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Towards the hydrogenation of oils in monolith reactor: methodology for washcoat development and performance evaluation

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Université
de Toulouse

Significant class of reactions:

for the production of fine chemicals, pharmaceuticals, flavors and fragrances, the conversion of biomass and the processing of raw food

But several issues:

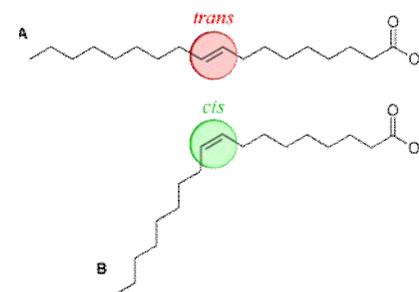
- **fast reactions**, thus prone to mass transfer limitations
- **highly exothermic reactions** ($\Delta H_R \approx -100-130 \text{ kJ/mol}$), resulting in possible thermal hazards
- **selectivity constraints**, due to consecutive reaction scheme and parallel side reactions (e.g. cis-trans isomerization)

ex. in food industry:



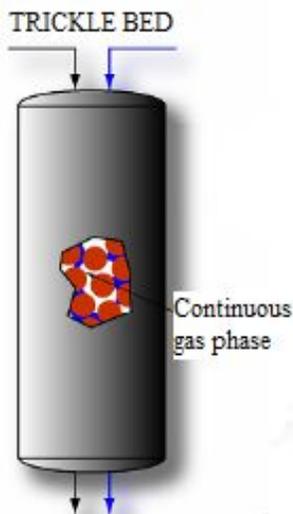
selectivity highly sensible to catalyst type, T & p_{H_2} , but also hydrodynamics & mass transfer limitations

- **need for efficient & sustainable catalysts**



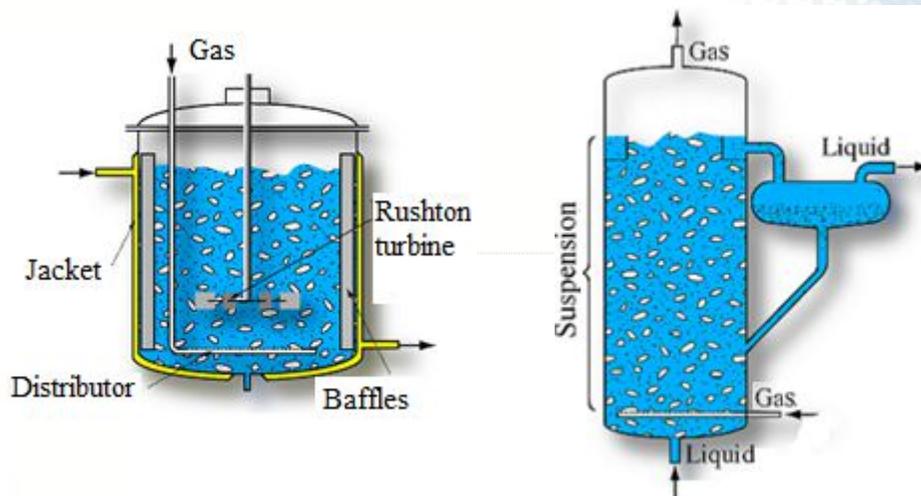
Drawbacks of conventional three-phase reactors:

Fixed bed reactor



- Liquid maldistribution (TBR)
- Partial catalyst wetting (TBR)
- Prone to hot spots and runaway (TBR)
- High resistances to mass transfer
- Limits of use for viscous/foaming fluids
- Plugging, high ΔP for small beads

Slurry reactor



- Uneasy catalyst separation, attrition
- Low ε_S & high mixing
 - * Reduced productivity
 - * Reduced selectivity (promotion of homogeneous side reactions & lower intermediate yields)
- High energy costs (mechanical stirring)

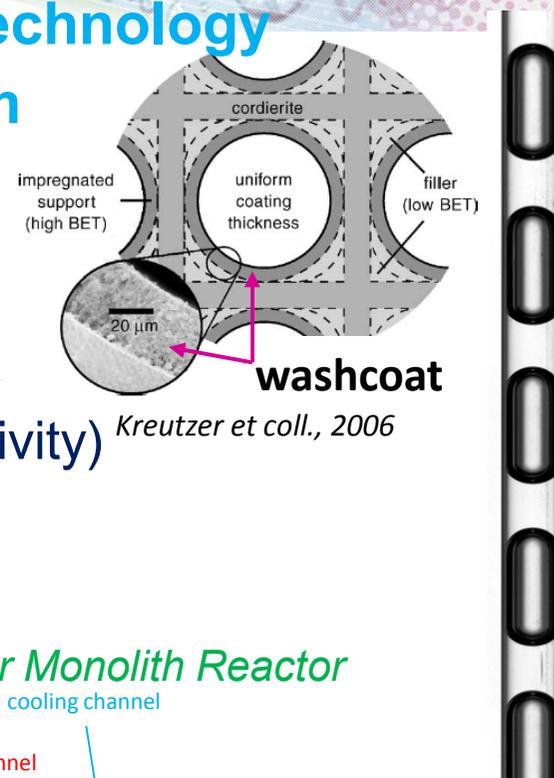
Development of an innovative reactor for three-phase catalytic hydrogenation: HYDROMoRe project (ANR CD2I 2012)

Proposed solution

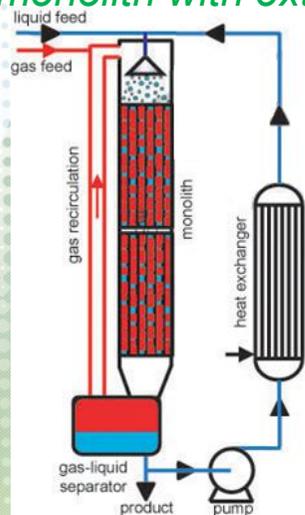
Innovative reactor inspired from monolith technology & equipped with *in situ* heat removal system

Expected features:

- Low ΔP
- Low diffusional limitations (**thin catalytic layer**)
- Good G-L & L-S mass transfer (**Taylor Flow**)
- Plug flow in channels (**TF**, \uparrow productivity & selectivity)
- Fast draining in case of runaway
- + Efficient temperature control (**quasi-isothermal**)

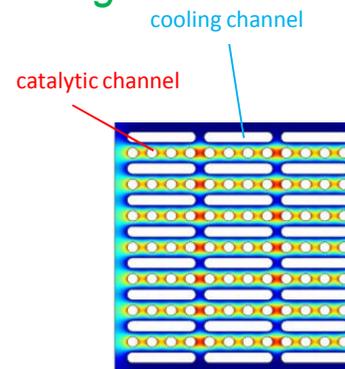


Ceramic monolith with external cooling



Kreutzer et coll., 2006 & US Patents, 1990s

Heat-exchanger Monolith Reactor



Catalytic channel walls:
heat conductive scaffold

Technological issues

Monolith type reactor equipped with *in situ* heat removal system

- Conception of such a reactor with millimeter size channels and metal scaffold?

