Gas-phase deposition (ALD) for highly efficient preparation of catalysts

J. Ruud van Ommen
Product & Process Engineering (www.ChemE.nl/ppe), ChemE
Delft University of Technology, the Netherlands
j.r.vanommen@tudelft.nl

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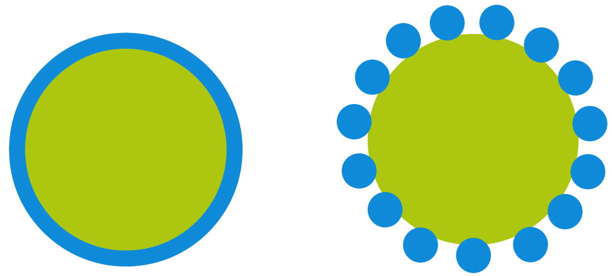
Introduction: ALD on fluidized powders

Efficiency of precursor usage

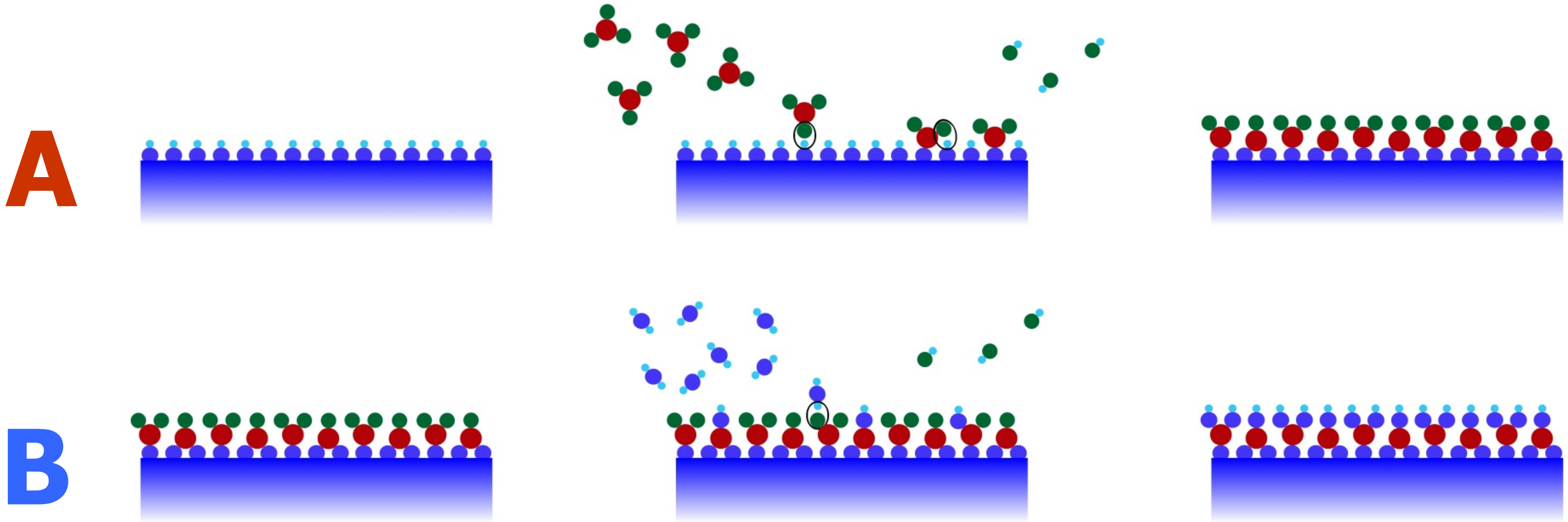
Batch and continuous reactor technology

Application examples

Atomic Layer Deposition (ALD) on Powders



ALD: a gas-phase deposition technique with sub-nm control



A – B – A – B – A – B – A – B – ... etc.

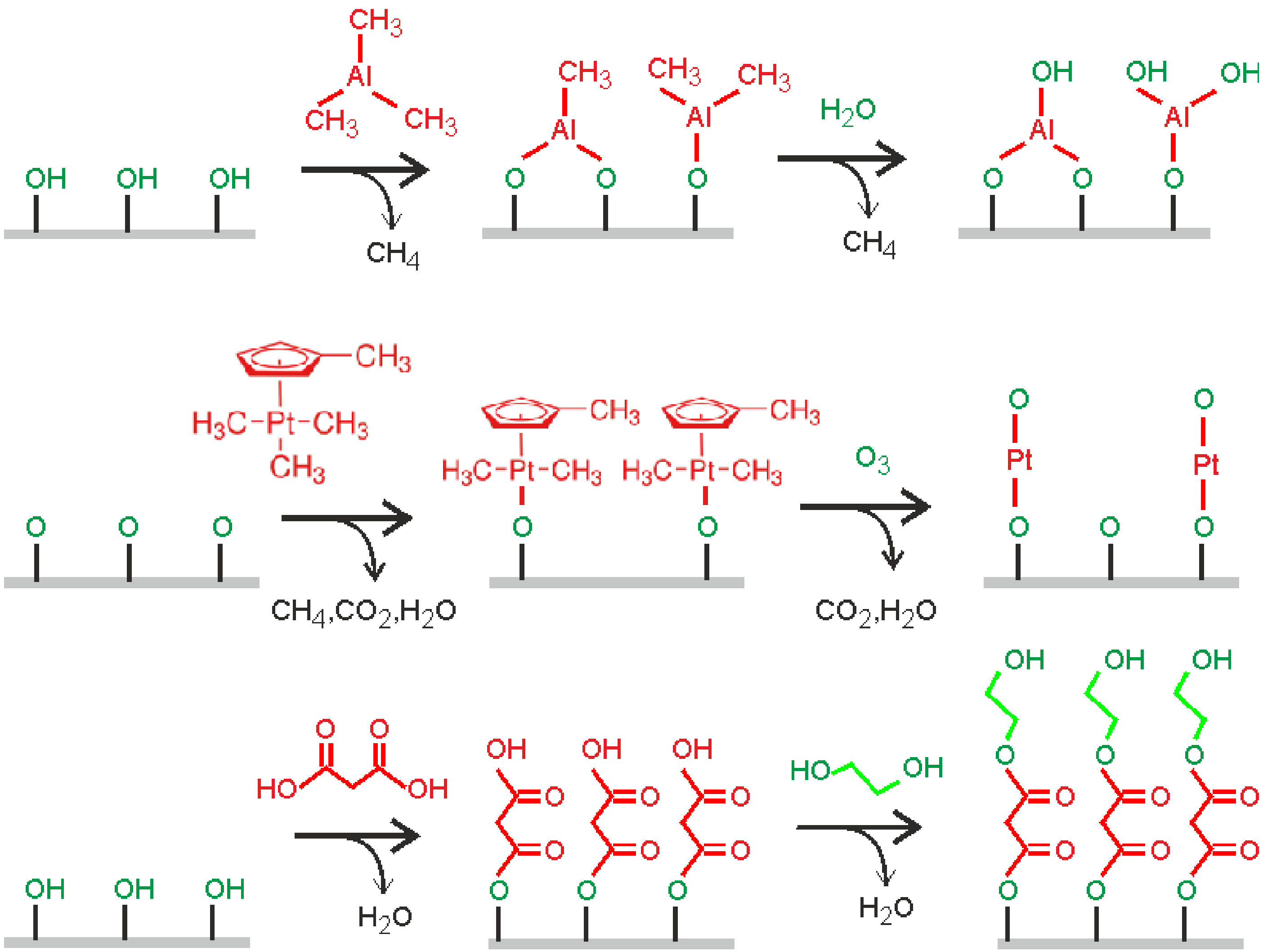
Number of cycles determines layer thickness

Chemistry of ALD

Al_2O_3

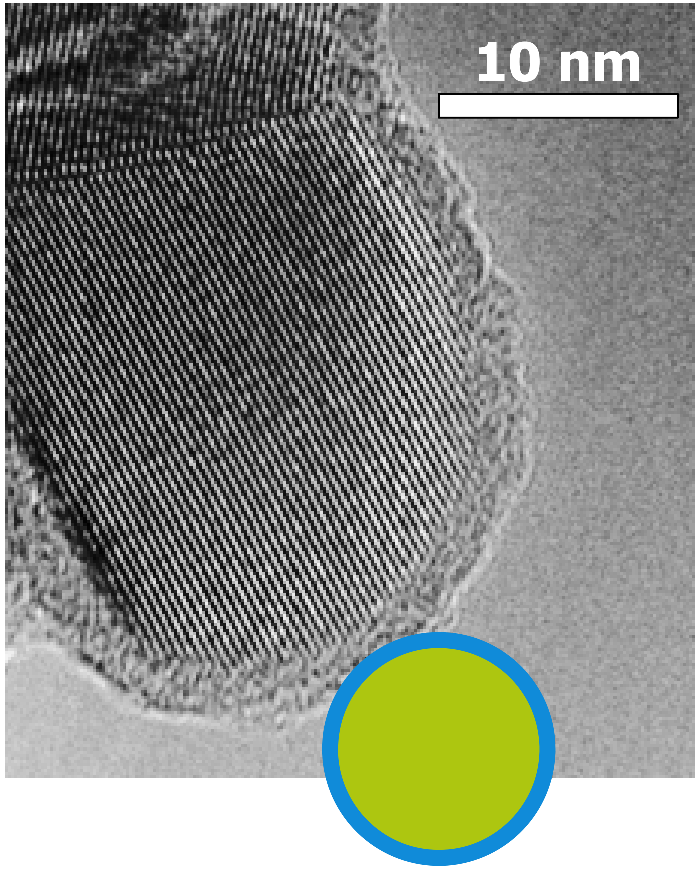
Pt

Polyester (molecular layer Deposition, MLD)

