Kinetics – Interaction between Reaction, Mass and Heat Transfer

Lecture Series "Modern Methods in Heterogeneous Catalysis Research", FHI, Berlin, 31.10.2014

Olaf Deutschmann, Karlsruhe Institute of Technology (KIT)

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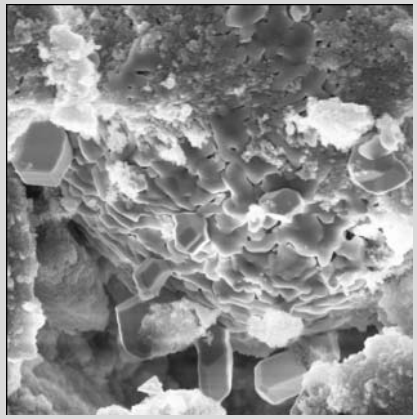
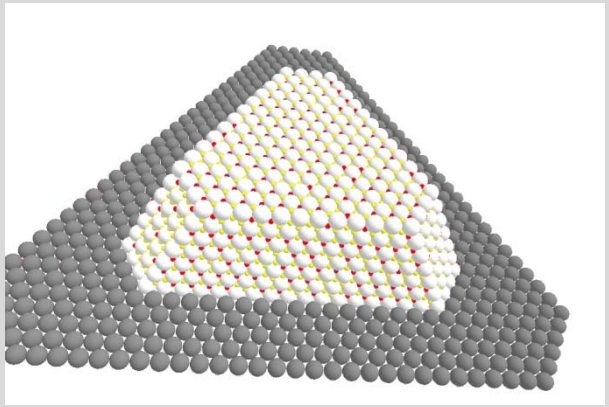
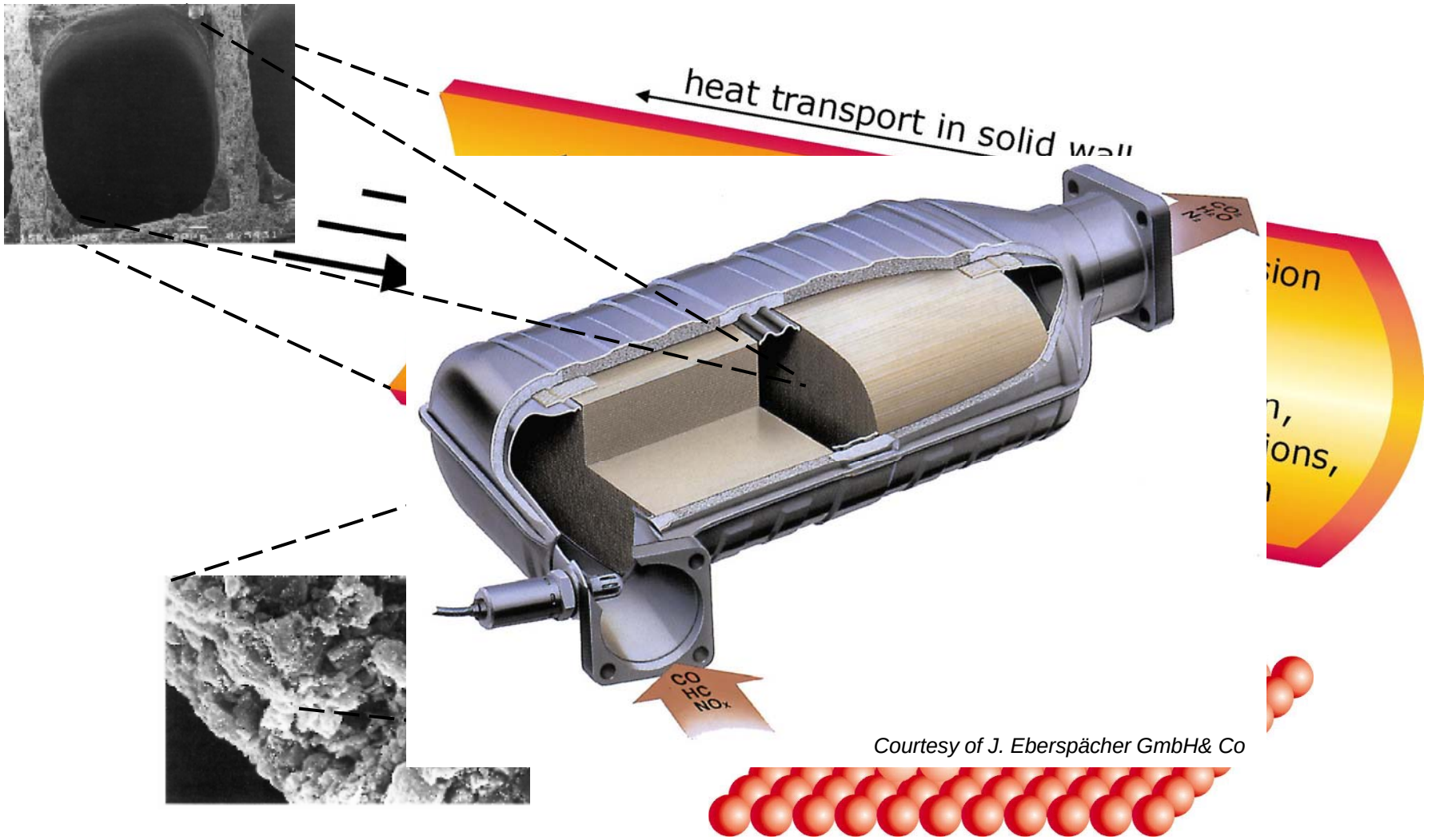