➤ **Manufacture by selective laser melting (Al alloy)**

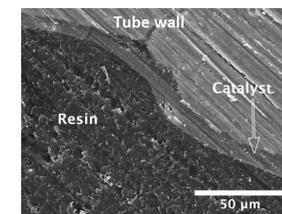
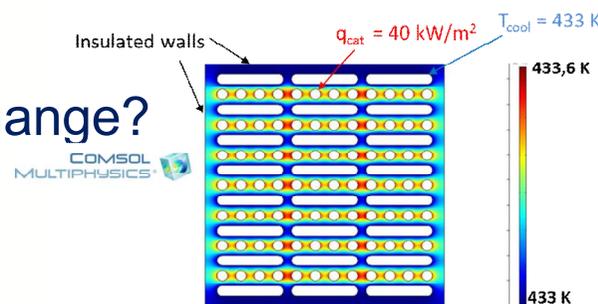


- Catalytic layer adherence, activity & stability?

➤ **Development of synthesis method & exhaustive characterizations**

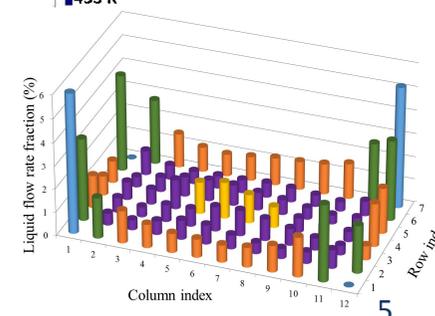
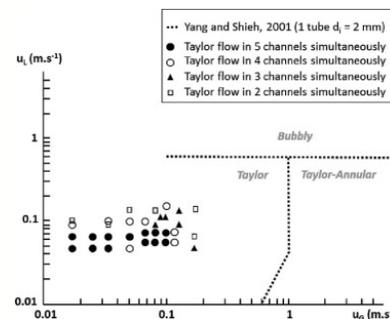
- Reactor design for efficient heat exchange?

➤ **Simulation of thermal behavior**



- Suitable flow regime?

➤ **Design of suitable GL distributor & Experimental characterization of individual channel hydrodynamics (cold mock-up)**



Methodology

Catalytic objects & reactor tools

Continuous reactor

- Efficient heat removal
- Single channel as relevant scale for the proof of concept

with coated jacketed tubes



• Is it enough?

- Overall monolith performance strongly linked to the catalyst activity/selectivity & the hydrodynamic / mass transfer behavior of **individual channels**
- Need for a model that could **discriminate involved phenomena**
- **Intrinsic catalyst performance to be evaluated separately**

Stirred batch reactor

with coated platelets



- 😊 more representative of monolith washcoat
- 😞 need to be recycled for kinetic study (deactivation?)
- 😞 more difficult to characterize (M content)

with catalytic powder



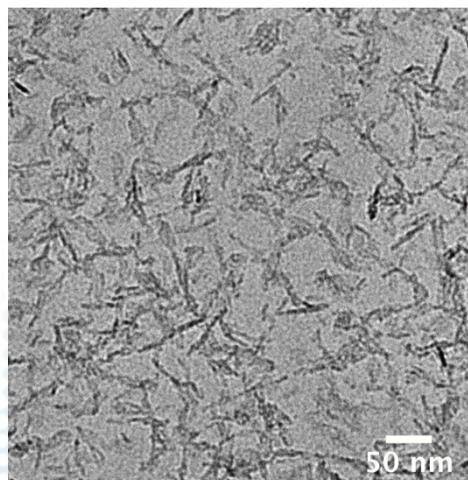
- 😊 homogenous lot, can be extensively characterized
- 😊 size and amount easily modified for kinetic regime
- 😞 same activity as washcoat?



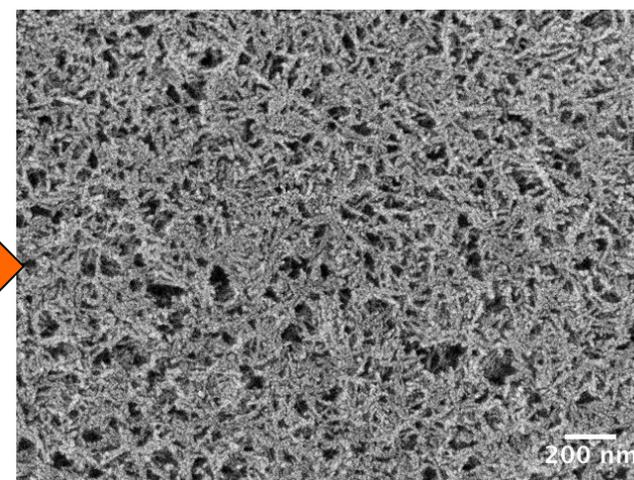
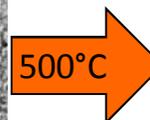
- ❖ Synthesis of colloidal dispersions (sols) of oxide nanoparticles in water
- ❖ Surface area and porosity are tuned through the addition of templating agents
- ❖ Sol deposition on the reactor walls (controlled filling and draining of the channel)
- ❖ Thermal treatment
- ❖ Impregnation with active metal precursor



AlOOH sol



AlOOH nanoparticles



Mesoporous alumina

Specific surface area : 300-500 m² g⁻¹

Average pore size : 5-40 nm

Pore volume : 0.3 - 2.6 cm³ g⁻¹



Impregnation with active metal precursor

1 - Selective impregnation of Pd precursor on support (alumina)

