Sustainable Energy &
Air Purification
University of Antwerp

Kinetic parameters for gas phase photocatalysis: analytic versus multiphysics approach

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COMSOL CONFERENCE
2014 CAMBRIDGE

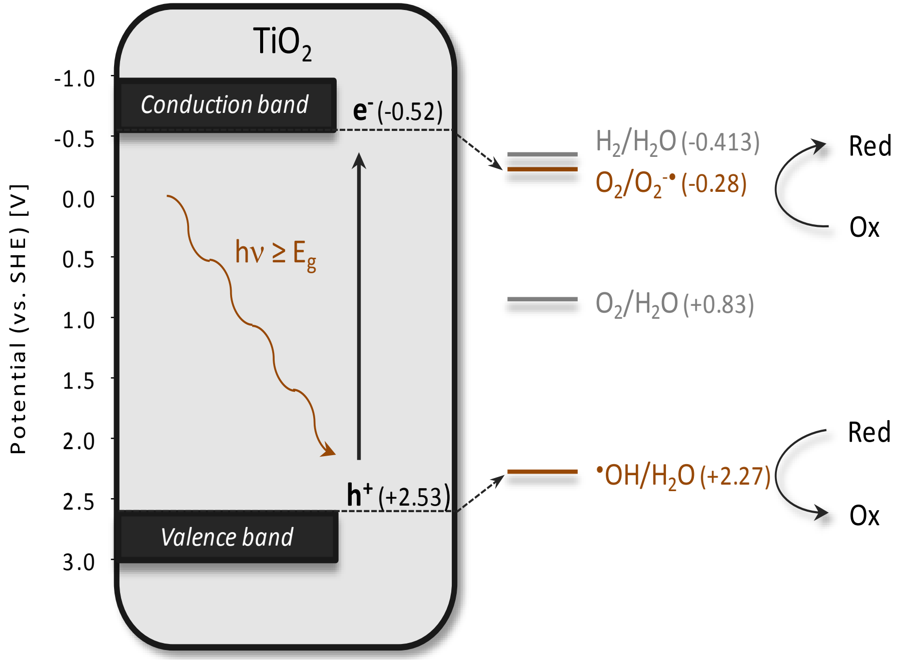
University of Antwerp

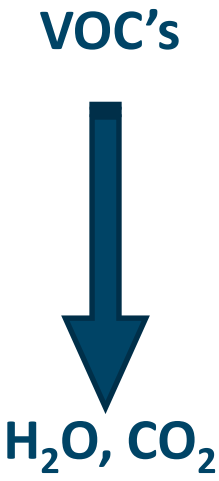
Photocatalysis

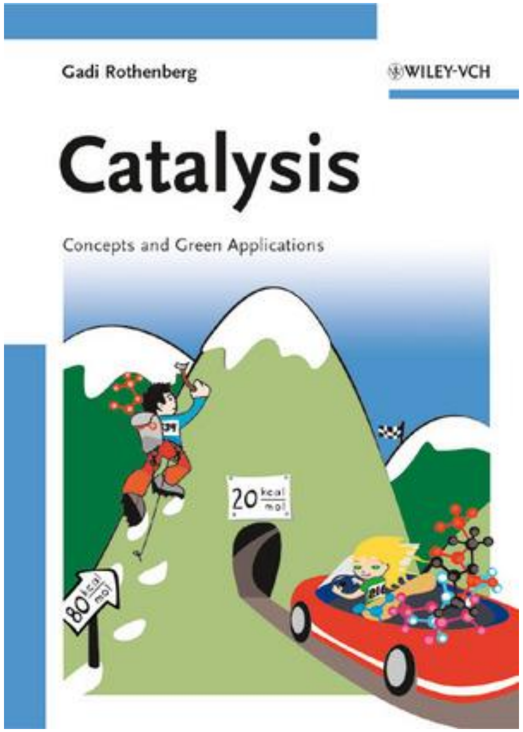
Catalyst: increases reaction rate without being consumed

Photo-catalyst: catalyst activated by (UV-)light

Most often titanium dioxide (TiO_2)





