Shadowing Effects of Monofunctional Catalysts in TAP Reactors

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INTRODUCTION: TAP micro-reactors reduce the complexity of industrial operating environments to characterize the catalyst's design. [1] However, the distribution of micron-sized catalyst particles plays a major role in extracting their distinctive reactivity palette and design optimization. [2-4]

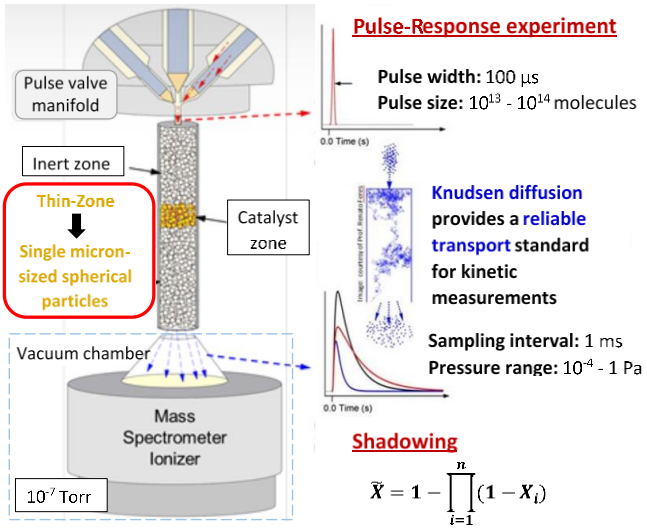


Figure 1. The TAP reactor system: a transient pulse response technique.

COMPUTATIONAL METHODS:

Reaction-Diffusion model (> ø 50 µm)

$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = 1 \rightarrow \frac{\partial c}{\partial t} = D_{cat}\frac{\partial^2 c}{\partial x^2} - kC_G \rightarrow c(t)|_{x=L} = 0$$

Steady-state study in 2- or 3-D **Mesh refinement study required**

Diluted thin-zone (ø 50 – 0.1 µm)

1-D model with a reactive pellet bed:

$$4\pi N_{pe}\left\{r^2 r_{pe}^2 \varepsilon_{pe}\frac{\partial c_{pe,i}}{\partial t} + \frac{\partial}{\partial r}\left(-r^2 D_{pe,i}\frac{\partial c_{pe,i}}{\partial r}\right) = r^2 r_{pe}^2 R_{pe,i}\right\},\ r = \frac{r_{dim}}{r_{pe}}$$

A homogenization approach: $A \Leftrightarrow B$ $\quad R_A = k_f c_A - k_r c_B$

$$k_f = \sqrt{\frac{R_g T}{2\pi M_g}}\,SSA_{zone}\exp\left(-\frac{E_a^f}{R_g T}\right) \qquad R_{A,eff} = R_A SSA_{pellet} r$$

Supported nanoclusters (ø 100 – 1 nm)

Inert support (2-D): $\frac{\partial c_s}{\partial t} = \alpha J_{cat} + D_s \Delta c_s - \frac{c_s}{\tau} \rightarrow \sigma_{cz} = \sigma\frac{A_{cz}}{A_{cat}}\left[\frac{mol}{m^2}\right]$

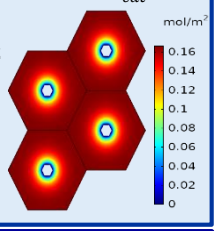
TAP reactor: $\frac{\partial c_{AZ}}{\partial t} + \nabla \cdot \left(D_s \nabla c_{AZ,tangent}\right) = R_{AZ}$

$A + Z_{sup} \Leftrightarrow AZ$

$A + Z_{cl} \Rightarrow B$

$A + Z_{cz} \Rightarrow B$

$$k_f = \frac{P_{stick}}{\sigma_i}\sqrt{\frac{R_g T}{2\pi M_g}}\exp\left(-\frac{E_a^f}{R_g T}\right)$$



Deterministic model	Stochastic model
Solution method: Finite elements Software: COMSOL Multiphysics 5.5	Solution method: Monte Carlo (MC) In-house software: C++ → Python

RESULTS: Simulations were conducted at 500 K and results were in agreement with the stochastic model.

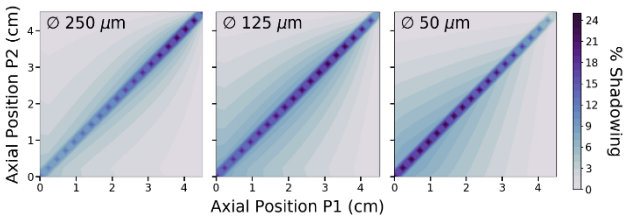


Figure 2. Shadowing of a highly active two-particle system with equal diameter in the axial direction of the TAP reactor.

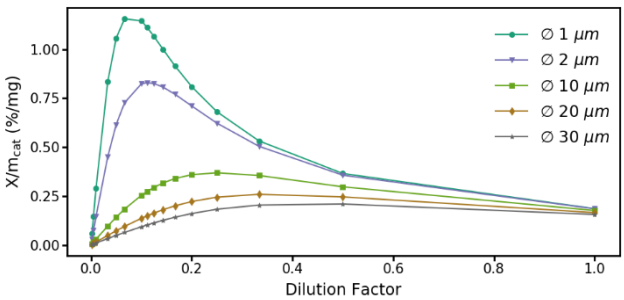


Figure 3. Dilutions of a centered reactive pellet bed of 2 mm long with highly reactive non-porous pellets ($\varepsilon_{pe} = 0, D_{pe,i} = 0$).

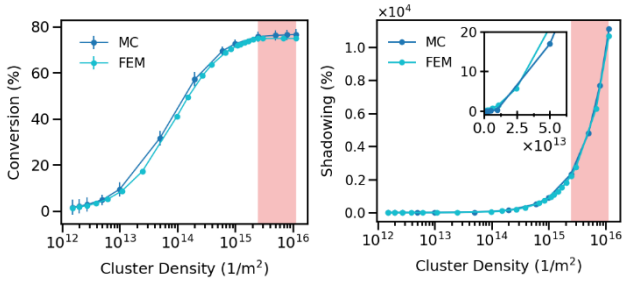


Figure 4. Centered particle (250 µm) deposited with nanoclusters of ø 10 nm at an inert support. Marked red zone = overlap of capture zones.

CONCLUSIONS:

- Two-Particle system shows most prominent shadowing in the axial direction with a shift towards the inlet of the reactor when decreasing their size.
- An optimal dilution of a thin-zone can be found at which performance outweighs shadowing.
- Capture zones extend the distance at which a shadowing effect sets in.
- Overlap of capture zones stabilizes the conversion, therefore leading to high amounts of shadowing.

A shadowing effect could be simulated for **highly active particles on a multi-scale.** A further step is to extend the models for non-homogeneous catalysts and fine-tune the mode of activity distribution within a catalyst particle with experimental validation.

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