❖ Pd acetylacetonate (Pd-acac) in toluene

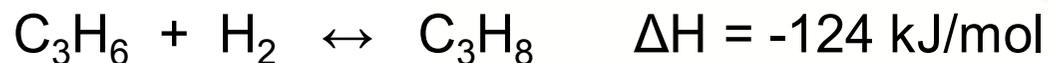
❖ $(\text{NH}_4)_2\text{PdCl}_4$ in water



2 - Drying overnight at 70°C

3 - Activation by thermal treatment in H_2 for 30 min at 250°C

Characterization of catalyst xerogel : propene hydrogenation



Conditions :

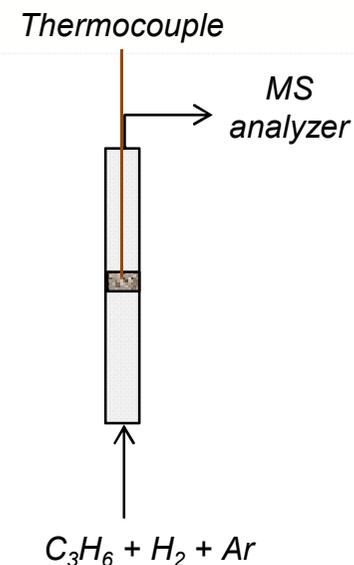
- Gas phase, $P \approx 1 \text{ atm}$
- Composition: 1% C_3H_6 + 1.5% H_2 in Ar
- Flow rate: 100 mL/min, temperature: $\approx 20^\circ\text{C}$
- Mass of catalyst = 10 mg mixed with 90 mg of alumina
- Analysis of outlet gas by mass spectrometry

Parameters :

- Active metal (Pd, Pt, Ru)
- Catalyst support (alumina vs. TiO_2)
- Addition of Pd (direct addition in sol vs. impregnation)
- Pd precursor : $(\text{NH}_4)_2\text{PdCl}_4$, Pd-acac in acetone, Pd-acac in toluene
- Thermal treatment temperature for decomposition (none to 300°C)
- Thermal treatment atmosphere for decomposition (Ar, O_2 , H_2)

Results :

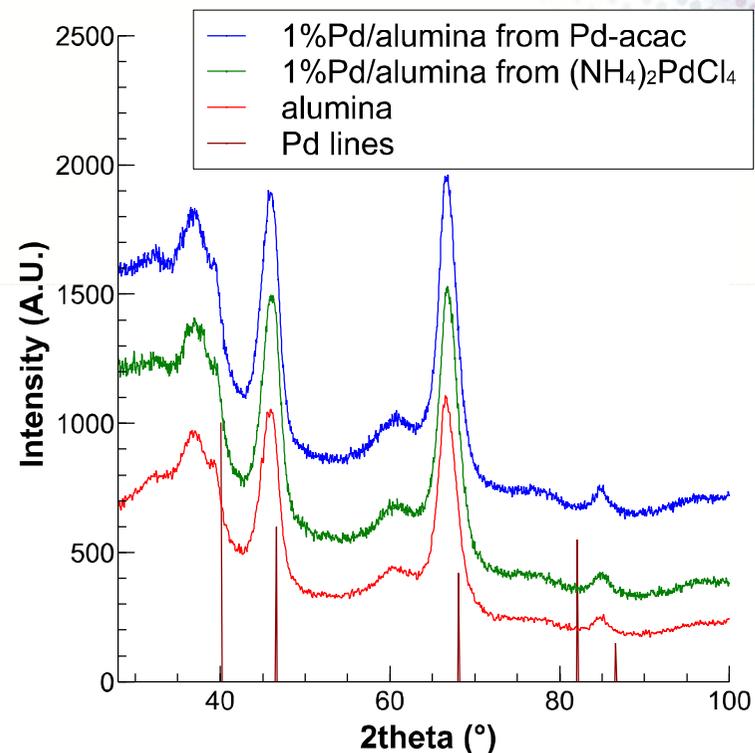
- Activity of catalysts prepared by impregnation \gg direct addition in sol
- Toluene is a better solvent for Pd-acac than acetone
- Pd-acac gives more active alumina supported catalysts than $(\text{NH}_4)_2\text{PdCl}_4$
- With Pd-acac precursor TiO_2 and alumina are equivalent
- Best thermal decomposition conditions = H_2 at 250°C



S_{BET} and V_{pore} are determined from adsorption isotherms of N_2 at 77.4 K

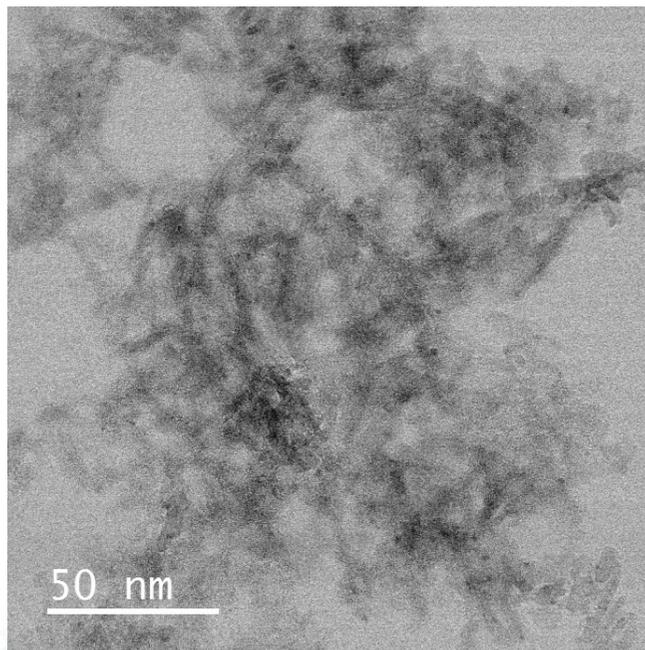
Xerogel	S_{BET} (m ² /g)	V_{pore} (mL/g)
Alumina	320 ± 20	1.2 ± 0.1
1%Pd/alumina from Pd-acac	320 ± 20	1.2 ± 0.1
1%Pd/alumina from $(\text{NH}_4)_2\text{PdCl}_4$	310 ± 20	1.2 ± 0.1