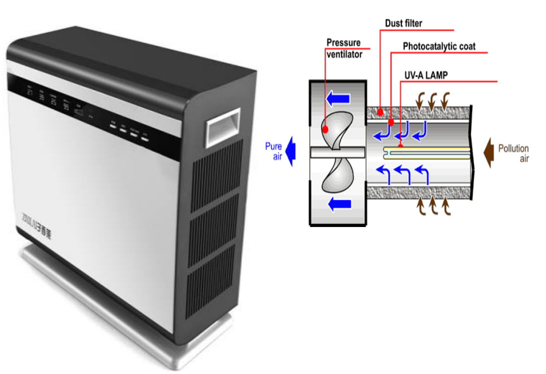


Photocatalysis: application fields

Water purification/desinfection

Self-cleaning materials

Air purification

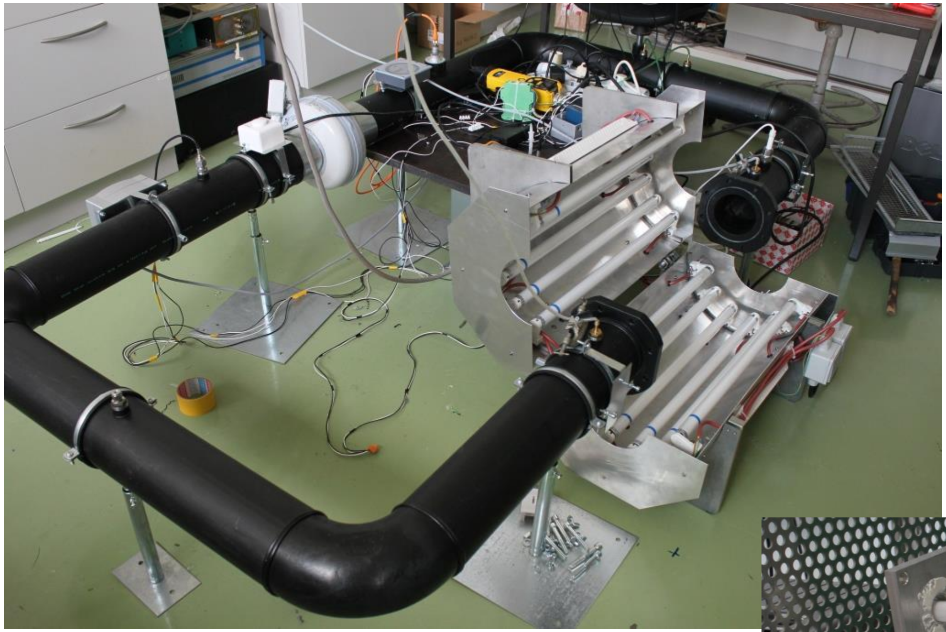


Research goals

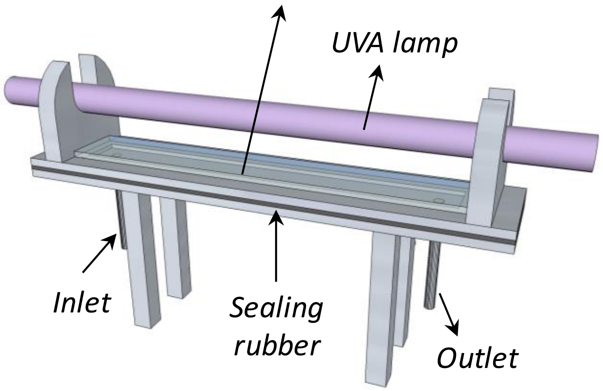
Main goal: development of suitable photoreactors for air purification

Sub goal: determination and exploitation of the main catalyst characteristics driving photocatalytic activity in the gas phase

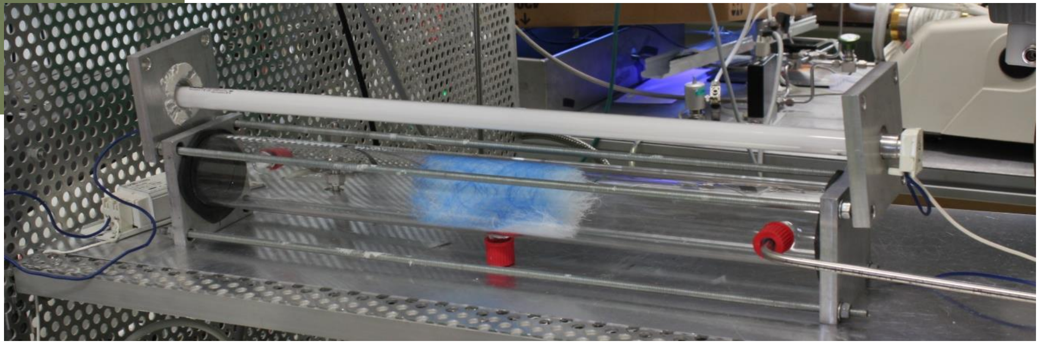
Intrinsic kinetic parameters



HVAC photoreactor



Flat bed photoreactor



Tubular photoreactor (glass fibre)