Complex interaction of physics and chemistry: Multi-scale modeling



Courtesy of J. Eberspächer GmbH& Co

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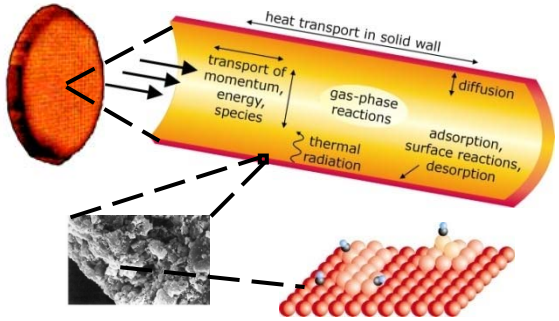
Objective of this lecture: Introduction into the impact of mass and heat transfer on chemical kinetics



Physical-chemical processes occurring in catalytic reactors

- Surface micro kinetics
- Internal and external diffusion
- Flow field
- Heat transport
- Gas-phase micro kinetics

Transient processes, Initial and boundary conditions

Experimental methods, Modeling, Numerical Simulation

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Kinetics – Interaction between Reaction, Mass and Heat Transfer: Outline

1. **Microkinetics of reactions on the catalytic surface**
2. Transport and reactions in porous media (internal diffusion)
3. Reactive flow and external diffusion
4. Gas-phase chemistry
5. Transient processes and heat transport