Negligible effect of impregnation on texture

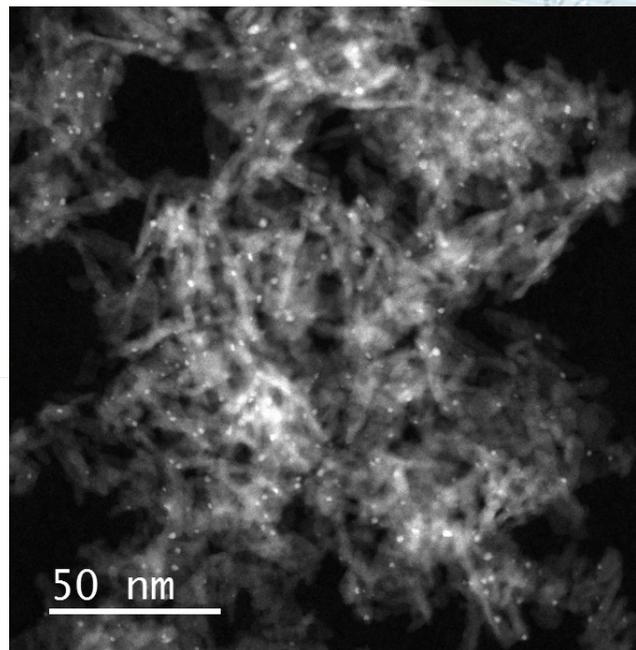


Crystallite size of Pd < 5 nm

Characterization of catalyst xerogel : TEM



TEM : bright field image

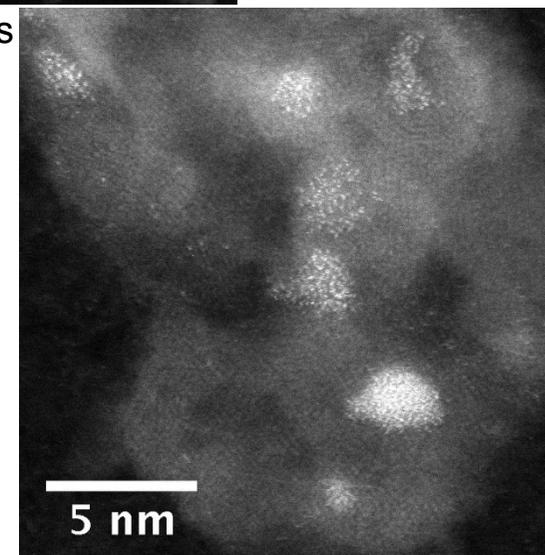


STEM : dark field images

Catalyst : 1%Pd/alumina (from Pd-acac)

activated in H₂ for 30 min at 250°C

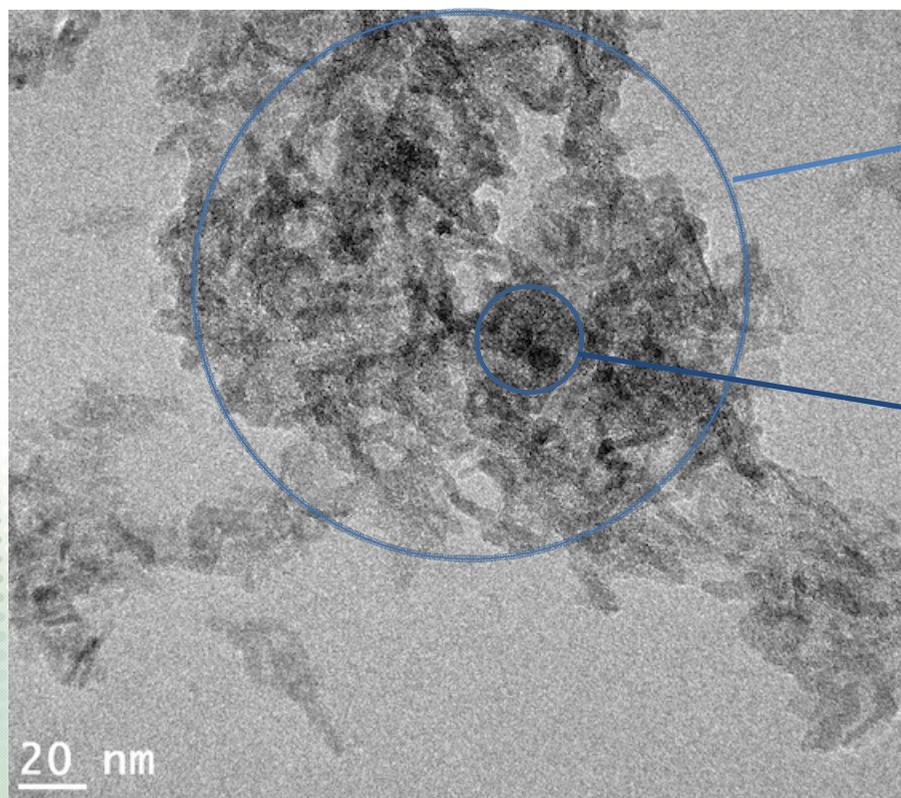
Microscope JEM-ARM200F Cold FEG



Characterization of catalyst xerogel : TEM

Catalyst : 1%Pd/alumina (from $(\text{NH}_4)_2\text{PdCl}_4$) activated in H_2 for 30 min at 250°C