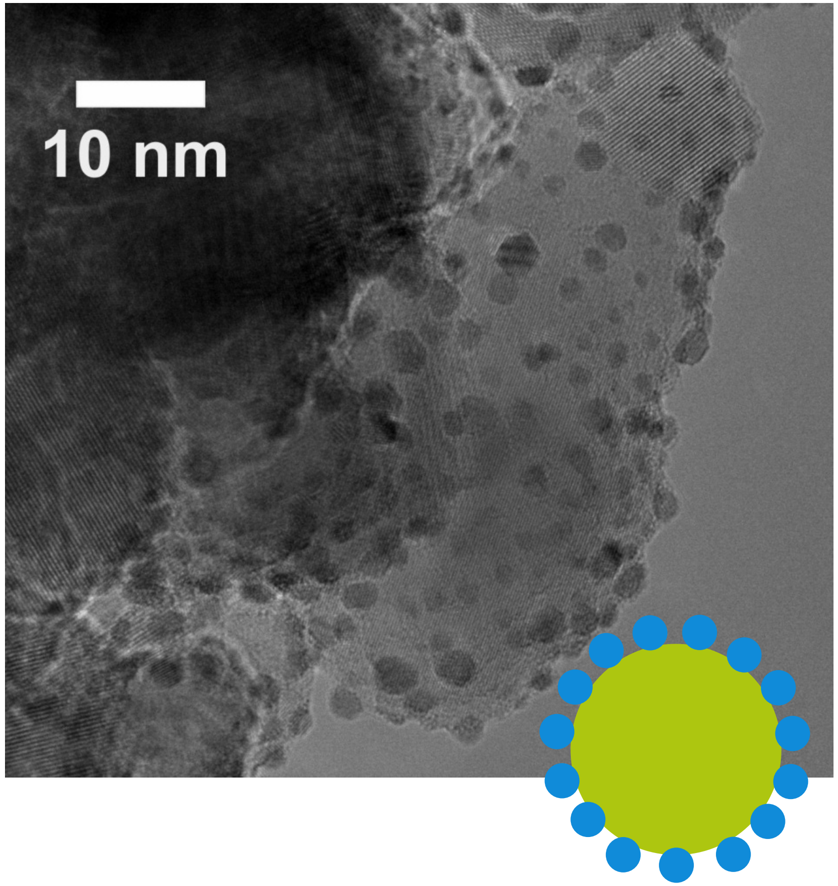


Film growth / island growth on (nano)particles

Al_2O_3 film ~ 3 nm



Pt clusters ~ 2 nm

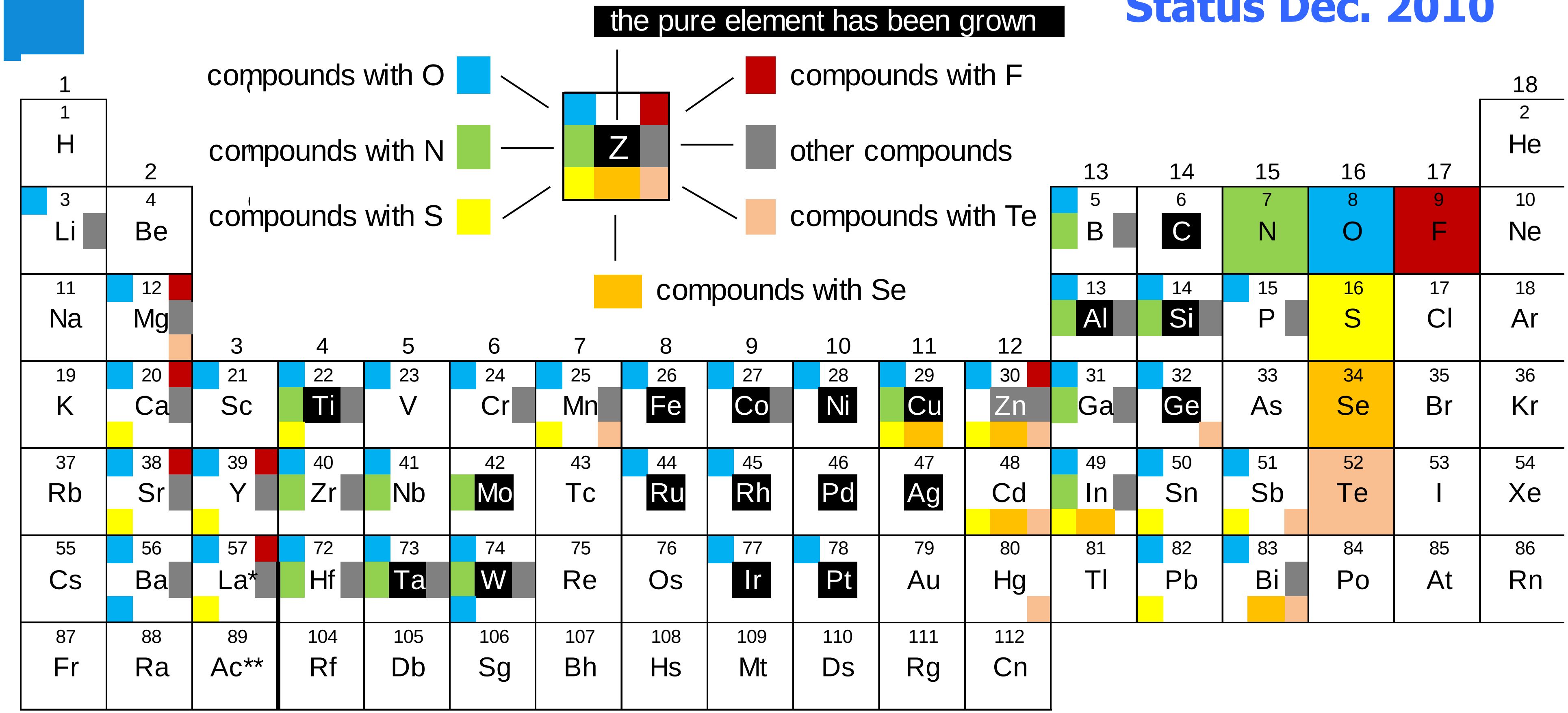


Wide range of coatings possible

'Periodic table of ALD'

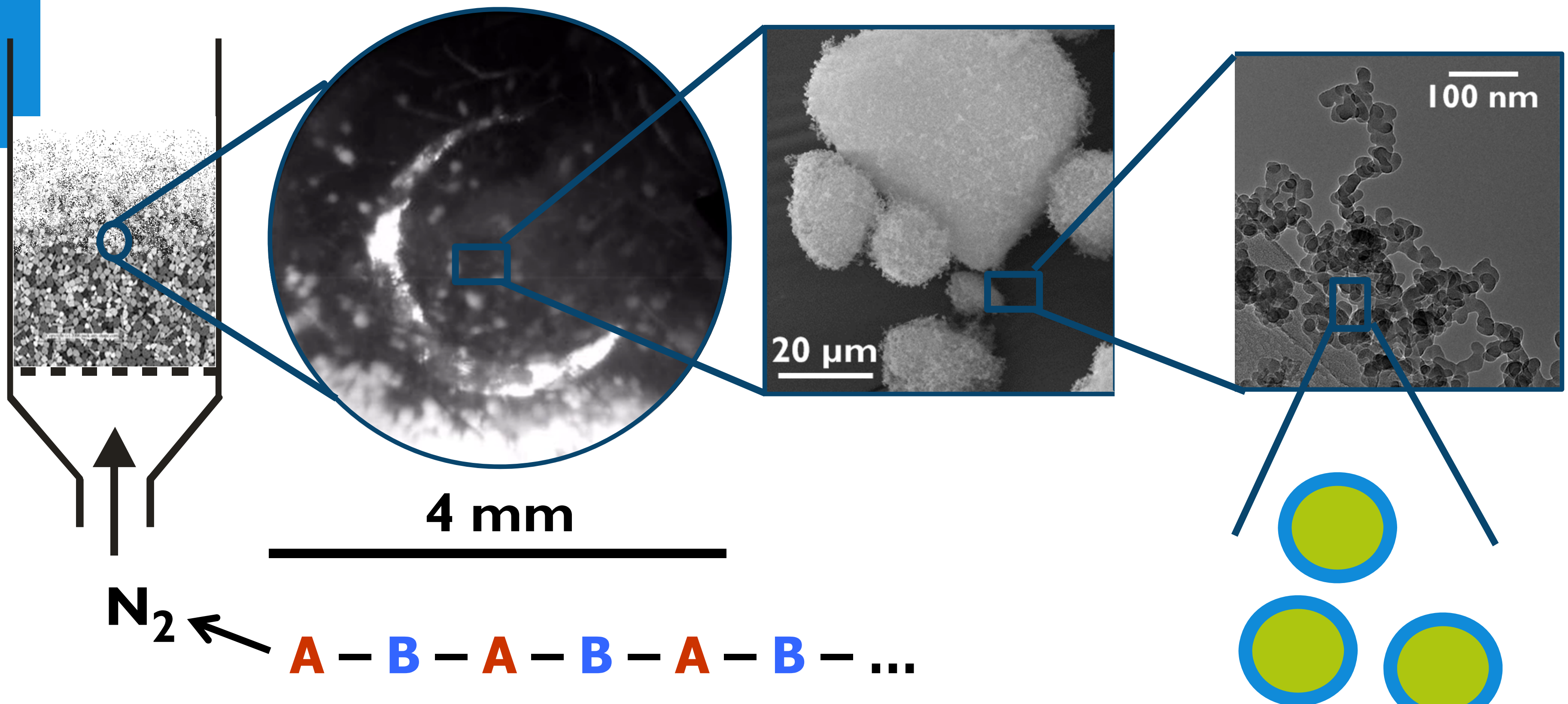
Miikkulainen et al., J. Appl. Phys. 113 (2013) 021301

Status Dec. 2010



Mostly applied to flat substrates (semiconductor industry)

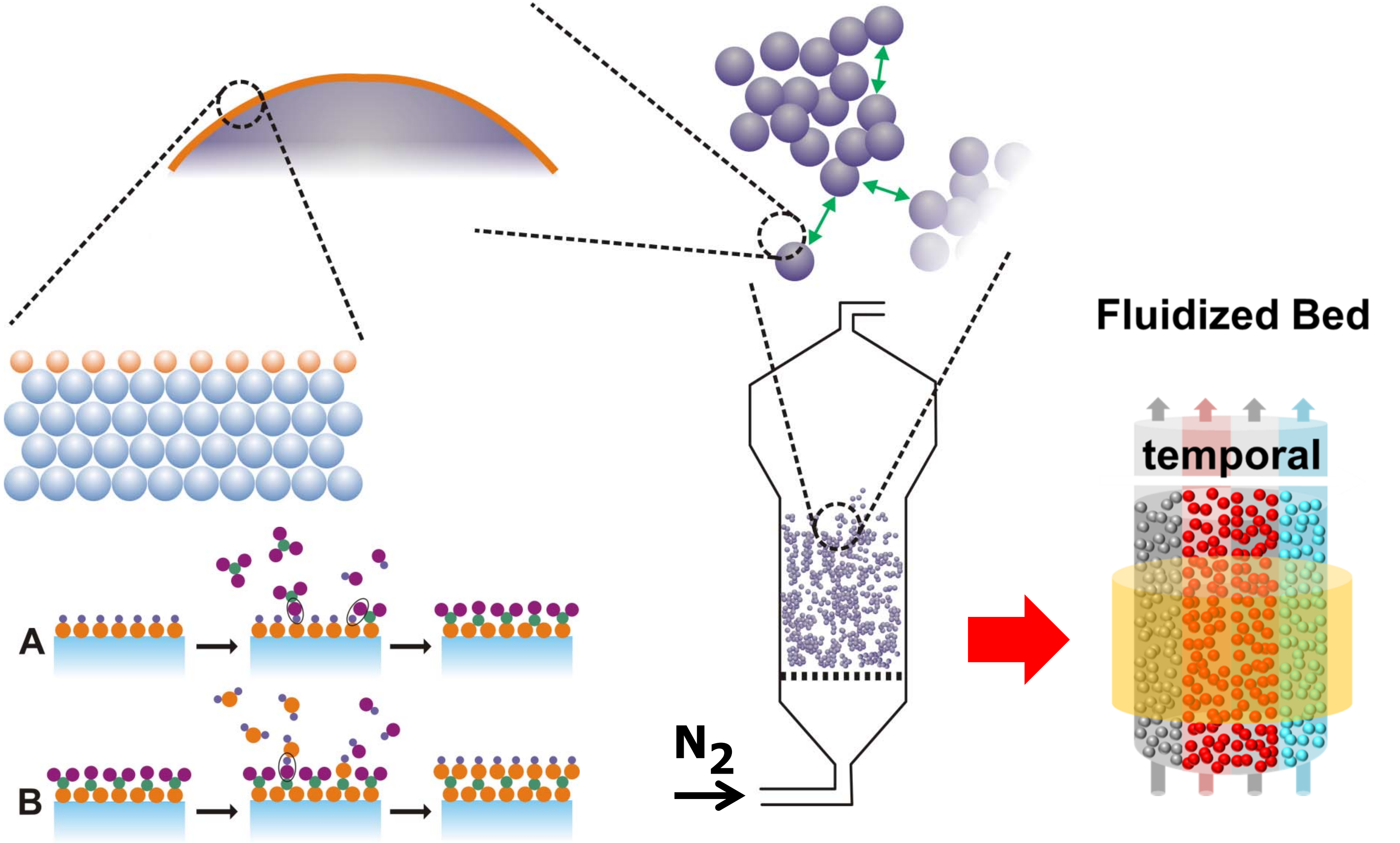
Fluidization of nanoparticles



van Ommen et al., J Nanoparticle Res 14 (2012) 737

De Martín et al., J Nanoparticle Res 15 (2013) 2055

Fluidized bed reactor for ALD



Yakovlev, Malygin et al., J Appl Chem USSR 52 (1979) 959

Hakim, Weimer et al., Chem. Vap. Dep. 11 (2005) 420 (1 mbar)

Beetstra, van Ommen et al., Chem. Vap. Dep. 15 (2009) 227 (1 bar)

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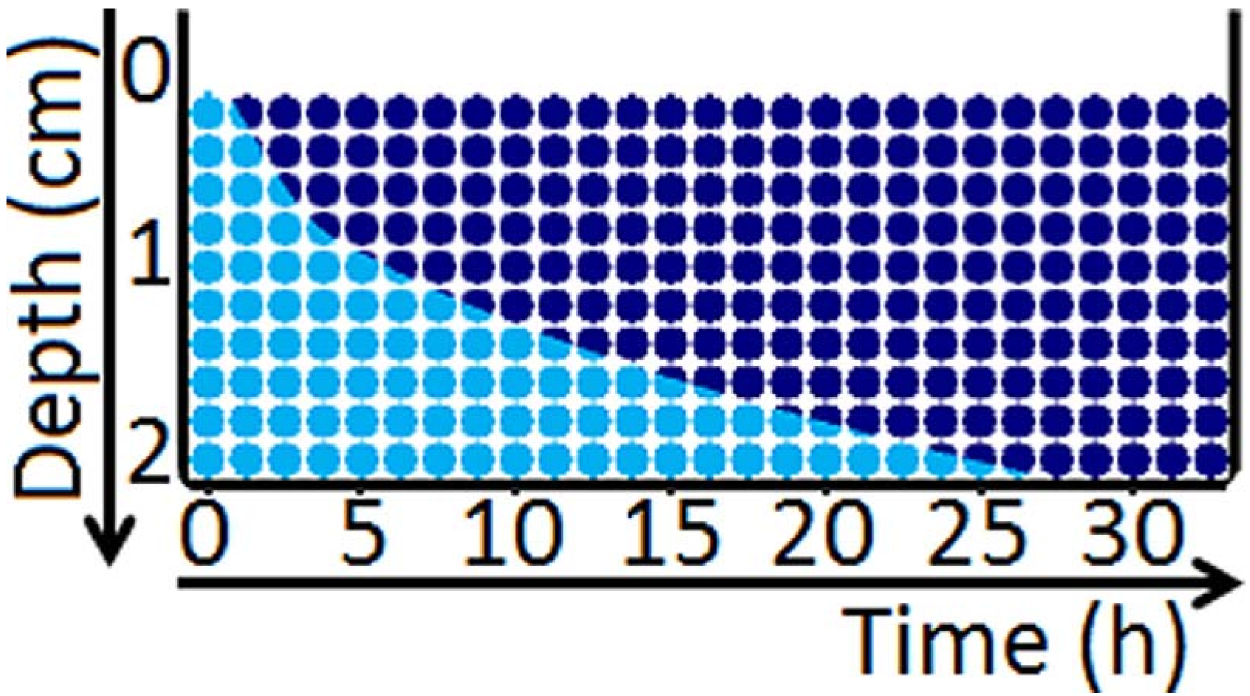
Packed particle bed not efficient!