Intrinsic kinetic parameters

$$VOC_{bulk} \underset{k_{des}}{\overset{k_{ads}}{\rightleftarrows}} VOC_s \xrightarrow{k_{LH}} H_2O, CO_2$$

Langmuir adsorption:

fractional coverage of VOC on an illuminated TiO_2 surface

$$\theta_{VOC} = \frac{K_L C_{VOC}}{1 + K_L C_{VOC}}$$

Unimolecular Langmuir-Hinshelwood mechanism:

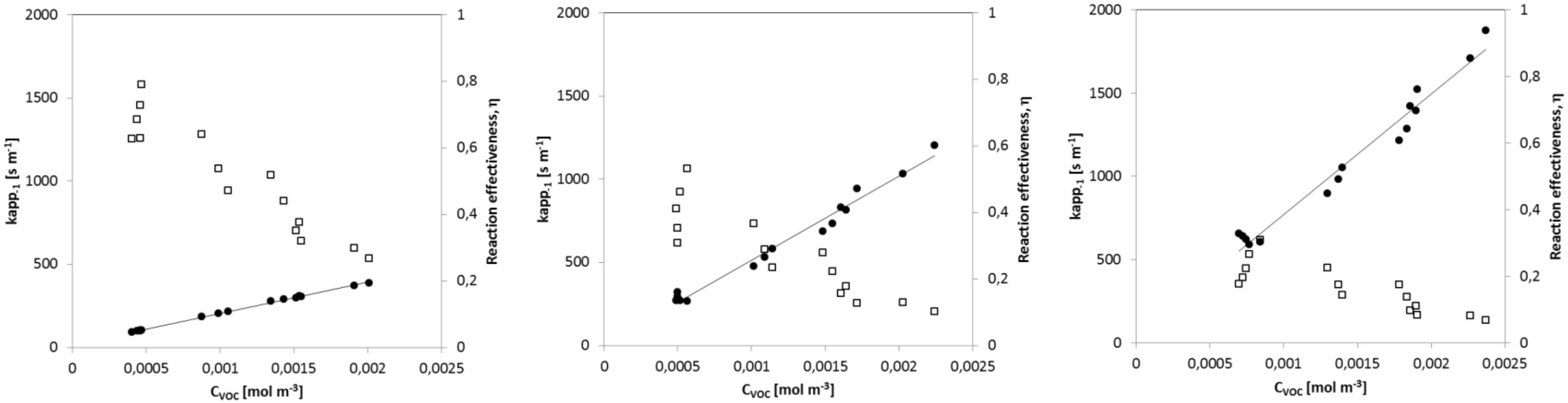
$$r = k_{LH}\,\theta_{VOC} = \frac{k_{LH} K_L C_{VOC}}{1 + K_L C_{VOC}} = k_{app} C_{VOC}$$

Intrinsic kinetic parameters

Analytic model

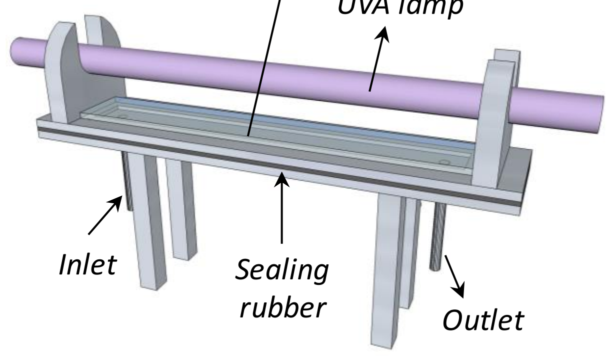
$$r = k_{LH}\,\theta_{VOC} = \frac{k_{LH}\,K_L C_{VOC}}{1 + K_L C_{VOC}} = k_{\text{app}}\,C_{VOC}$$