Microscope JEM-2100F

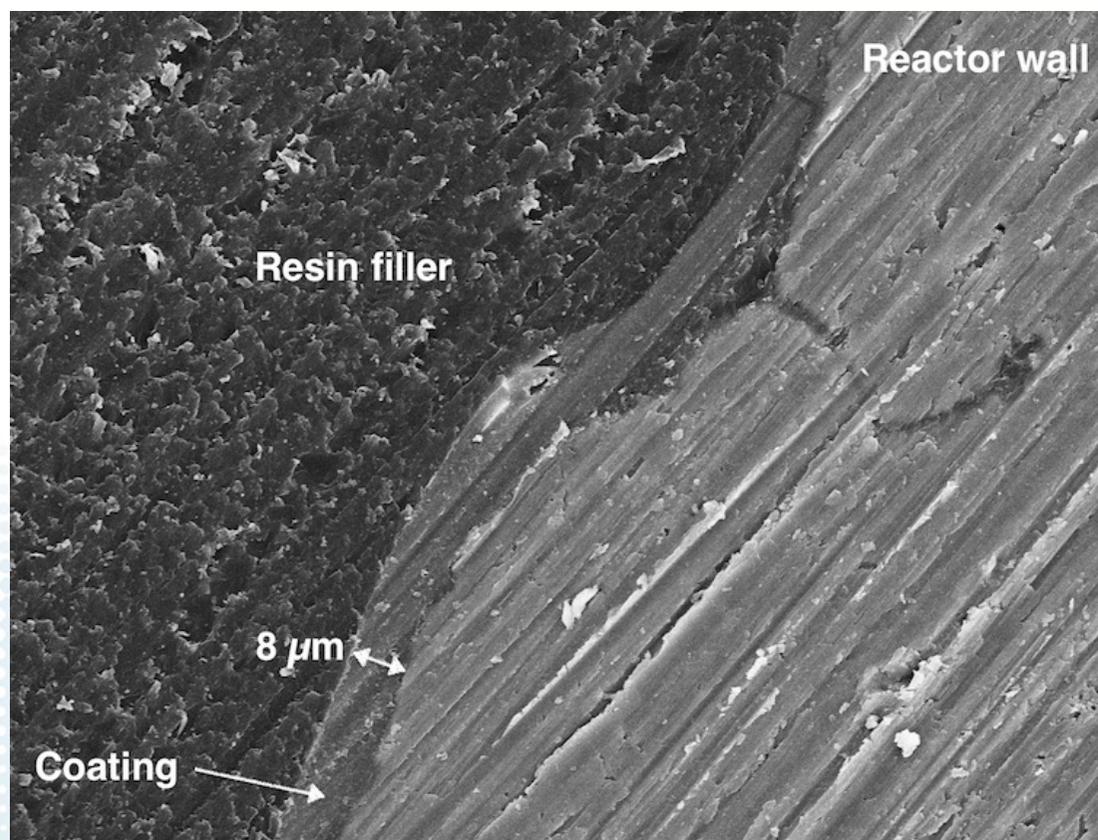
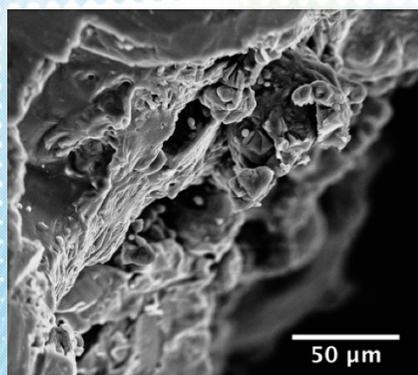
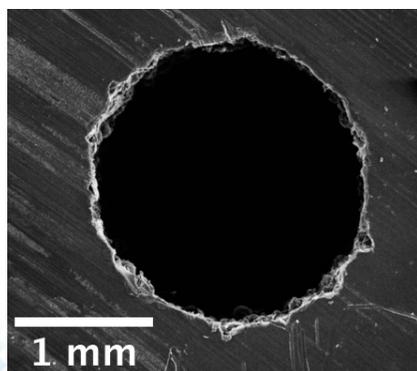


EDX analysis
gives 1%Pd

EDX analysis
gives 1.7%Pd

Determination of uniformity and thickness of the coating

- 1 - Filling the tube with epoxy resin
- 2 - Inspection by SEM of cross sections



The coatings are well anchored, no loss was observed after adhesion tests

Coated amount of alumina (m/S) was evaluated by weighting

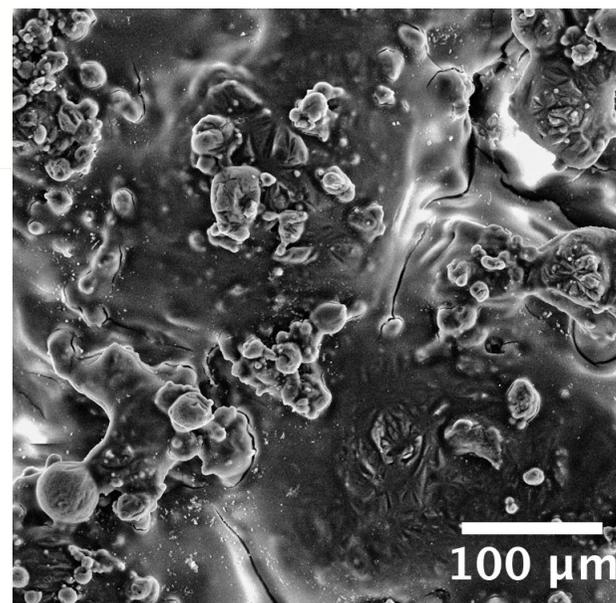
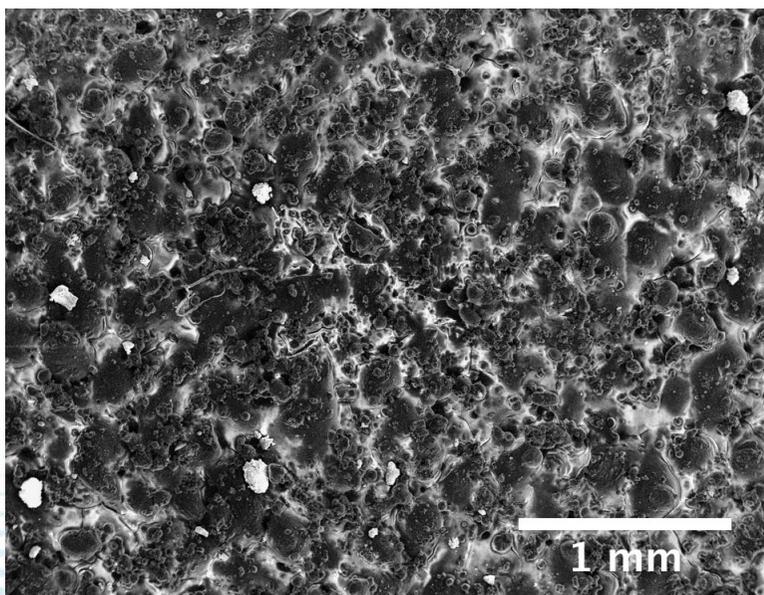
Substrate	Coated mass (mg)	m/S (g/m ²)
Al3003 platelets	3.6 ± 0.3	2.6 ± 0.2
AlSi10Mg platelets (SLM)	9.1 ± 0.3	3.8 ± 0.1
AlSi10Mg monotubes (SLM)	17 ± 5	14 ± 4