Longrie et al., J. Vac. Sci. Technol. A 32 (2014) 010802

Amount of waste produced

$$E - \text{factor} = \frac{\text{mass of waste}}{\text{mass of desired product}}$$

Industry segment	Annual product throughput [log kg]	E-factor [-]	Typical amount of waste [kg]
Oil refining	8-10	~0.1	1E8
Bulk chemicals	7–9	<1–5	2E8
Fine chemicals	5–7	5–50	1E7
Pharmaceuticals	4–6	25–>100	5E6
Nanomaterials	2–3	100–100,000	1E6

Sheldon, Green Chem (2007); Eckelman, J. Ind. Ecol (2008)

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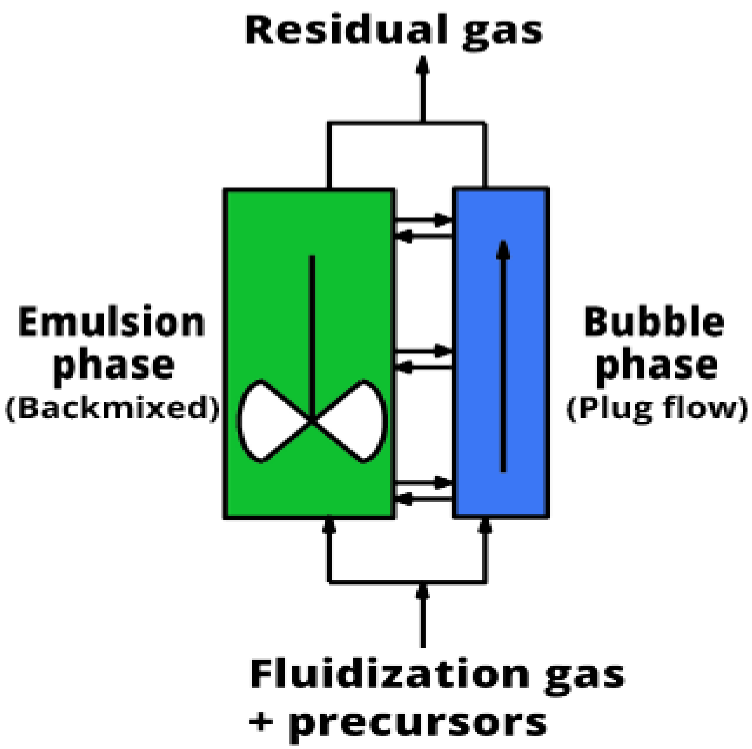
Pharmaceuticals	4–6	25–>100	5E6
Nanomaterials	2–3	100–100,000	1E6
Particle ALD	?	**1-10**	

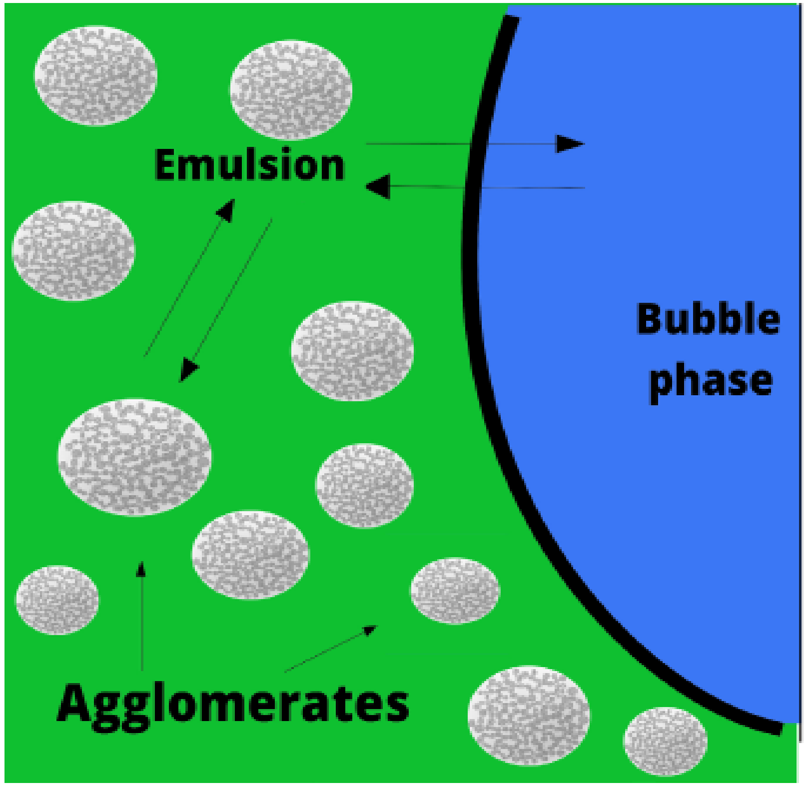
TU Delft Goulas & van Ommen, KONA Powder and Particle J. 31 (2014) 234

Modelling precursor usage

Objective: assessing the precursor utilization efficiency

Conservative assumption: CSTR + PFR; re-agglomeration not considered





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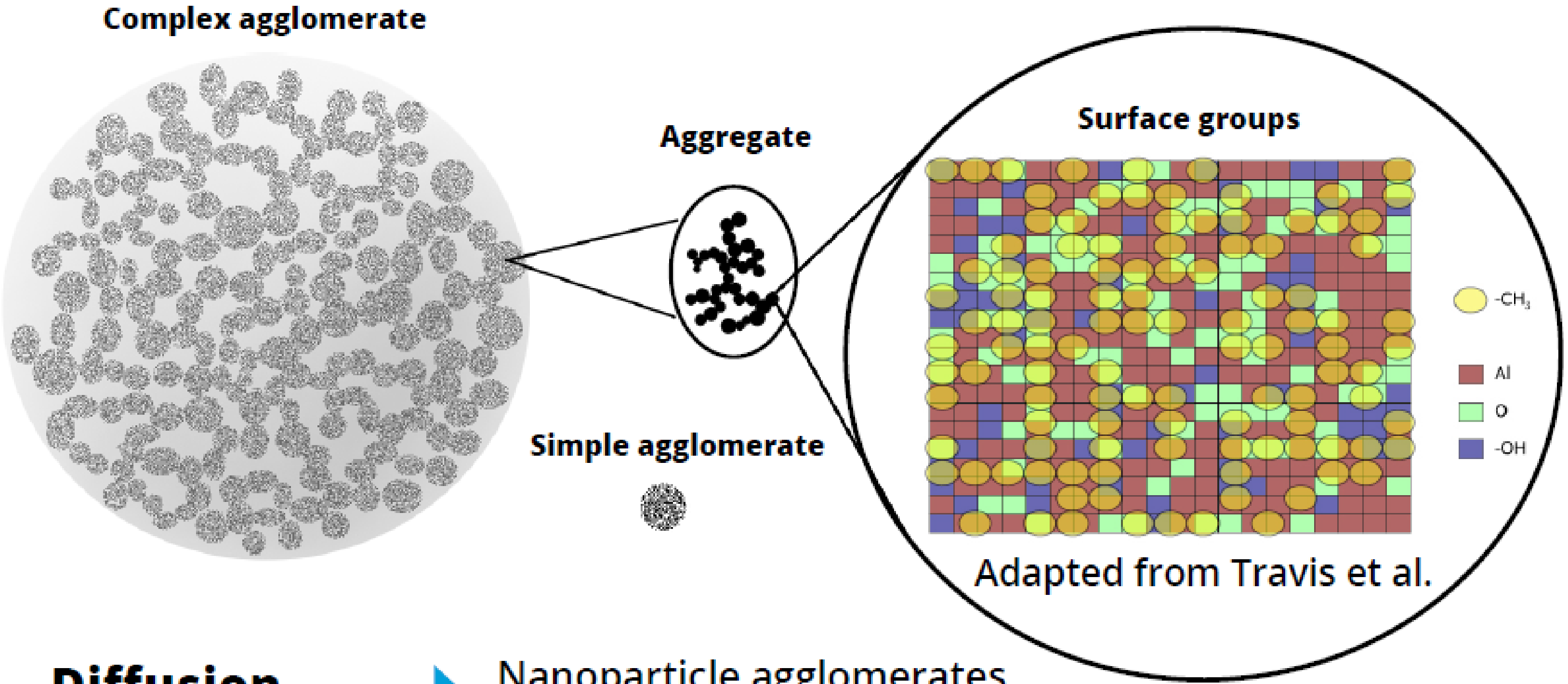
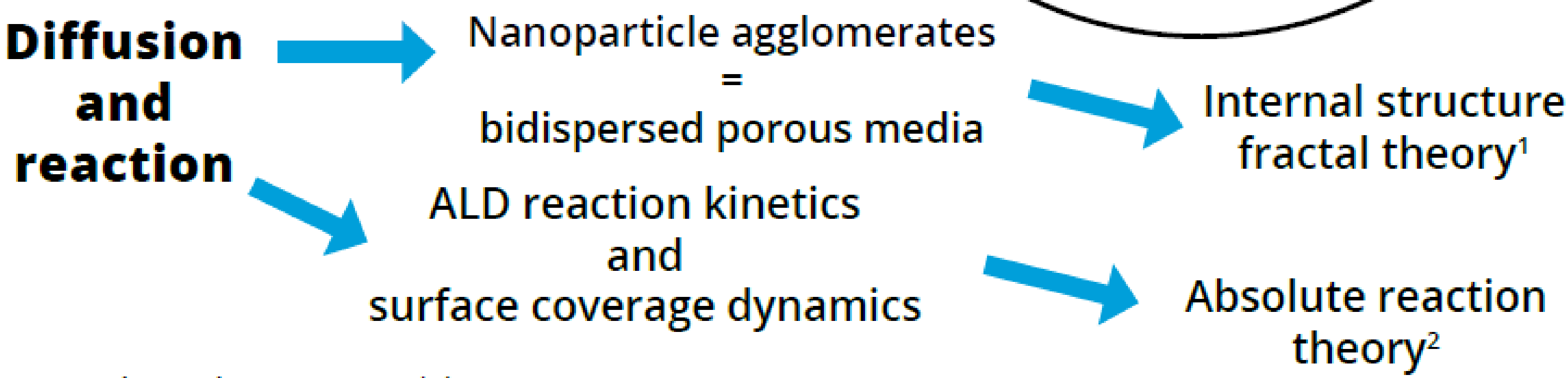
Paper in preparation: Grillo et al.

Modelling precursor usage

Microscale and surface coverage dynamics

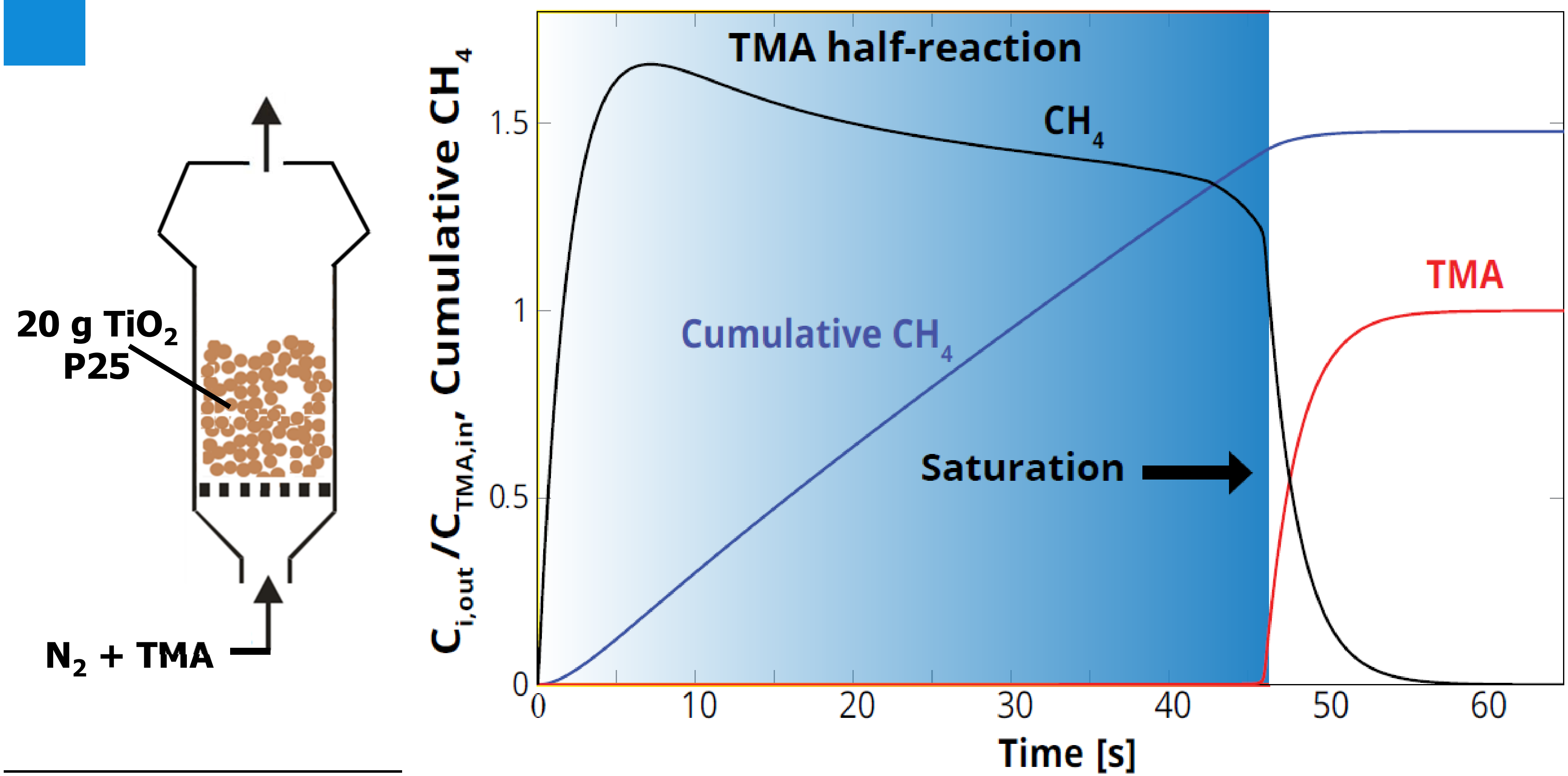




[1] De Martín et al., J Nanoparticle Res 15 (2013) 2055
[2] Travis et al., Chem. Vap. Deposition 19 (2013) 1521-3862