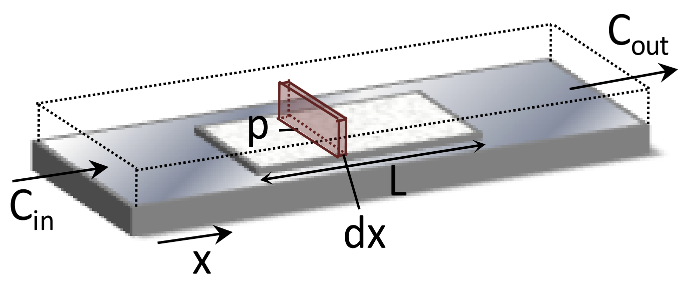
$$\frac{1}{k_{app}} = \frac{1}{K_L k} + \frac{1}{k} C_{VOC}$$



Plot of k_{app}^{-1} (●)and h (□) *versus* the average surface concentration C_{VOC} for a) 1.1 mW cm^{-2}, b) 1.8 mW cm^{-2} and c) 2.6 mW cm^{-2} incident UVA intensity

Analytic model: mass transfer





Mass conservation:

$$G\frac{\partial C_{VOC,\infty}(x)}{\partial x}dx = -j(x)\,p\,dx$$

Mass convection at the boundary:

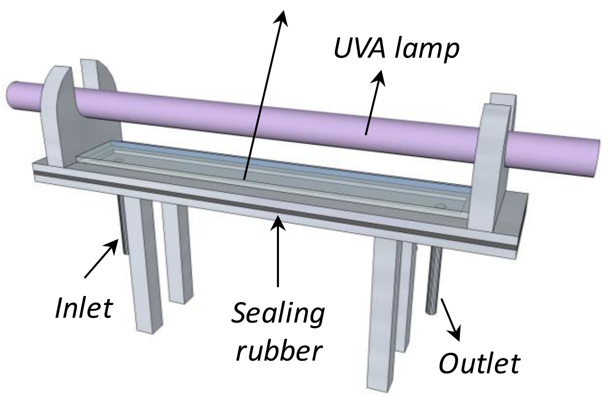
$$j(x) = \frac{C_{VOC,\infty}(x)}{1/h_{mass}(x) + 1/k_{app}(x)}$$

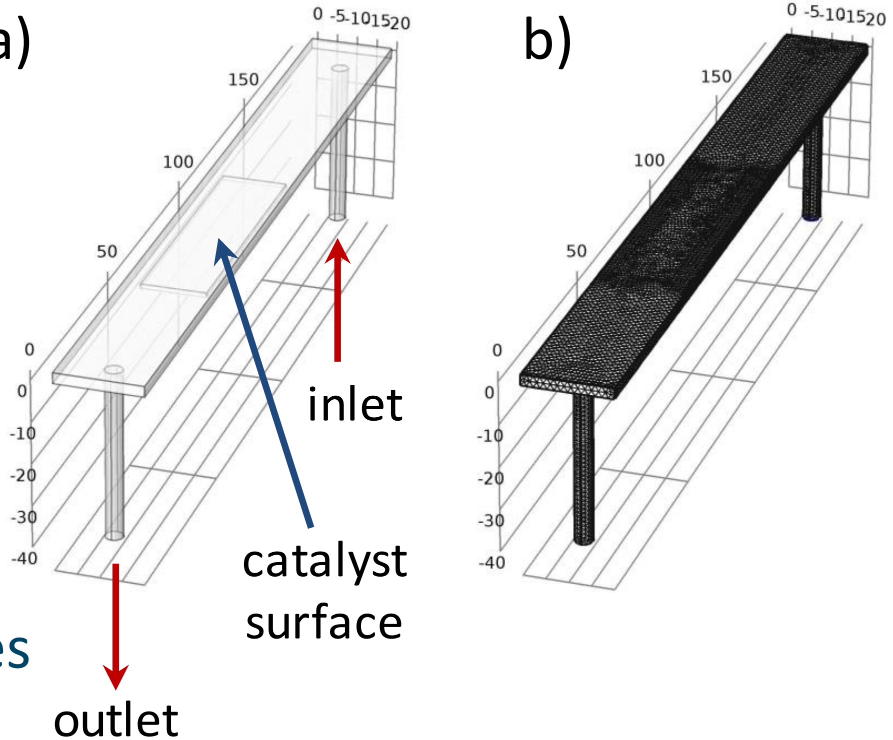
Solution:

