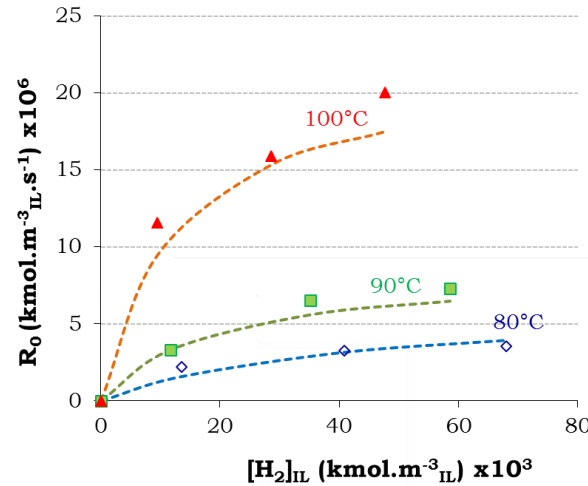
no limiting step, only the release of aldehyde product is an irreversible step

Kinetic modeling

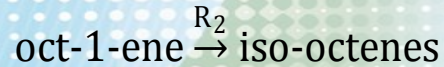
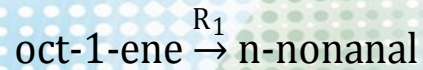


Initial reaction rates

[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

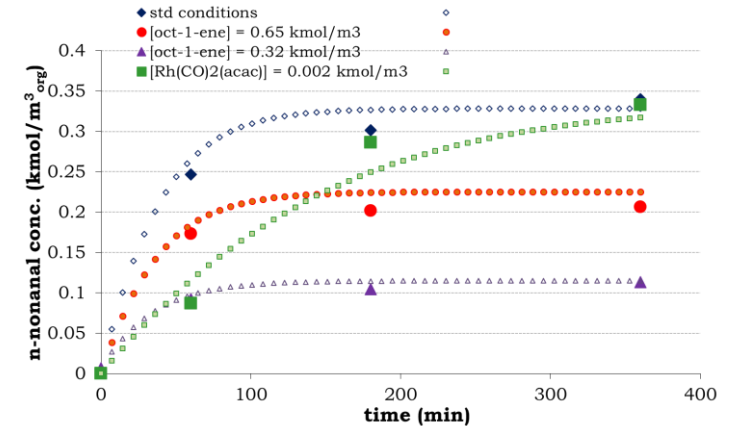
[Sharma et al. (2010)]

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

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

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

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



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

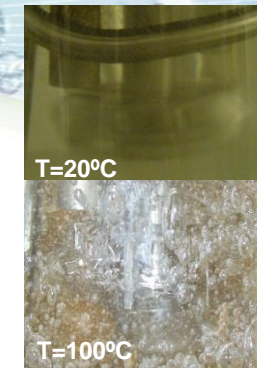
➤ Dynamic pressure step method: $P_{\text{reac}} = f(t)$

➤ **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

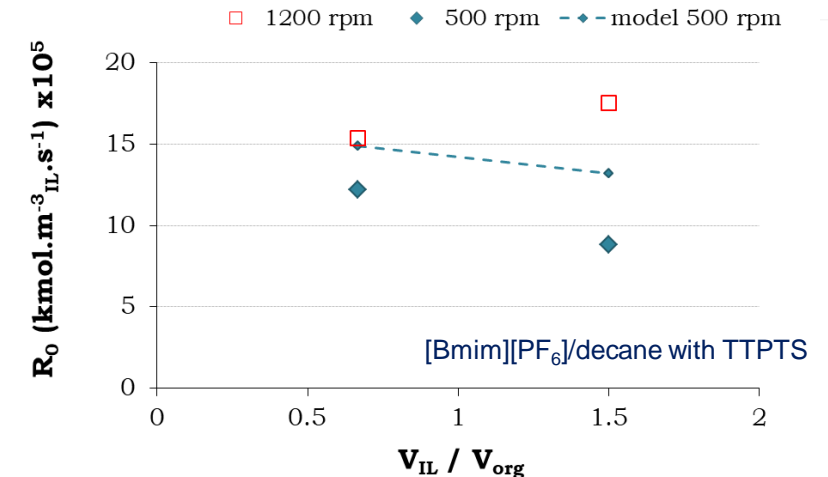
[Sharma et al. (2009)]