Simulation of residual gas analysis

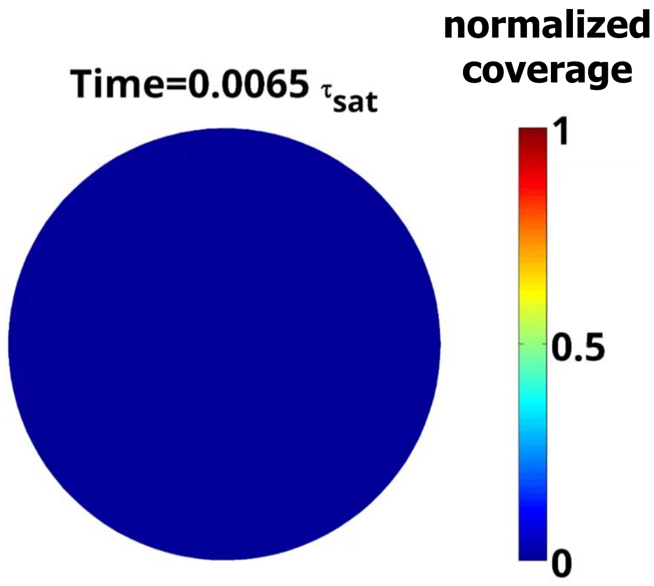
1 bar



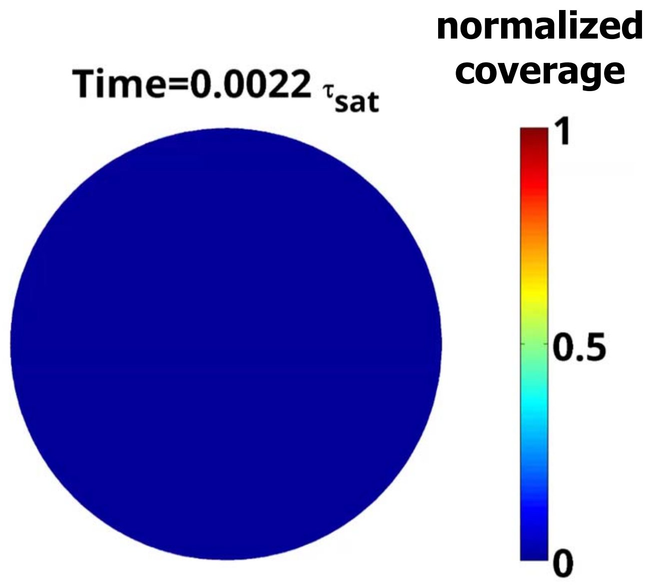
-CH_3 surface coverage inside NP agglomerate

Agglomerate diameter: 300 μm

1 mbar

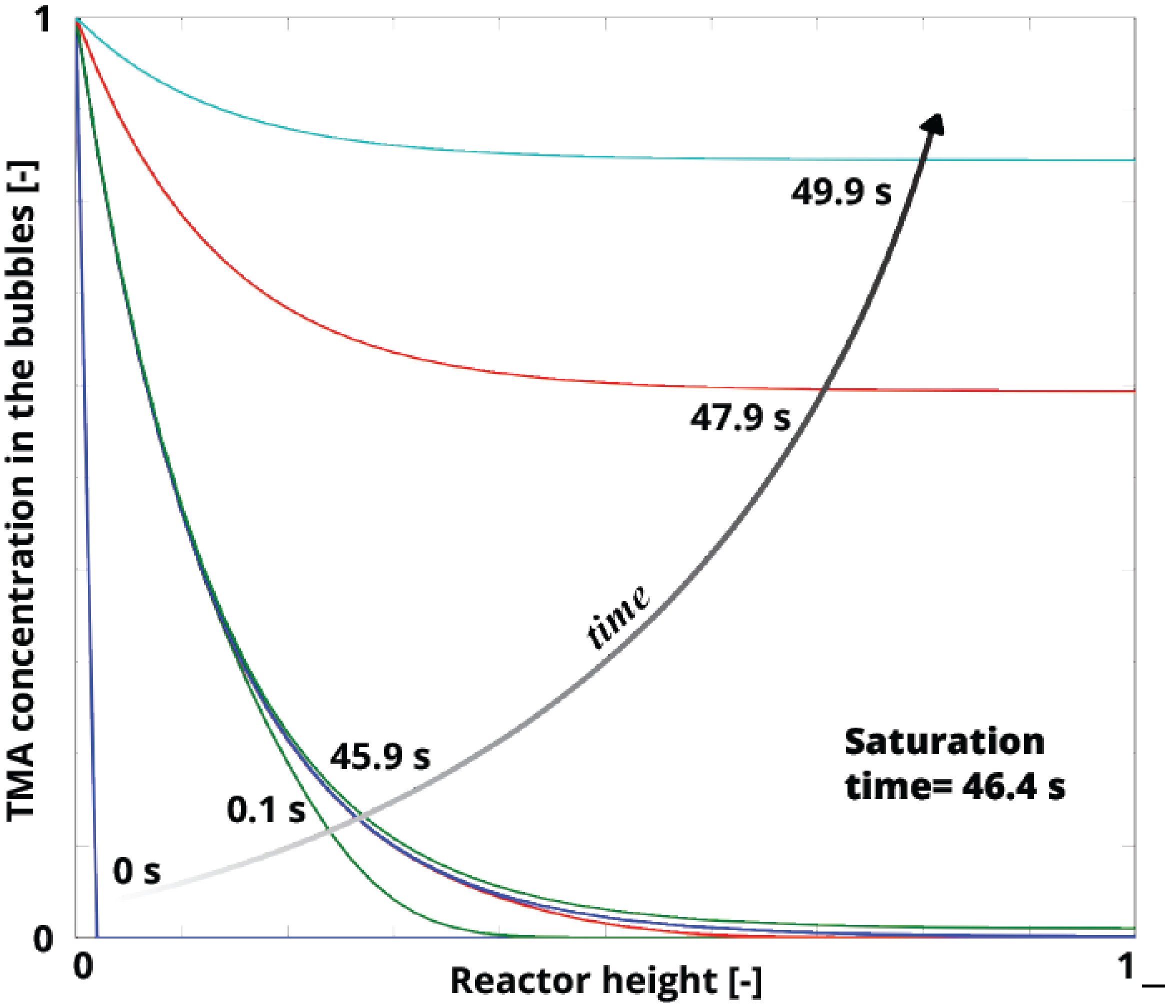


1 bar



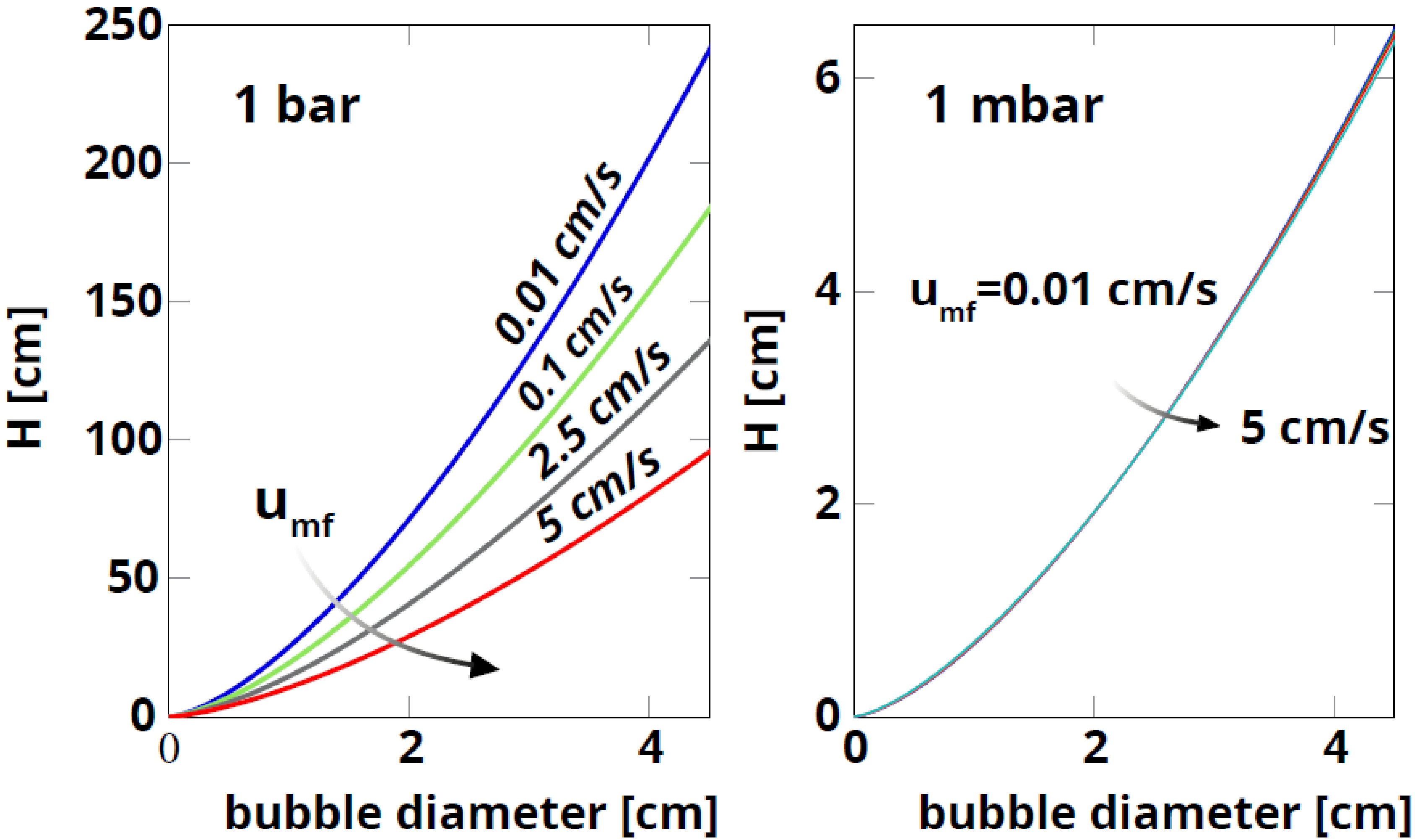
TMA concentration in the bubble phase

1 bar



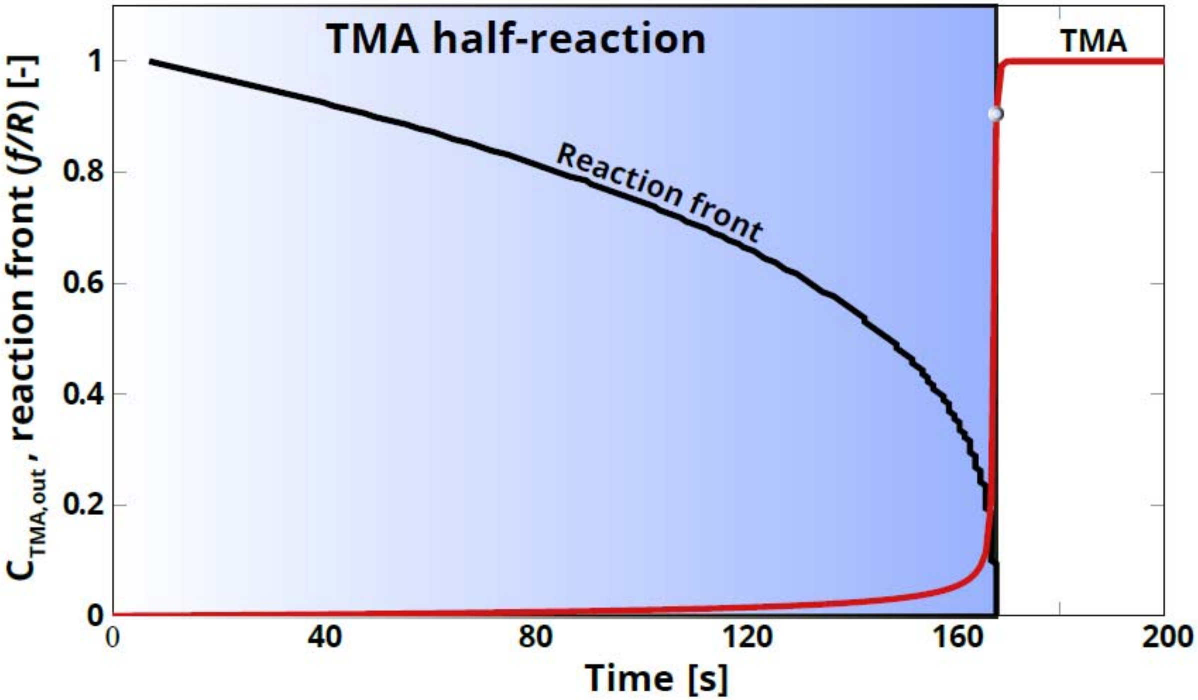
Effect of operating conditions on efficiency