$$C_{VOC,\infty,out} = C_{VOC,\infty,in}\,e^{-K_t A/G}$$

$$K_t = \frac{1}{1/h_{mass} + 1/k_{app}}$$

Comsol model





- 250,000 cells
- Laminar flow
- Transport of diluted species
- Surface reaction

$$r = \frac{k_{LH} K_L C_{VOC}}{1 + K_L C_{VOC}}$$

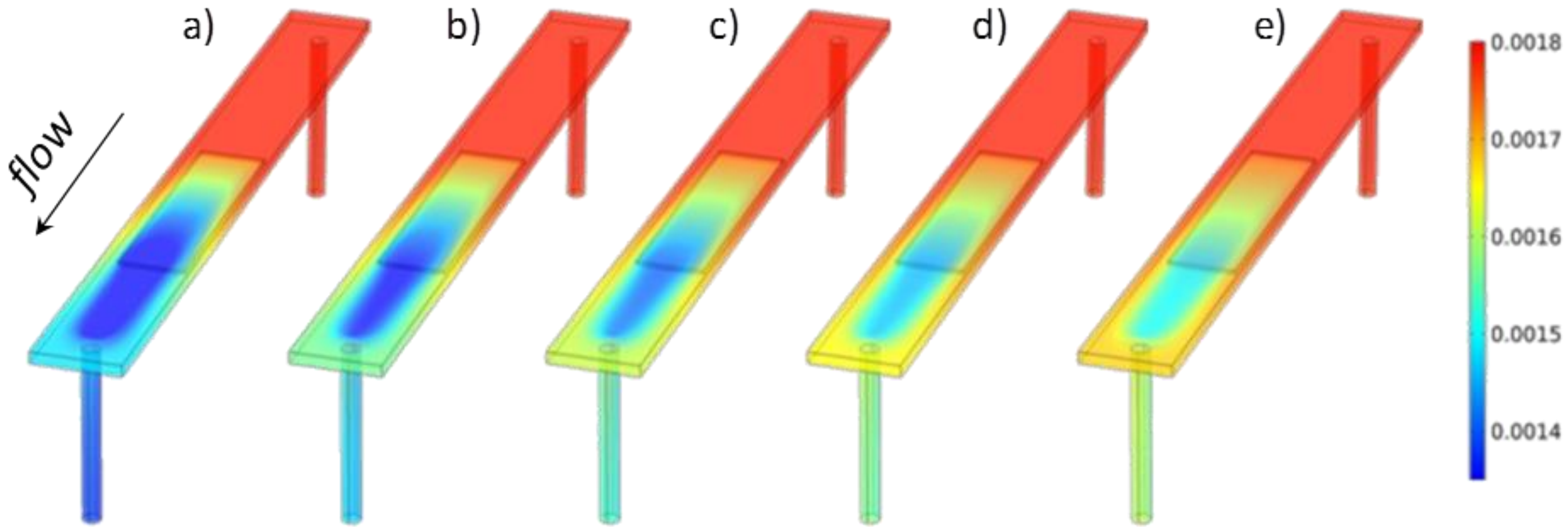
c)

Comsol model: optimization

- Step 1: Stationary solver: laminar flow
- Step 2: transport of diluted species and optimization
- Nelder-mead
- Optimization variables: K_L and k_{LH}
- objective function:

$$Obj = \left| C_{VOC,\infty,out,exp} - C_{VOC,\infty,out,CFD} \right|$$

Comsol model: results



Acetaldehyde concentrations in steady state condition. The acetaldehyde inlet concentration was 43 ppmv (0.00179 mol m^{-3}), at an effective total inlet gas flow rate of: a) 300 cm^3 min^{-1}, b) 375 cm^3 min^{-1}, c) 450 cm^3 min^{-1}, d) 525 cm^3 min^{-1} and e) 600 cm^3 min^{-1}

Comsol model: results

Summary of the kinetic parameters calculated in accordance with the analytic mass transfer based method and the Comsol method after an optimization procedure

Intensity [mW cm^{-2}]	k_{LH} [mol s^{-1} m^{-2}]		K_L [m^3 mol^{-1}]	
	Mass transfer based (analytic)	*Optimized numeric (CFD)*	*Mass transfer based (analytic)*	*Optimized numeric (CFD)*
1.1	1.38 x 10^{-6}	(1.58 ± 0.13) x 10^{-6}	1.45 x 10^{4}	(1.78 ± 0.15) x 10^{4}
1.8	2.11 x 10^{-6}	(2.40 ± 0.20) x 10^{-6}	1.47 x 10^{4}	(1.65 ± 0.11) x 10^{4}
2.6	5.35 x 10^{-6}	(6.23 ± 0.47) x 10^{-6}	1.02 x 10^{4}	(1.16 ± 0.08) x 10^{4}