➤ **In emulsion:**

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

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

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

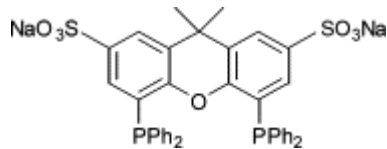


Coupling of reaction and G-L mass transfer

- **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



sulfoxantphos

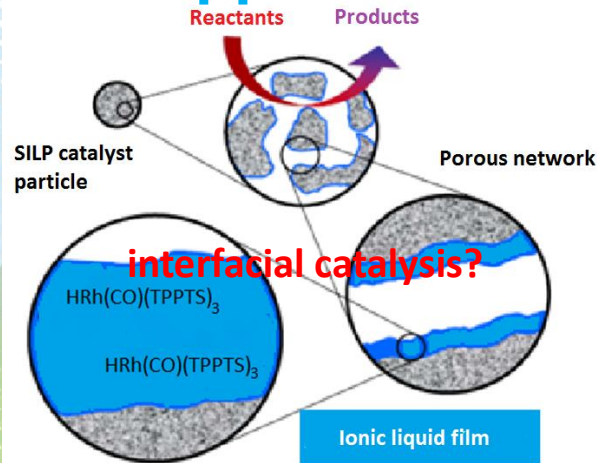
Conditions: $[Rh(CO)_2(acac)] \sim 7.0 \cdot 10^{-3} \text{ kmol.m}^{-3}_{IL}$, $SX:Rh = 5:1$,
 $[oct-1-ene]_0 \sim 0.9 \text{ kmol.m}^{-3}_{org}$, $p_{H_2} = p_{CO} \# 20 \text{ bar}$, $IL:org = 40:60 \text{ v/v}$

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

| Solvent | T (°C) | R 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)

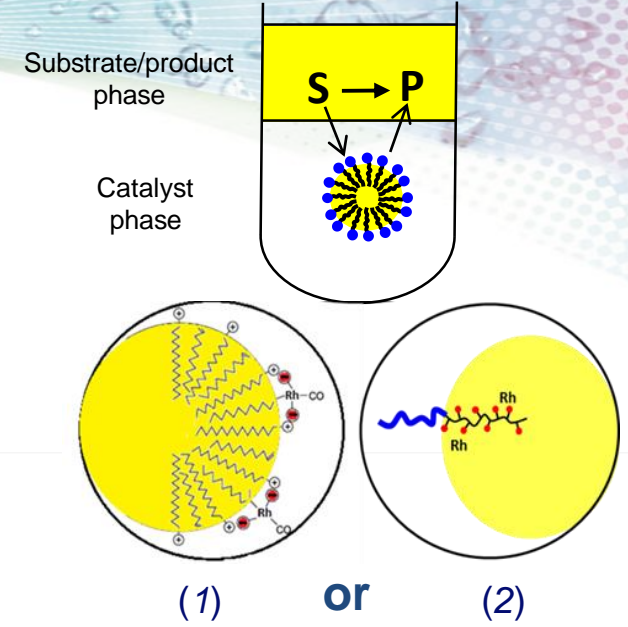
☺ Stable activity under recycling (Rh loss: 1-2 ppm)

Ex.2: Biphasic catalysis with CCM

From micellar catalyst ...