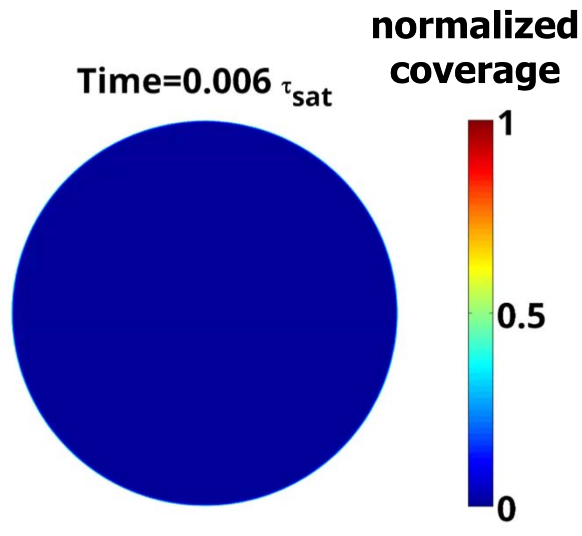
Bed height to obtain ~100% efficiency



ALD on nanoporous micron-sized particles

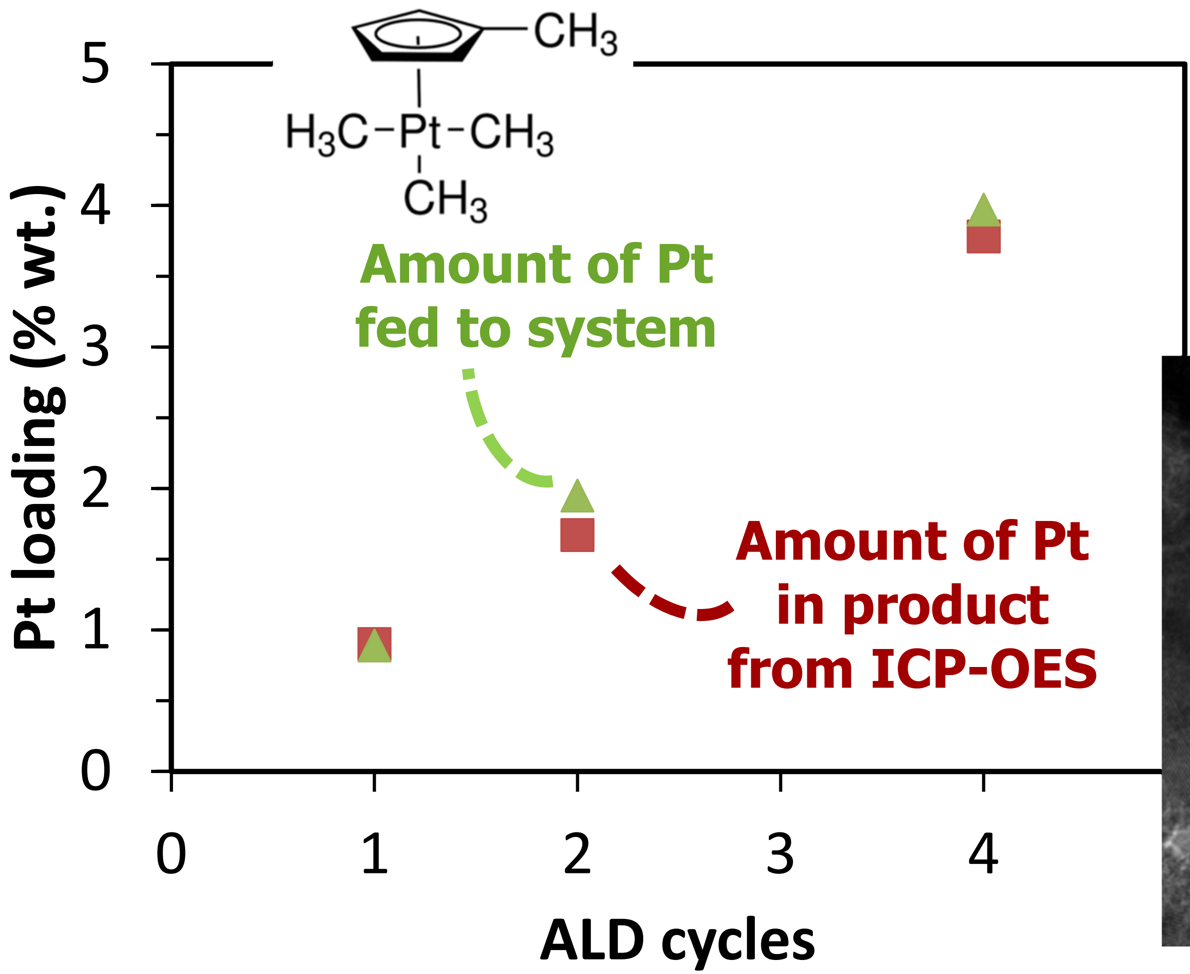
120 μm nanoporous γ-alumina particles, at 1 bar

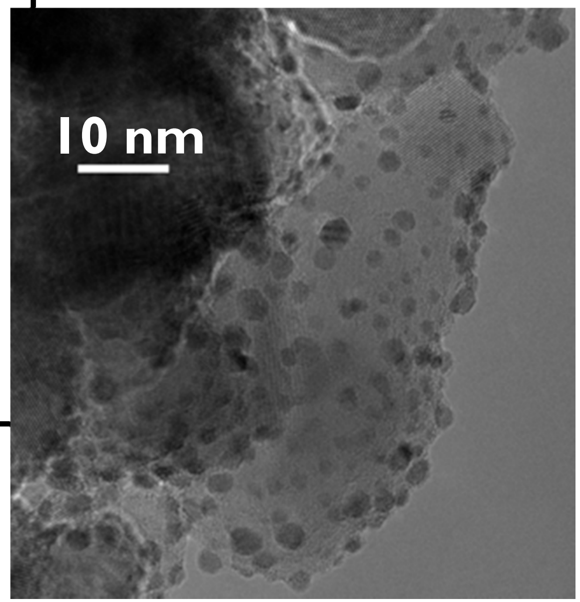




Efficiency of precursor use: exp. results

Deposition of Pt on TiO_2 nanoparticles





Goulas & van Ommen , *J. Mat. Chem. A* 1 (2013) 4647

Summary modelling results

ALD on NPs in FBRs:

- 1 bar: 100% efficiency possible, but bubbles can reduce it
- 1 mbar: 100% efficiency in most cases

ALD on nanoporous micron-size particles:

- 1 bar and 1 mbar: sharp reaction fronts, lower efficiency at lab-scale, but still high (>90%)

Results are in qualitative agreement with exp. findings

Paper in preparation: Grillo et al.

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Exhaust gas neutralization system
ALD reactor
Precursors TMA and H_2O
Infrared Heating Lamp
Control system

Deposition of Pt on TiO_2 nanoparticles

Experimental conditions

250 mg TiO_2 P25 (Evonik), diam.: 25 nm

Reactants: $MeCpPtMe_3$ & O_3

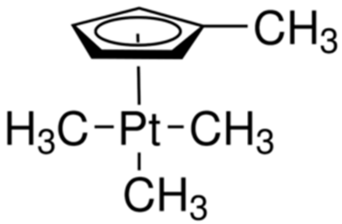
T = 250^{o}C; p = 1bar

column diameter: 10 mm

gas flow: 0.20 L/min / 4.2 cm/s

typical pulse time: 1-10 min

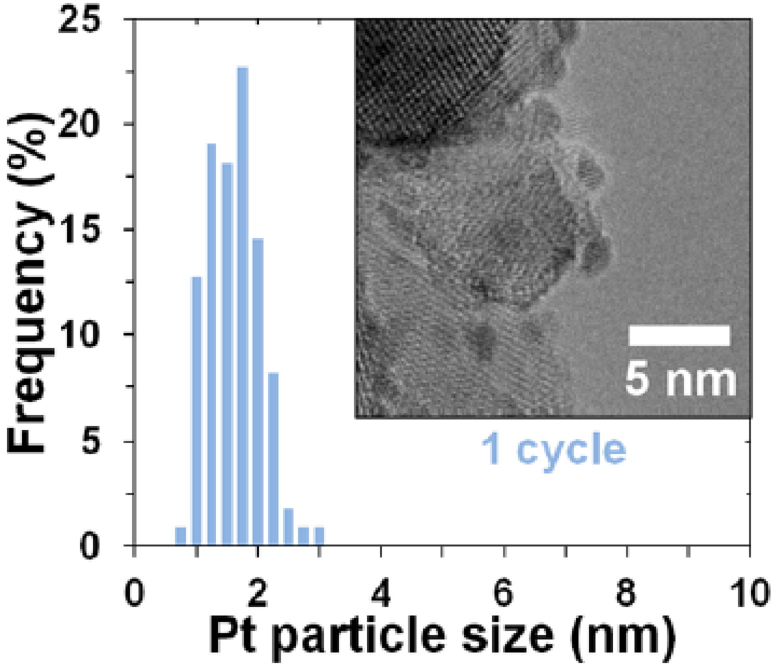
Pt on TiO_2 nanoparticles: photocatalyst