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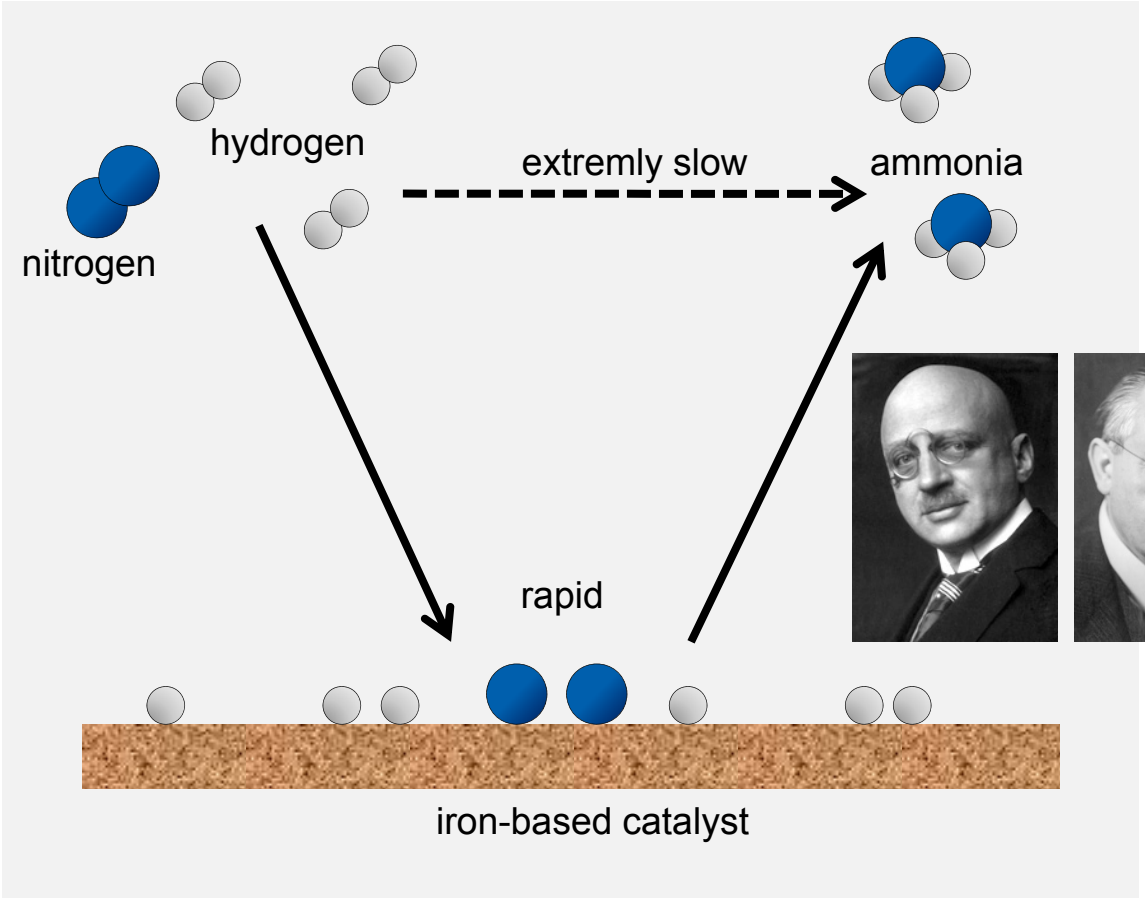
Micro kinetics of heterogeneous catalysis: ammonia synthesis studied since 1905
Haber/Karlsruhe, Bosch/BASF, Ertl/Berlin



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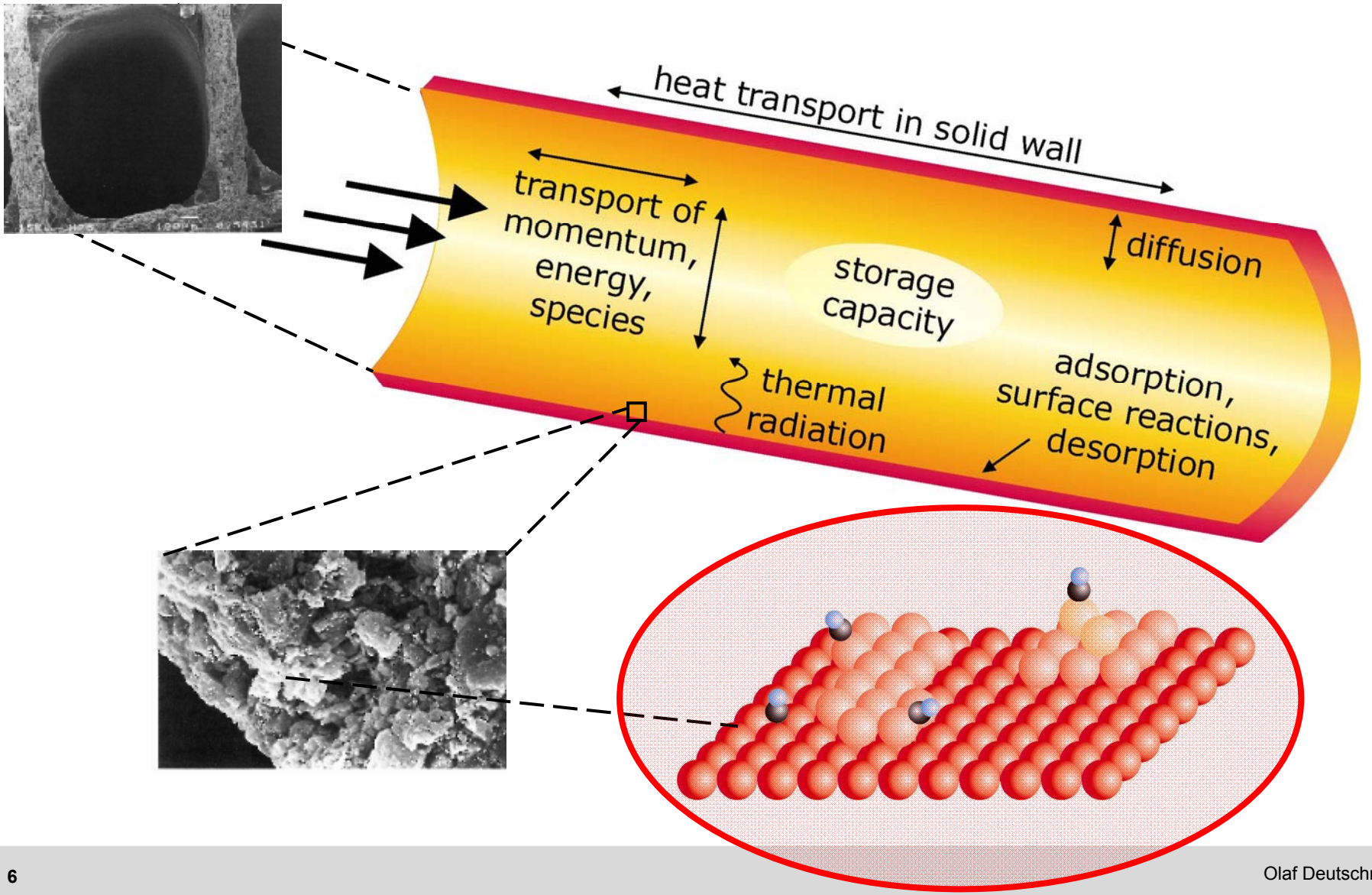
Heterogeneous catalytic reactions