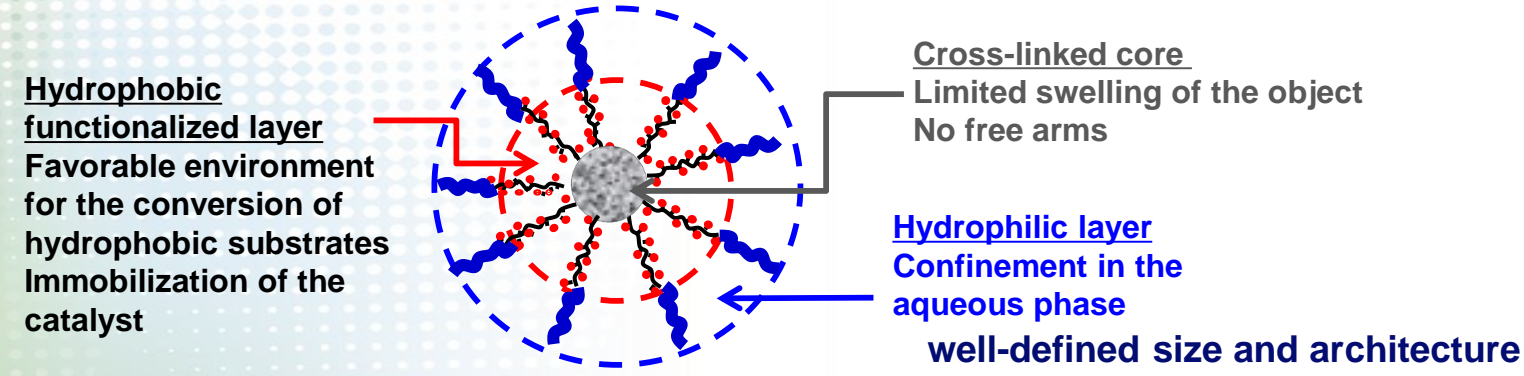
- using *cationic surfactants* (1) or *amphiphilic ligands* (2)
- ☺ TOF up to 1000 h⁻¹ (1, 100°C) or 2500 h⁻¹ (2, 100°C)
- ☹ stable emulsions by excessive swelling of the micellar core
- ☹ Loss of catalytic objects at the interface

Loss of metal (Rh)

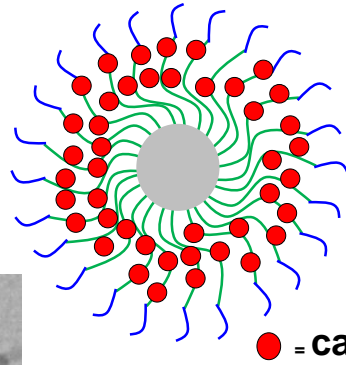


... to polymeric core-shell catalyst

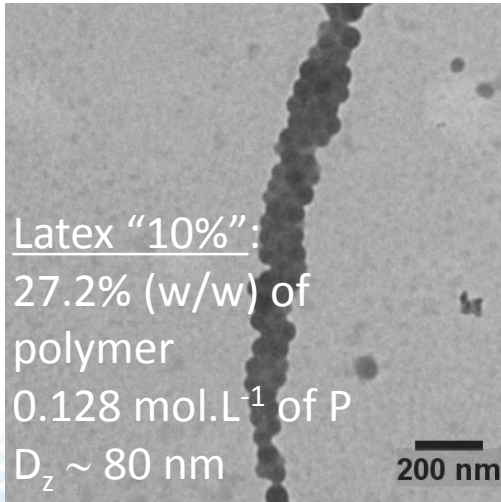
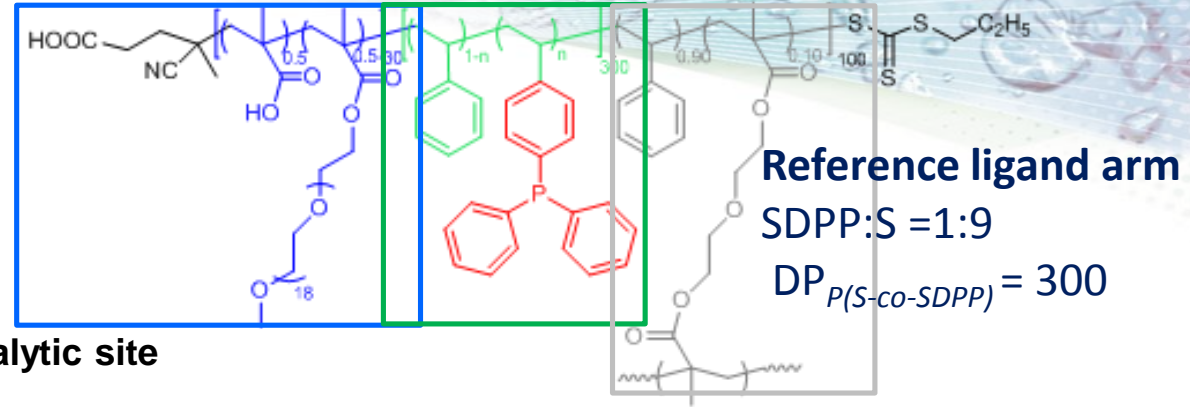
by cross-linking the hydrophobic segments of self-assembled amphiphilic block copolymers synthesized by “controlled” radical polymerization