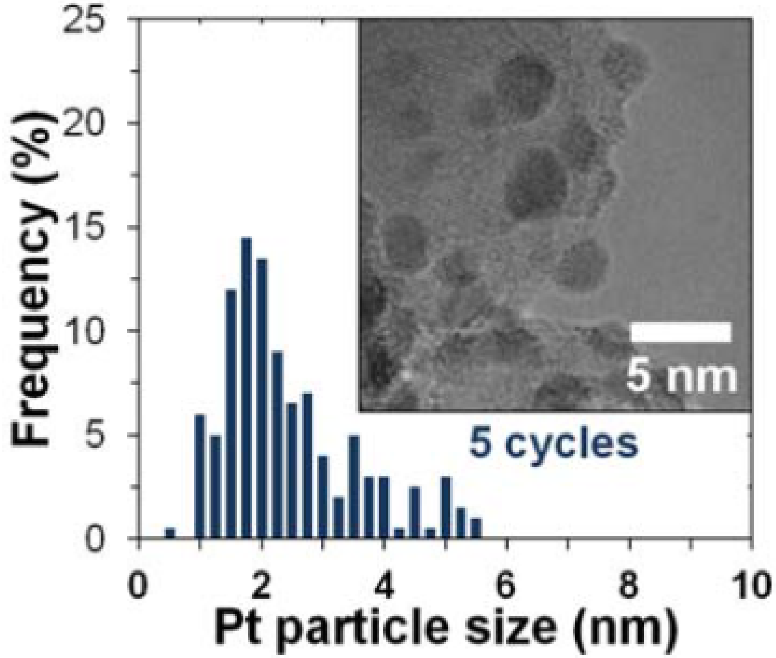
deposition control: # cycles

narrow particle size distribution

$d_{p,1}$=1.5±0.35nm for 1.6 wt% Pt



$d_{p,5}$=2.3±0.87nm for 5.8 wt% Pt

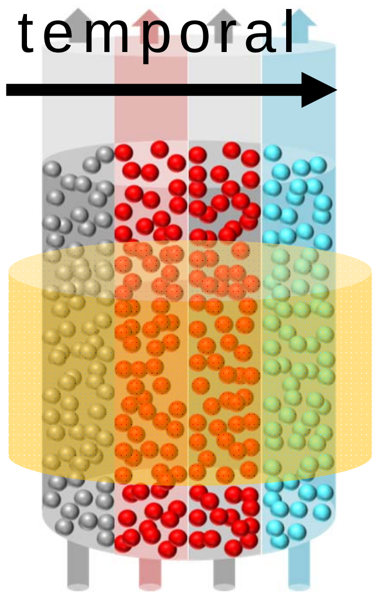


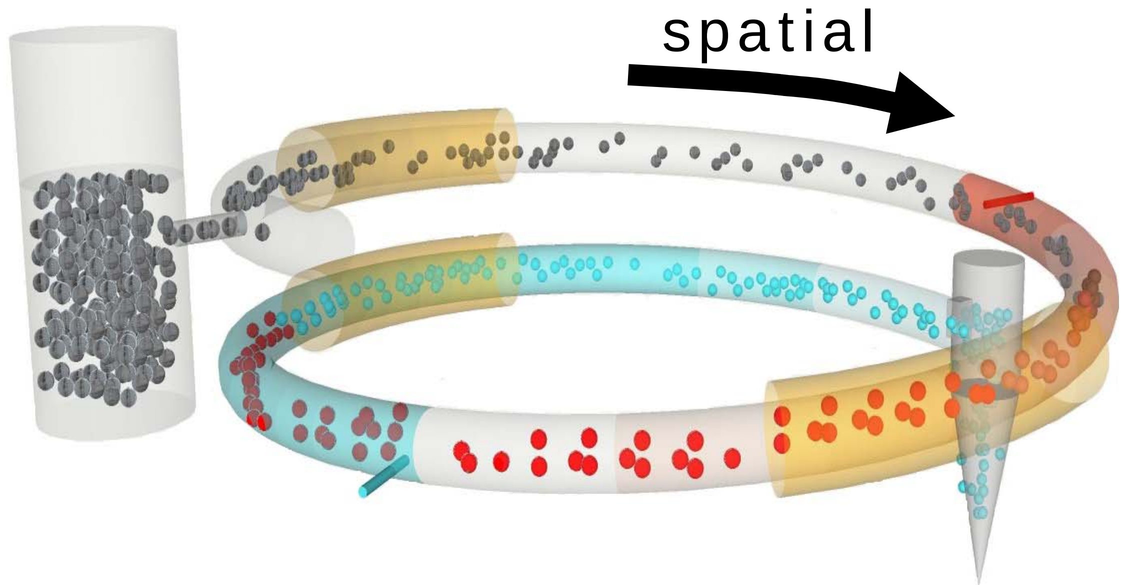
Goulas, *J. Mat. Chem. A* 1 (2013) 4647

ALD on powders

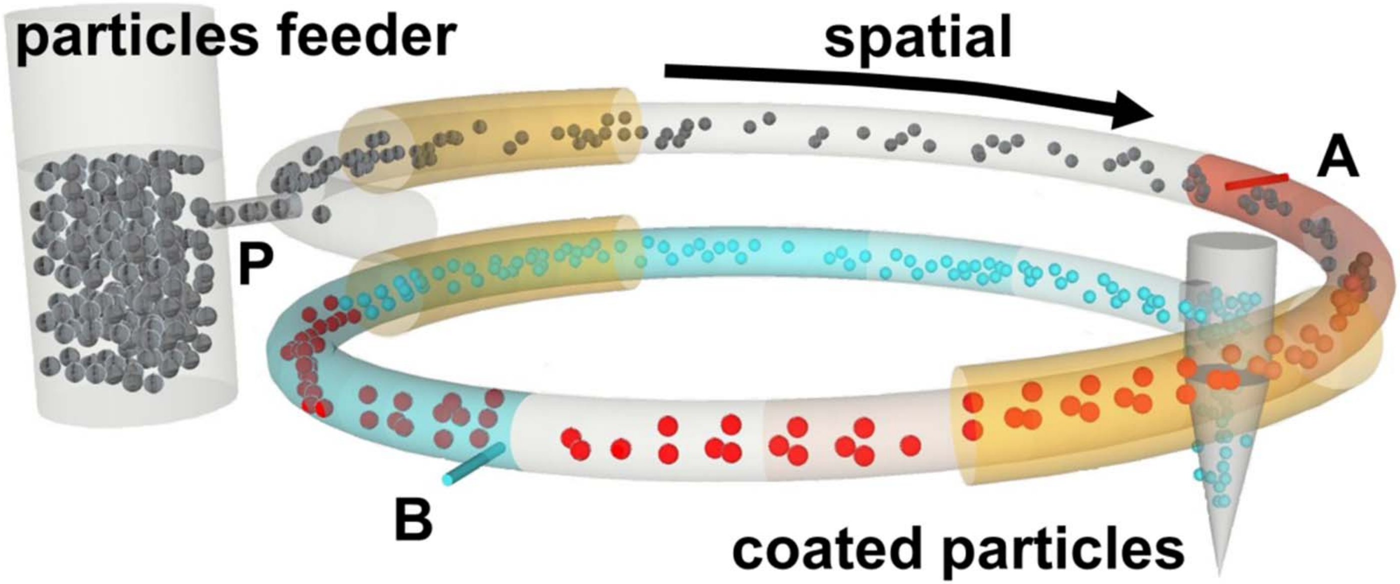
- simple & robust
- mild conditions
- nm to µm particles
- many different materials
- low waste footprint
- scalable

Different reactor technologies possible:



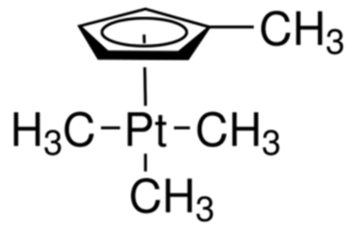


A continuous reactor for ALD on particles



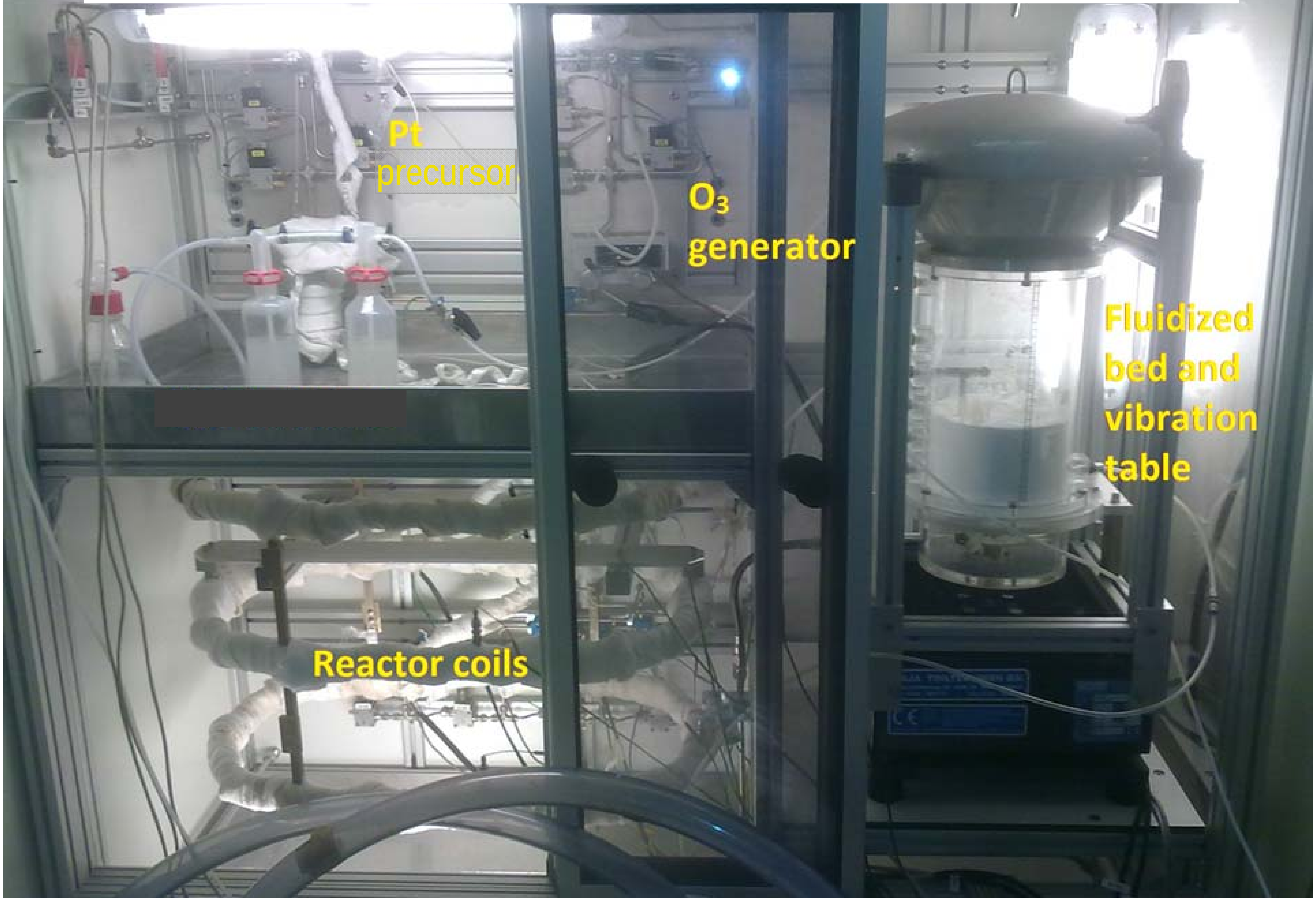
- 4 mm diam.
- 27 m long
- ~10 m/s
- ~1 g/min

- $MeCpPtMe_3$ & O_3
- Pt on TiO_2
- 1 bar, 1 cycle



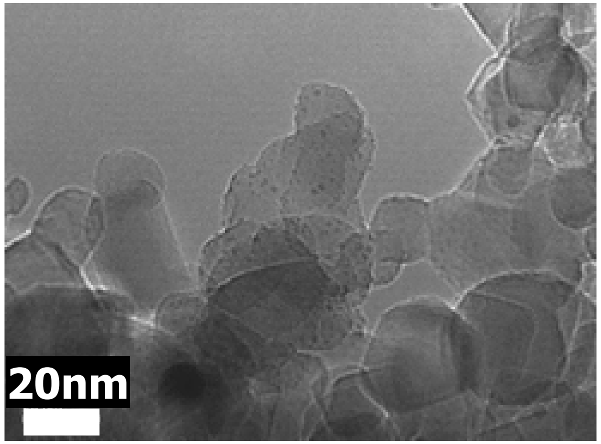
Patent Pending: WO2010/100235

A continuous reactor for ALD on particles



Pneumatic reactor: homogeneous product?

1 ALD cycle



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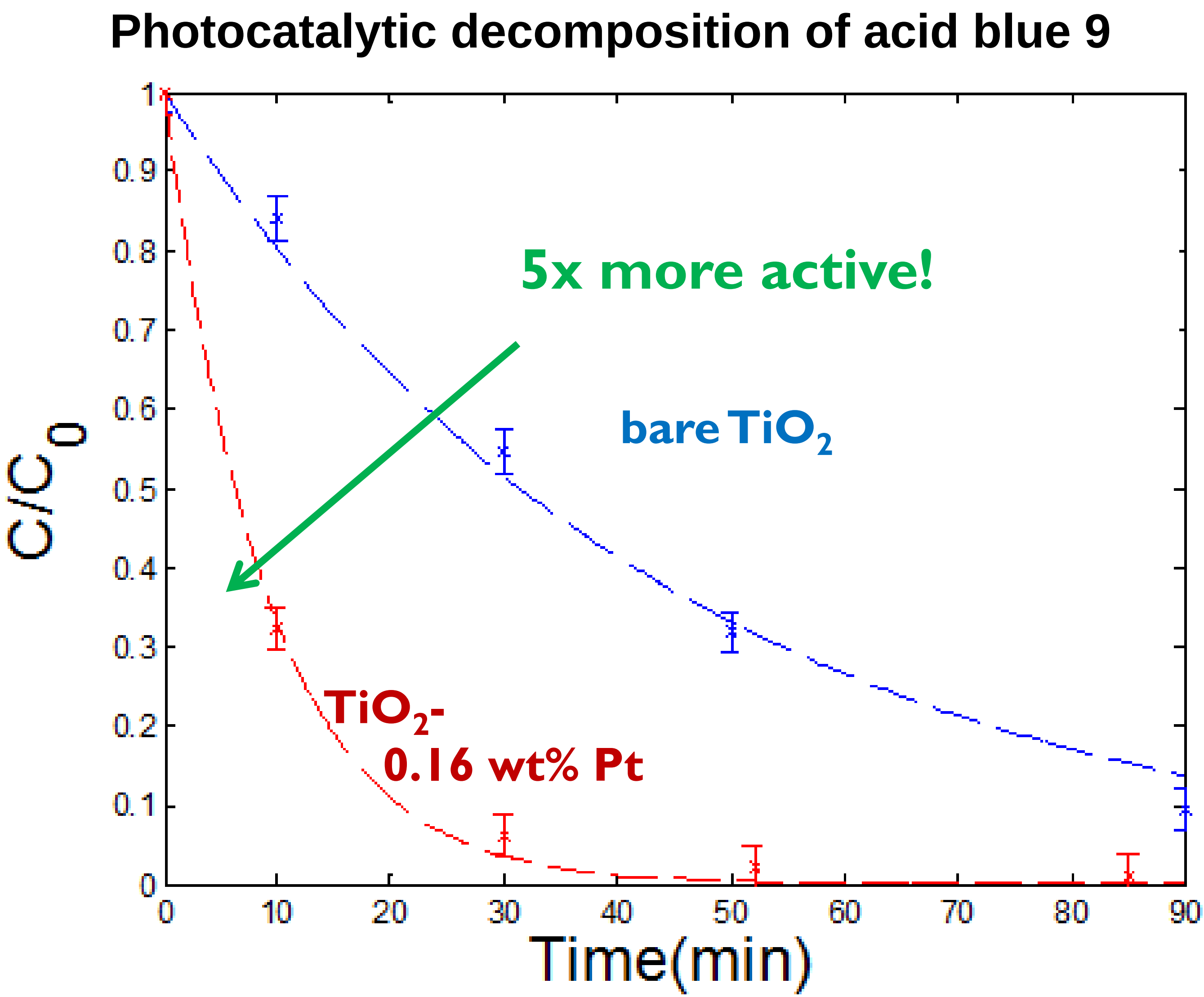
Photocatalysis: Pt on TiO_2 nanoparticles