Surface area was determined from adsorption isotherms of Kr at 77.4 K

Substrat	Coated mass (mg)	Measured Surface (m ²)	Specific Surface Area (m ² /g)
AL3003 platelet	4	1.2	300
¼ AlSi10Mg monotube (SLM)	4	1.1	280

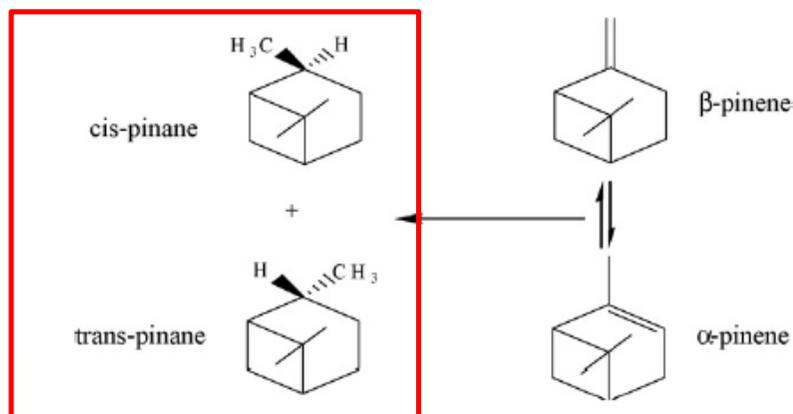
EDS analyses done on SLM platelets after catalytic hydrogenation of α -pinene

- Check if the coating was damaged by the catalytic test
- Element analysis of Pd and S



EDS analysis	S (wt.%)	Pd (wt.%)
Plate #1	0.33 ± 0.01	1.2 ± 0.3
Plate #2	0.0	1.6 ± 0.1
Plate #3	0.0	1.6 ± 0.3

α -pinene hydrogenation:



Typical operating conditions:

p_{H_2} = 1-100 bar, T = 50-200°C,
 pure or diluted pinene (P),
 Ni or noble metal catalyst

cis/trans selectivity reduced by an increase in temperature, but favored by increasing hydrogen pressure up to 10 bar (negligible effect beyond)

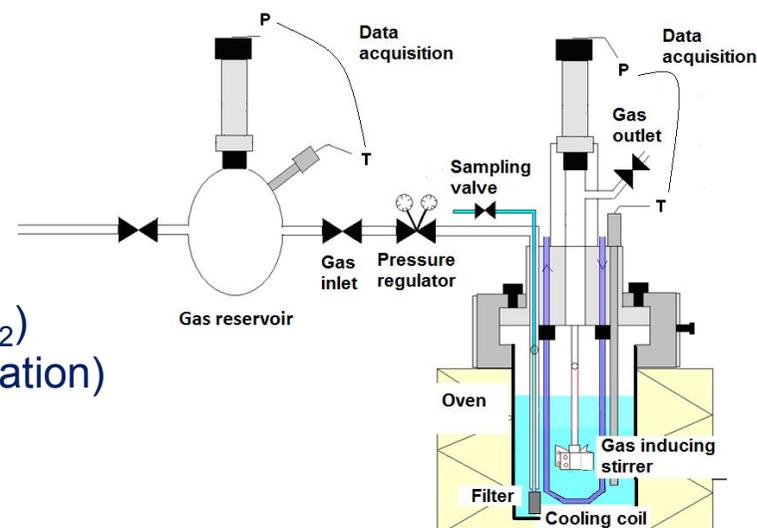
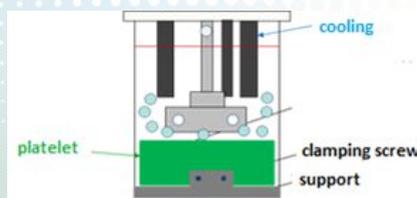
[Il'ina et coll., 2002; Simakova et coll., 2009; Wang et coll., 2015]

Kinetic investigation:

Stirred autoclave reactors (100 & 250 mL)
 with **gas ballast & addition funnel**

- Controlled atmosphere (p_{H_2}) and T
- Gas auto-dispersing stirrer (1200 rpm)
- Continuous recording of H_2 consumption (R_{0,H_2}) + GC/FID analysis of L samples (product speciation)

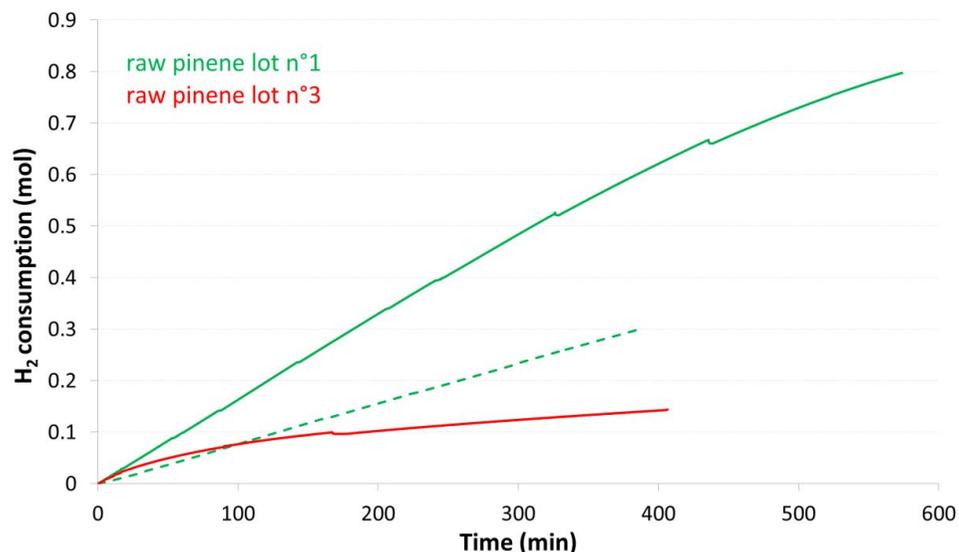
Catalytic platelet
 (5-20 mg of coating)
 or **powder** (5-50 mg)