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:

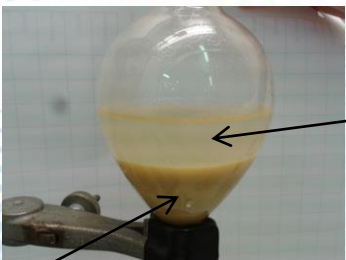
- Performance of CCM for aqueous biphasic catalysis?
- Driving mechanisms? Any limitation by mass transfer to/in the objects?
- How to optimize the objects?
- Content of the swelled CCM & phase separation dynamics?

Catalytic performance of CCM

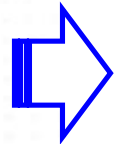
Std conditions: Ref. TTP@CCM, $[Rh] = 6.5 \cdot 10^{-3} \text{ kmol} \cdot \text{m}^{-3}_{\text{aq}}$, $[\text{oct-1-ene}] = 1.1 \text{ kmol} \cdot \text{m}^{-3}_{\text{org}}$ (solvent: n-decanal), $P/Rh = 4$, $V_{\text{org}} = 75 \text{ mL}$, $V_{\text{aq(ns)}} = 25 \text{ mL}$, $T = 363 \text{ K}$,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



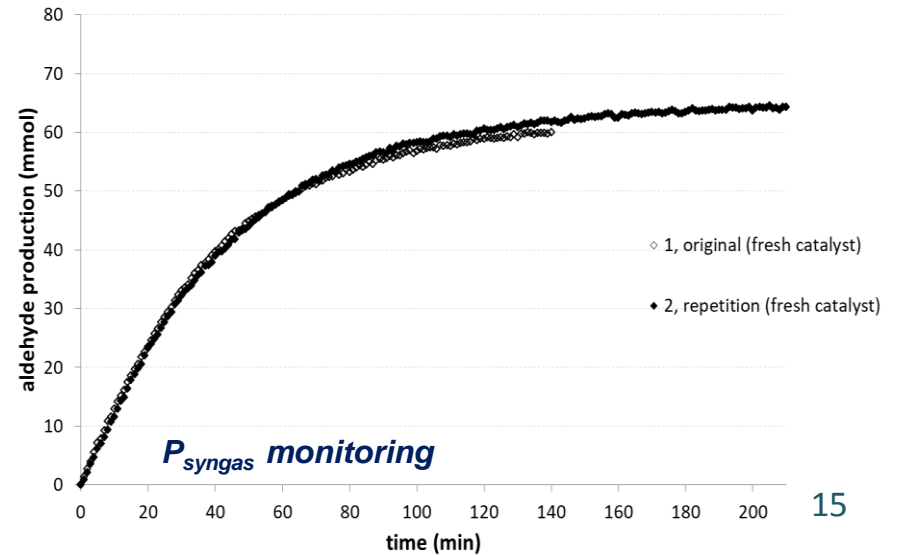
- High catalytic activity (**TOF ~ 500 h⁻¹** vs. 1000 h⁻¹ for homogeneous reaction with TPP functionalized star polymer), l/b ratio of ~ 5
- No hydrogenation and nearly no isomerization
- Low Rh leaching (~2 ppm measured by ICP/MS) and negligible activity of recovered organic phase
- **Excellent catalytic 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