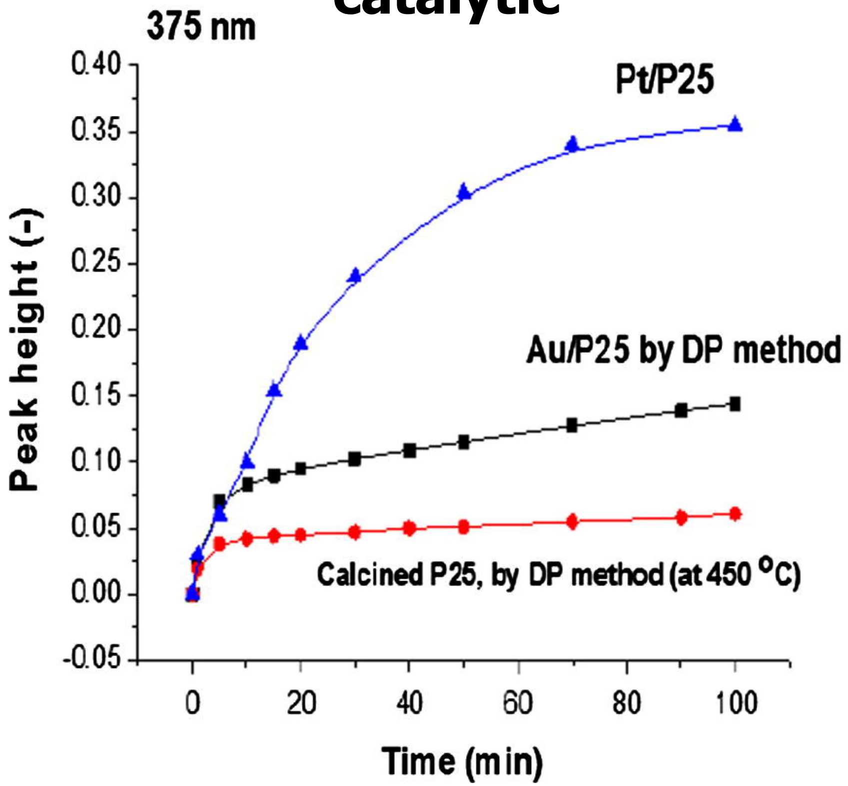


Methylcyclohexane oxidation: Pt/TiO_2 vs Au/TiO_2

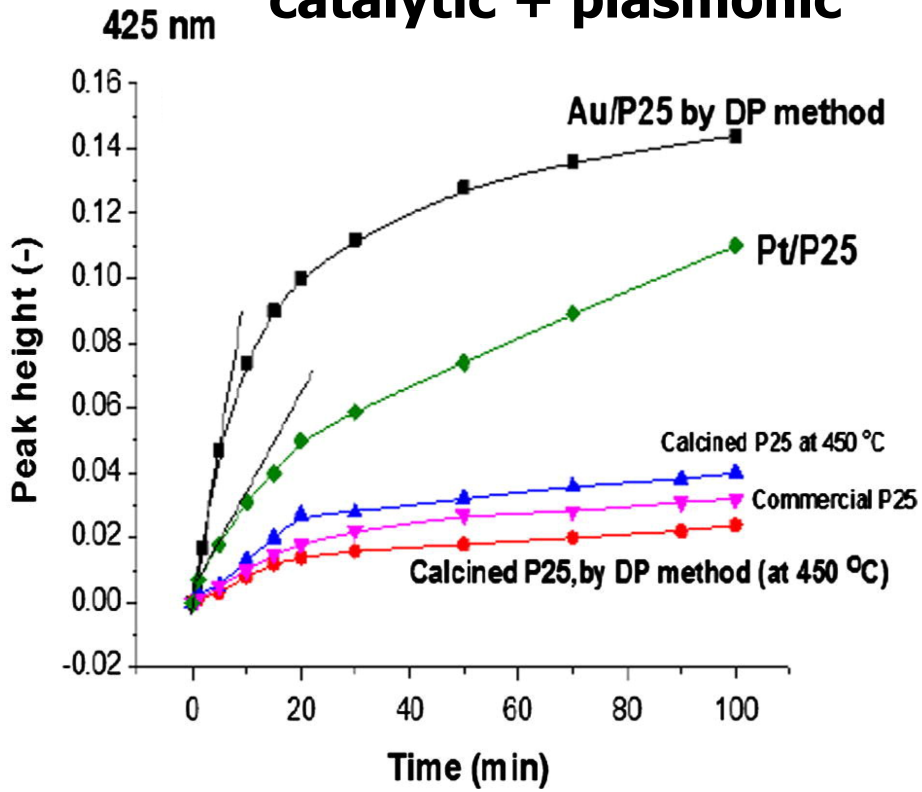
Photocatalysis with Pt/P25 (ALD) vs Au/P25 (deposition-precipitation)

Time evolution of the peak height of the ketone (1710 cm^{-1}) vibration

catalytic



catalytic + plasmonic



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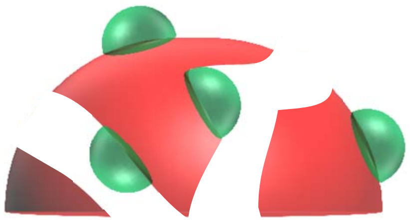
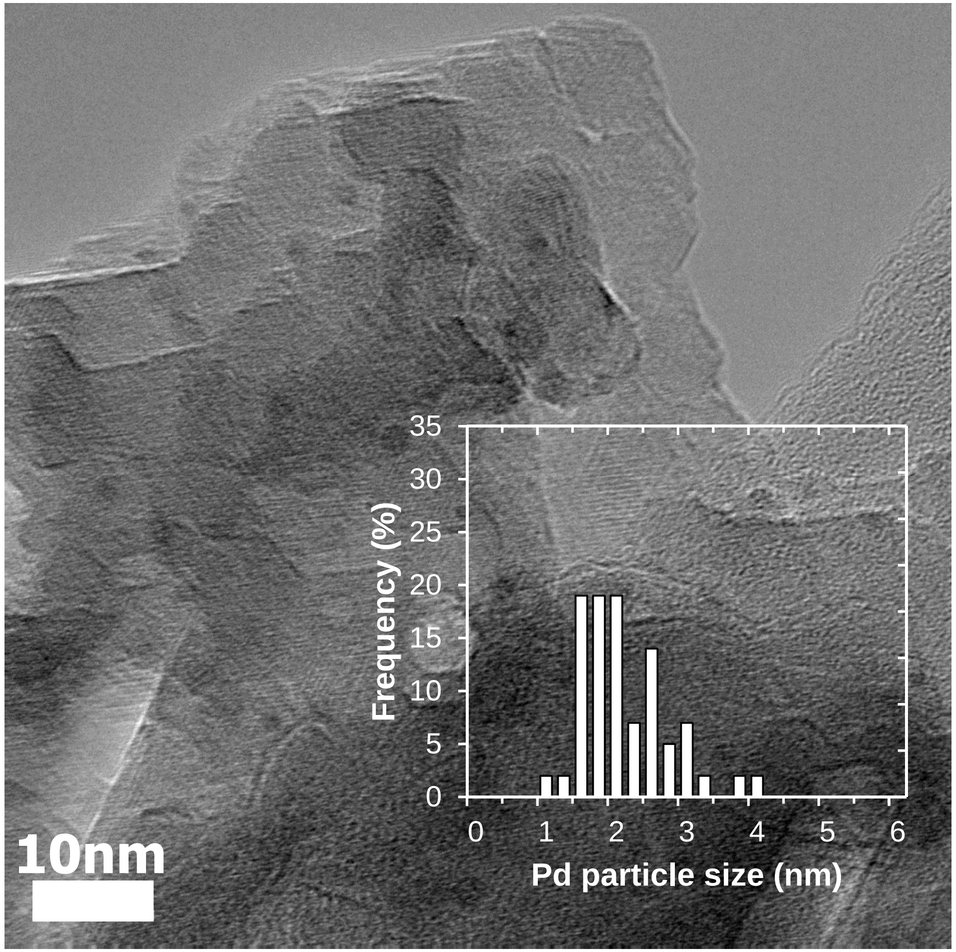
R. Amrollahi et al., Journal of Catalysis 319 (2014) 194

Suzuki-Miyaura c-c cross-coupling: Pd/Al_2O_3

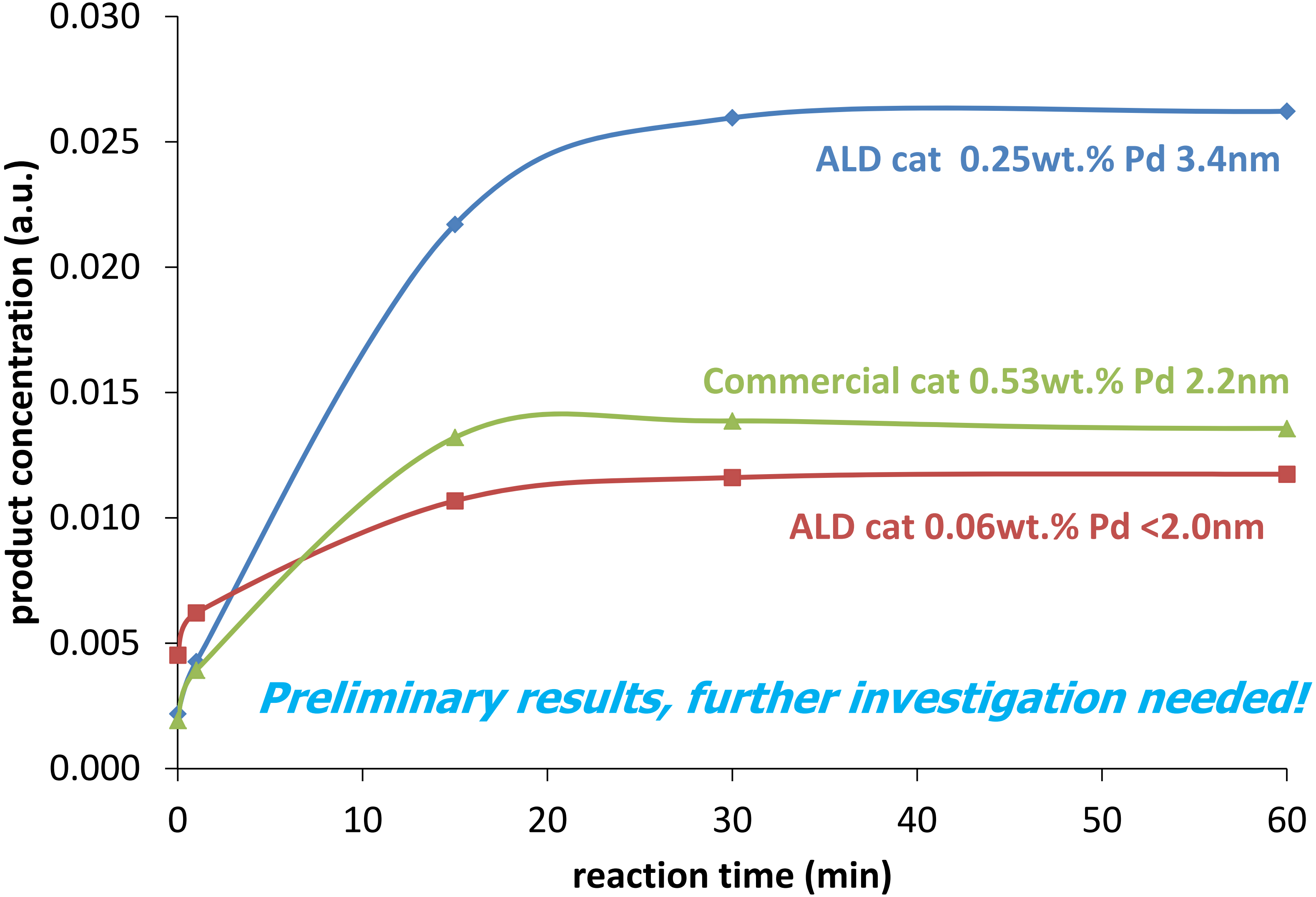
ALD of Pd with $Pd(hfac)_2$ and HCHO on micron-sized, nanoporous Al_2O_3 particles