Application to 3 ϕ system

Deactivation issue

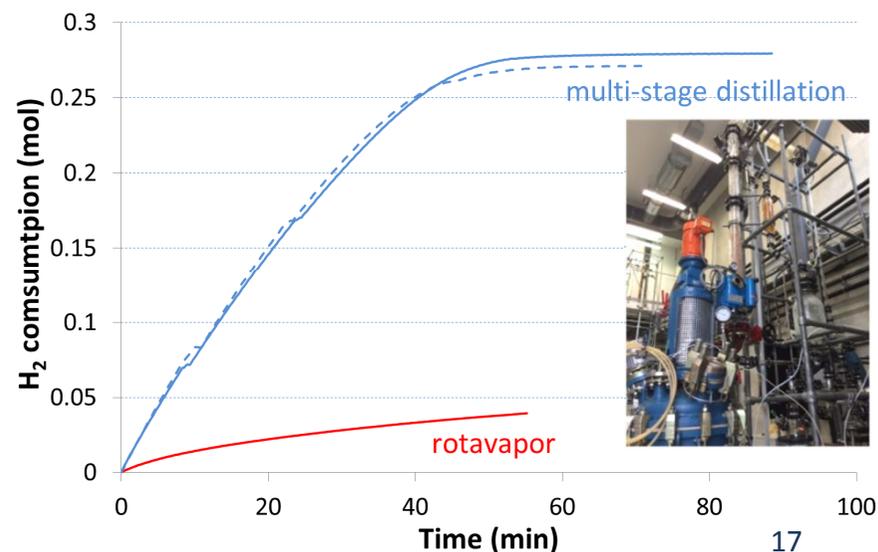
Preliminary tests (catalytic platelets):



- Deactivation during the reaction or under recycling (---)
- Sulfur compounds and water traces initially suspected, but S content < 0.4 ppm ∇ pretreatment of pinene, and molecular sieve not effective

Tests after distillation of raw pinene (powder):

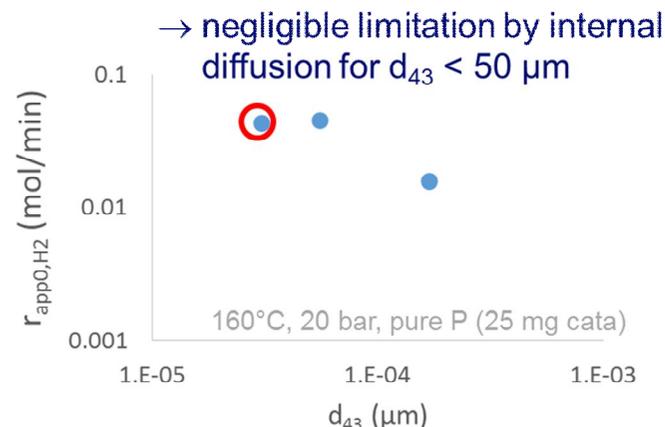
- Significant improvement of catalyst stability after batch **multi-stage distillation of pinene** (100 mbar)
- **Reproducible tests** (---)
- Deactivation by pinene oxidation products?



Pinene hydrogenation

Kinetic study (with powder):

- Experimental verification of **kinetic regime** (G-L mass transfer & internal diffusion)



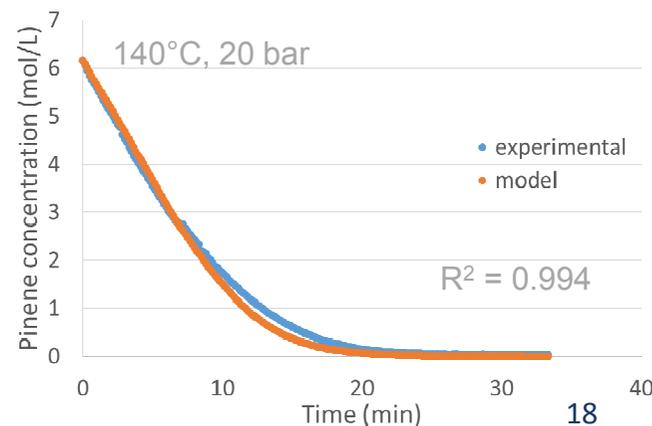
- **Experimental database:** $T = 100\text{-}160^\circ\text{C}$, $p_{\text{H}_2} = 10\text{-}30 \text{ bar}$, $C_P = 1.5\text{-}6 \text{ mol/L}$, 50 mL liquid, 25 mg cata ($d_{43} = 30 \mu\text{m}$) → 18 experiments
 - **Parameter study:** “apparent” E_A & react° orders in accordance with literature values
 - **Reaction selectivity:** < 5% of β -pinene, cis-pinane selectivity: 60-70%
- Evolution with T & p_{H_2} in accordance with literature trends

Modelling of intrinsic hydrogenation rate:

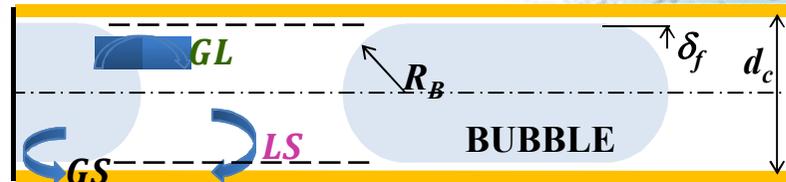
- Model discrimination & parameter estimation based on R_{0, H_2} then **complete kinetic curves**
- **Selected model:**

$$R_{\text{H}_2} = \frac{kK_{\text{H}_2}K_P P_{\text{H}_2} C_P}{(1 + \sqrt{K_{\text{H}_2} P_{\text{H}_2}} + K_P C_P)^3}$$

(dissociative adsorption of H_2 , surface reaction as rate-determining step)

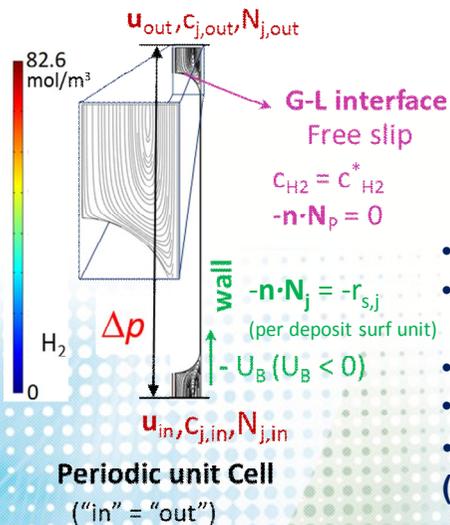


Capillary reactor modelling



Complex interplay in between mass transfer, local hydrodynamics & catalytic reaction