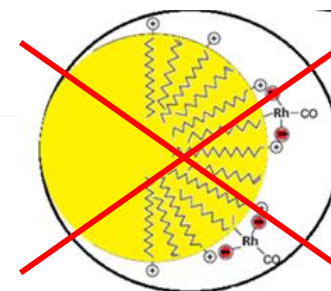
Driving mechanisms

➤ ~~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 »

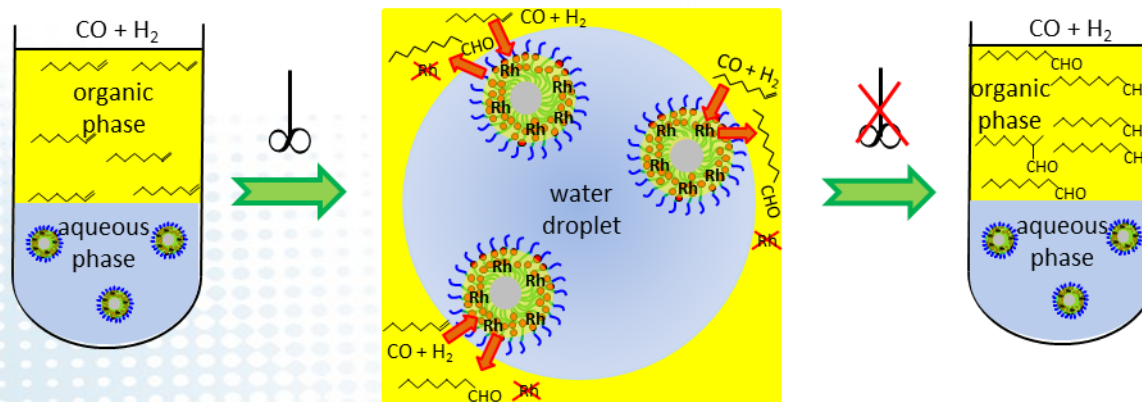
Catalysis within the hydrophobic microenvironment gathering catalyst and substrate

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 I/b ratio or metal leaching (CCM or nanogel)

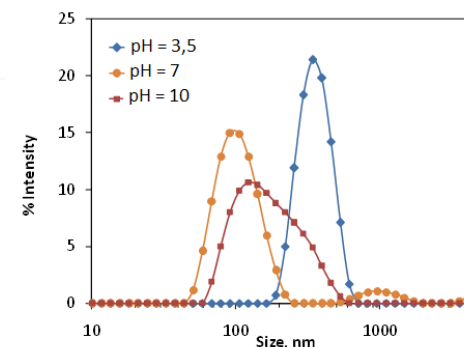
Cross-linking extent +



→ 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 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



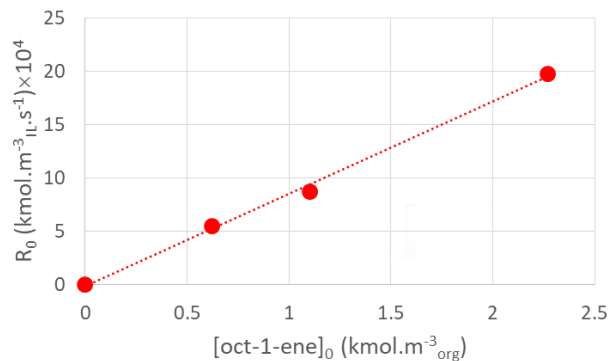
DLS aq ϕ with CCM 1

Towards a kinetic model

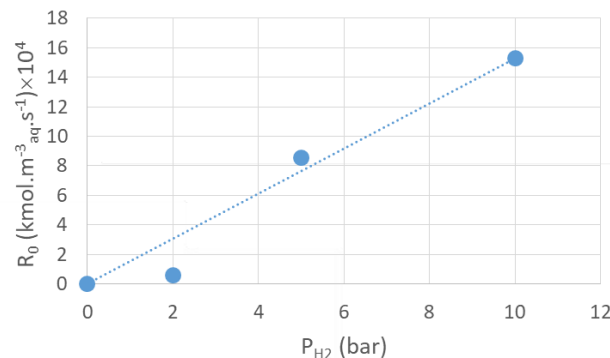
Selection of nanogel with 5% SDPP (pH=7)