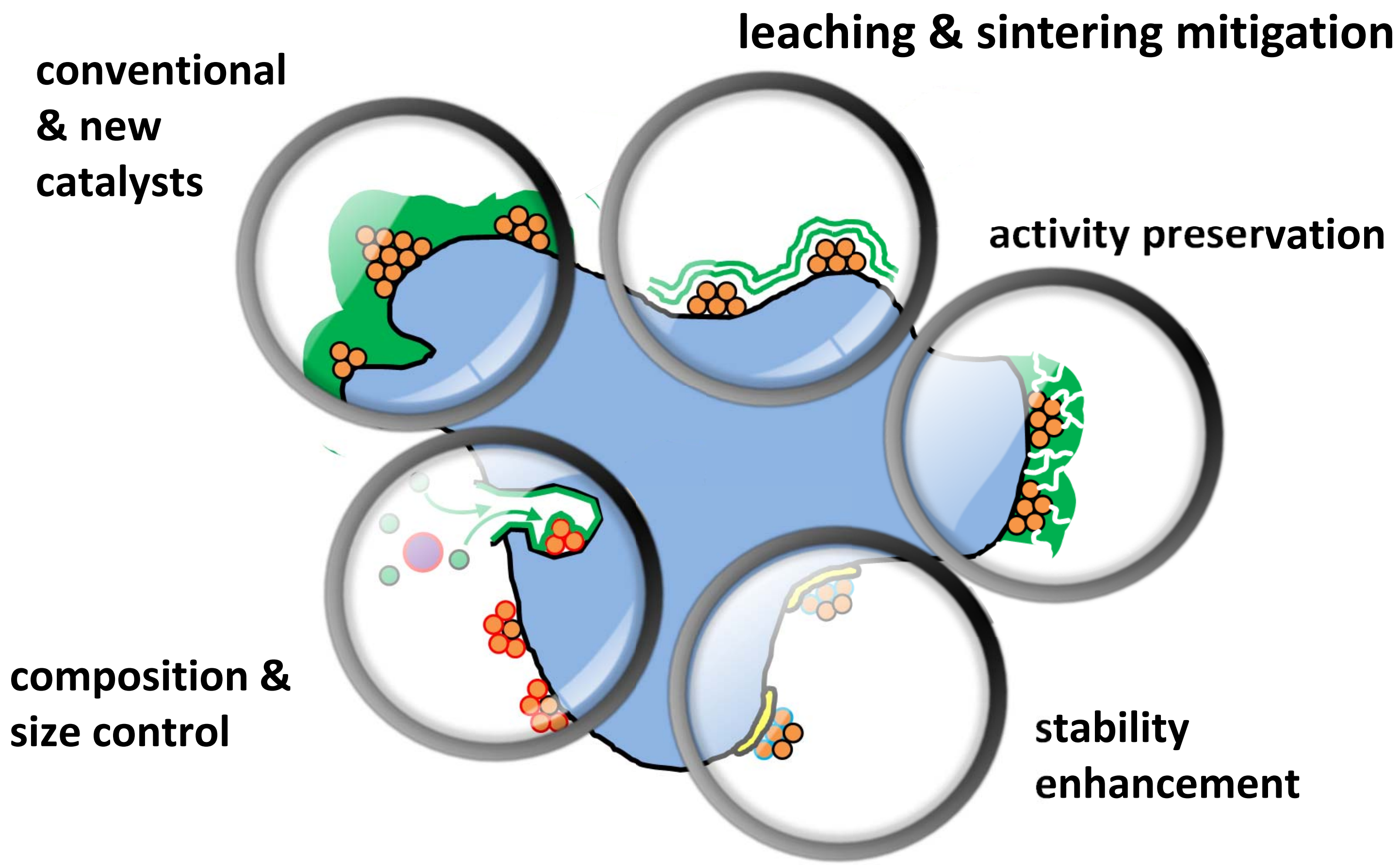
Suzuki-Miyaura c-c cross-coupling: Pd/Al_2O_3

C-C bond formation between iodobenzene and phenylboronic acid



With Aris Goulas, Nastya Bavykina & Jorge Gascon

Opportunities for ALD in catalysis

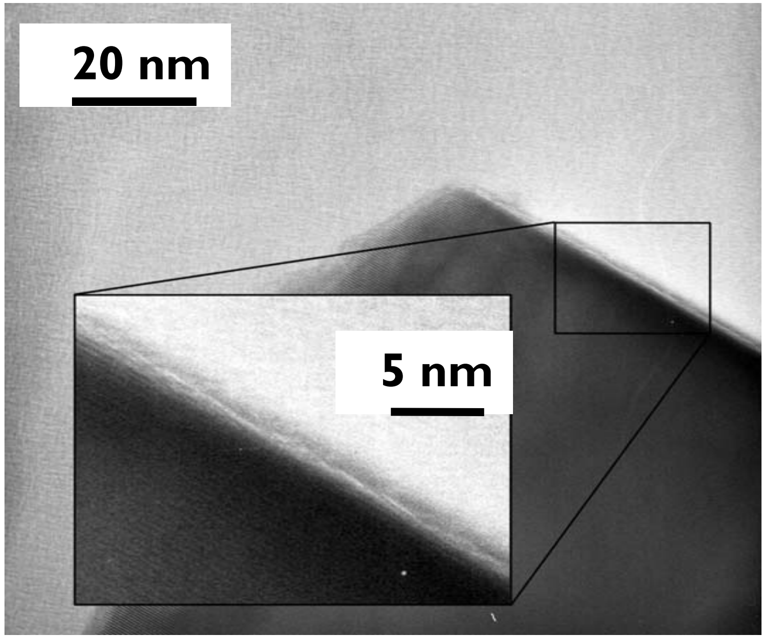


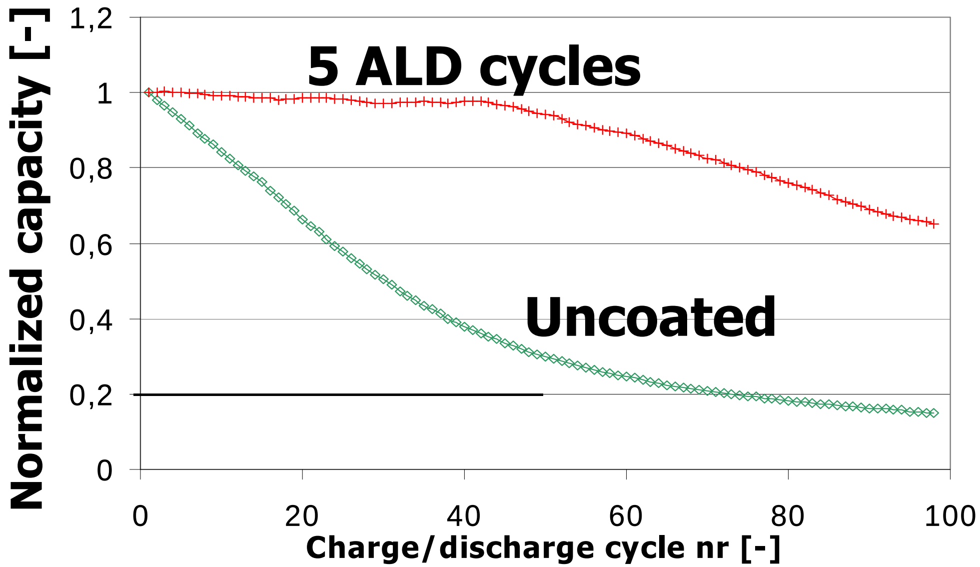
We will explore these opportunities partly in our research group, and partly via a spin-off company (as of 1/1/2015)

Li-ion batteries: reduced charging time & aging

Sub-micron particles: faster charging, but increased aging
Ultrathin coating needed to improve the lifetime
120 g powder, coated at 160°C & 1 bar

Al_2O_3 film on $LiMnO_2$ particles



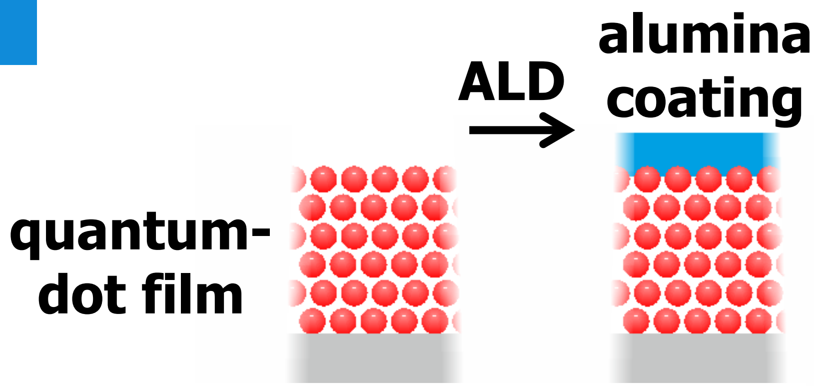


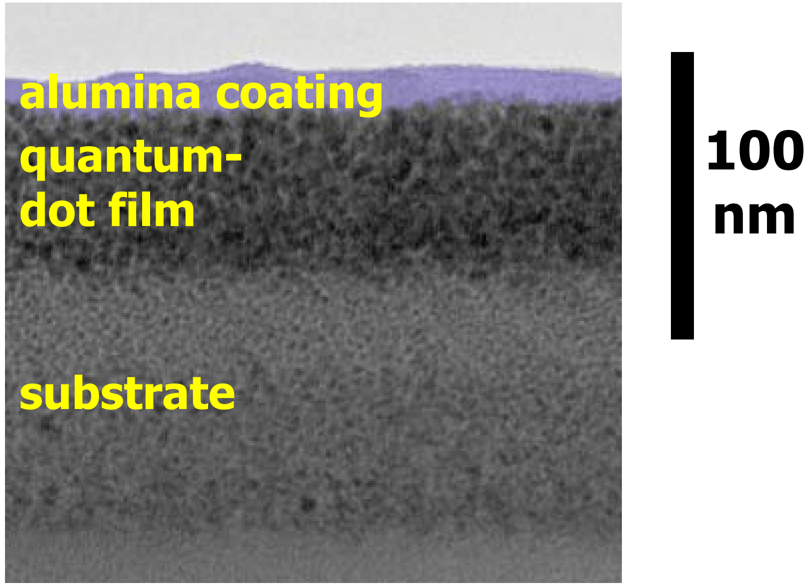
Beetstra, Lafont, Nijenhuis, Kelder, van Ommen; *Chem. Vap. Dep.* 15 (2009) 227

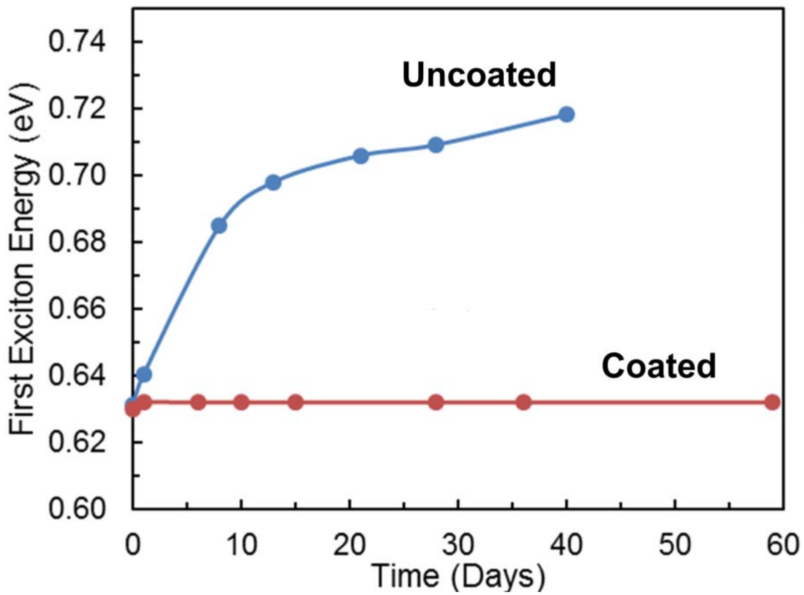
Quantum-dot films for solar cells

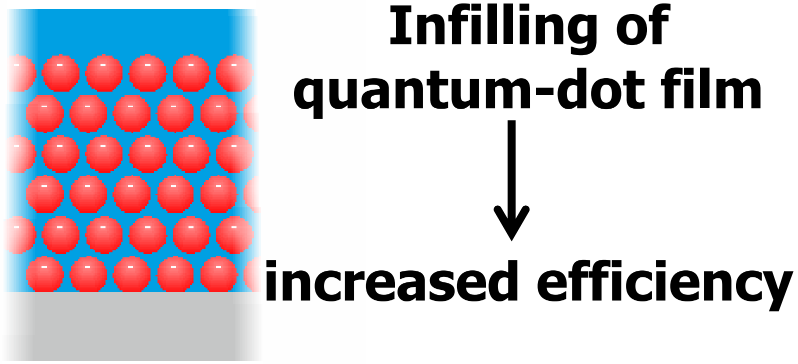
Solar cells based on quantum dots:
theoretical efficiencies of close to 50% possible

Coating needed to increase durability and efficiency









with Guerra, Valdesueiro, Chandramathi Sukumaran , Houtepen

Conclusions

- Coating of fluidized particles (10 nm-1mm) with ALD at 1 bar
- Many different core and shell materials can be used
- Both continuous films & cluster growth
- Highly efficient use of resources
- Fluidized bed: scalable process
- Continuous process is also feasible
- Wide range of possibilities in catalysis,
  but also for other applications
- We will explore these via academic research + spin-off

Thanks to all co-workers & students who contributed!

j.r.vanommen@tudelft.nl

MARIE CURIE ACTIONS

nanonextnl
innovating with micro and nanotechnology

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