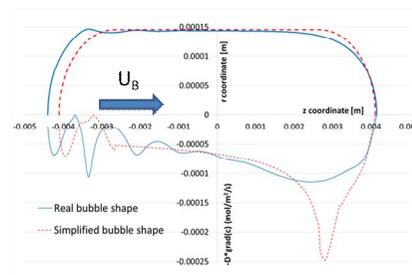
CFD model:



- Transient calculation
- No limitation by internal diffusion ($e_{wc} \sim 10 \mu\text{m}$)
- Isothermal cell
- Constant bubble shape & ϵ_G
- **1-phase or 2-phase calculations** (\rightarrow relevant bubble shape)

Individual mass transfer coefficients in agreement with literature, except k_{LS} for α -pinene (resistance underestimated by tested correlations)

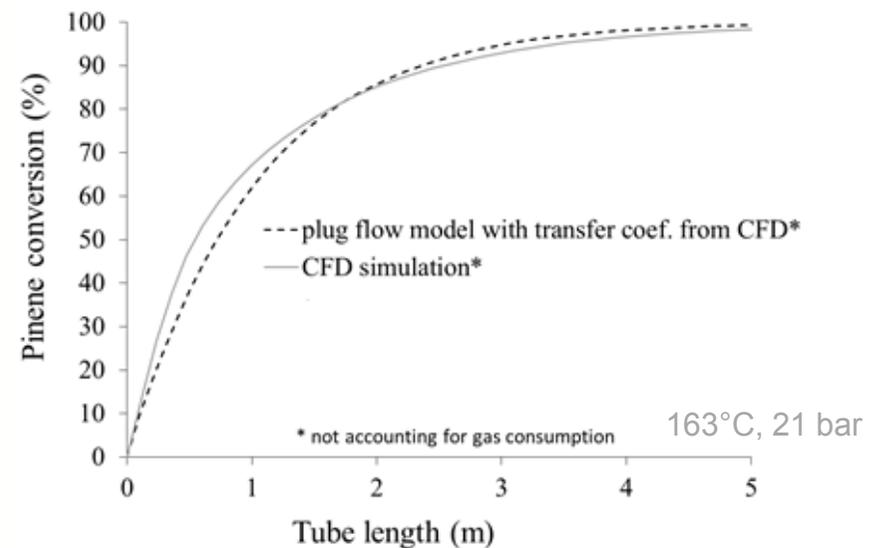
Similar behavior of CFD & 1D models with adequate mass transfer coefficients



1D heterogeneous model:

Plug flow model describing external mass transfer resistances

\rightarrow can easily account for the effect of H_2 consumption

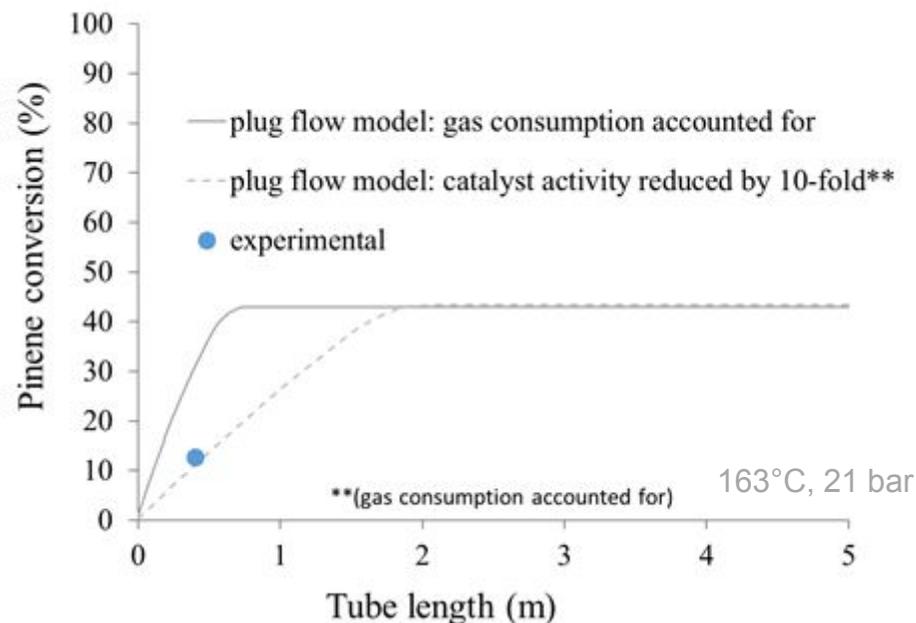


Comparison to reactor data & open questions

➤ Too optimistic predictions vs. measured conversion



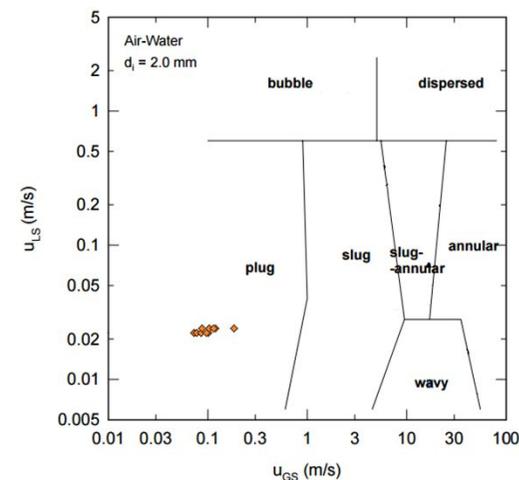
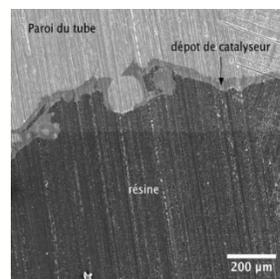
Rem: cis-pinane selectivity= 35-70%



➤ Possible hypotheses:

- Taylor regime? (initial high ϵ_G ? effect of wall roughness?)
- Overestimated $k_L a$ value? (geometry effect, arbitrary L_{UC})
- Impact of catalyst deactivation?
- Different activity of washcoat & powder?

Any suggestions?



20

Acknowledgements



Agence Nationale de la Recherche
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Total Oil & Gas company,

Our students & collaborators (*F. Durán-Martínez, M. Brun-Kreczman, L.S. Garcia Landois Fernandez, C. Leleu*),
for their valuable contribution;

Our technical staff: J. Labadie, J.L. Labat, B. Boyer & I. Coghe,
for designing & setting up the reactor pilots

Thank you for your kind attention!