Parametric study

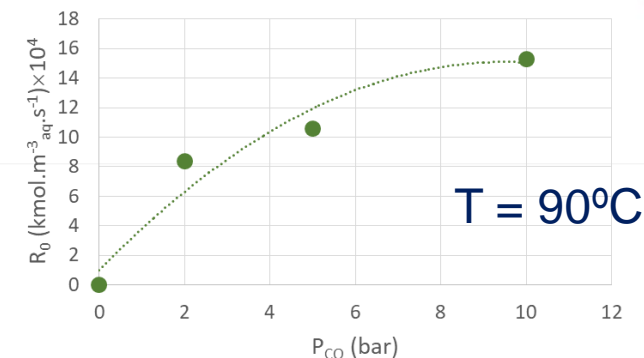
Initial conc. of oct-1-ene



Partial pressure of H₂



Partial pressure of CO



T = 90°C

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

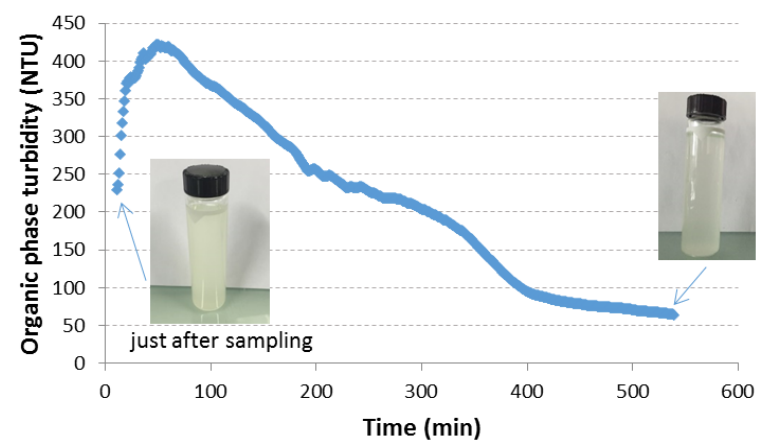
Evaluation of the nanogel composition

- 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)



Dynamics of ϕ separation

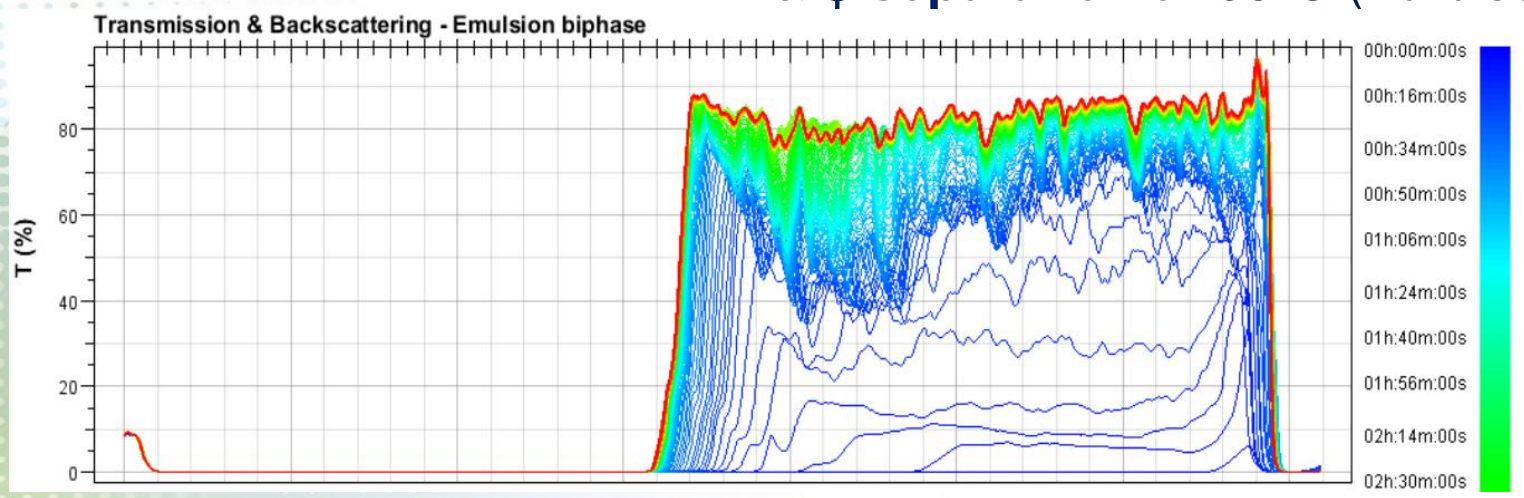
Turbidity evolution



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

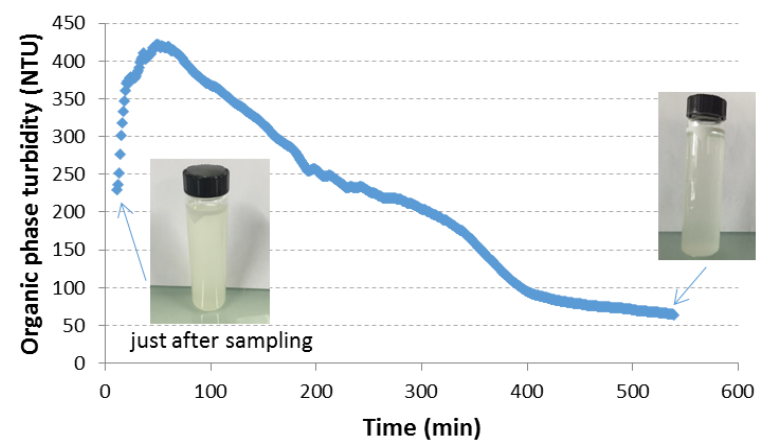
Stability evolution

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



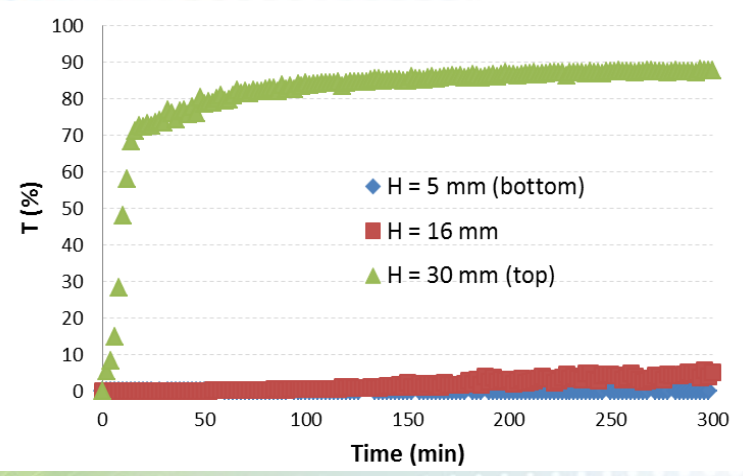
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Stability evolution



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**

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Jean-Louis Labat



Pr. Rinaldo Poli



Dr. Eric Manoury



Dr. Carine Julcour



Dr. Laurie Barthe



Marie Morere



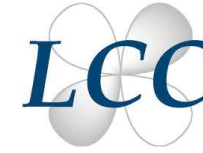
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Dr. Andrés Cardozo



Dr. Florence Gayet



Dr. Si Chen

The teams



Dr. Amit Sharma



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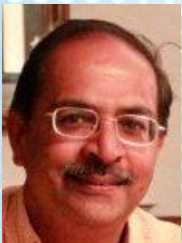
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