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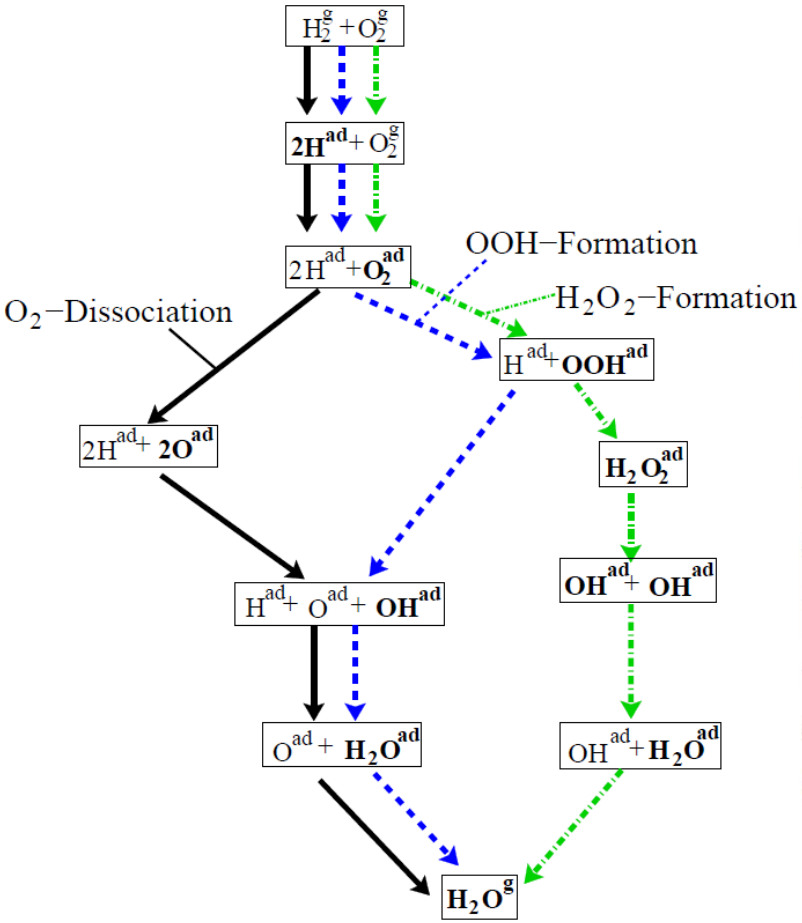
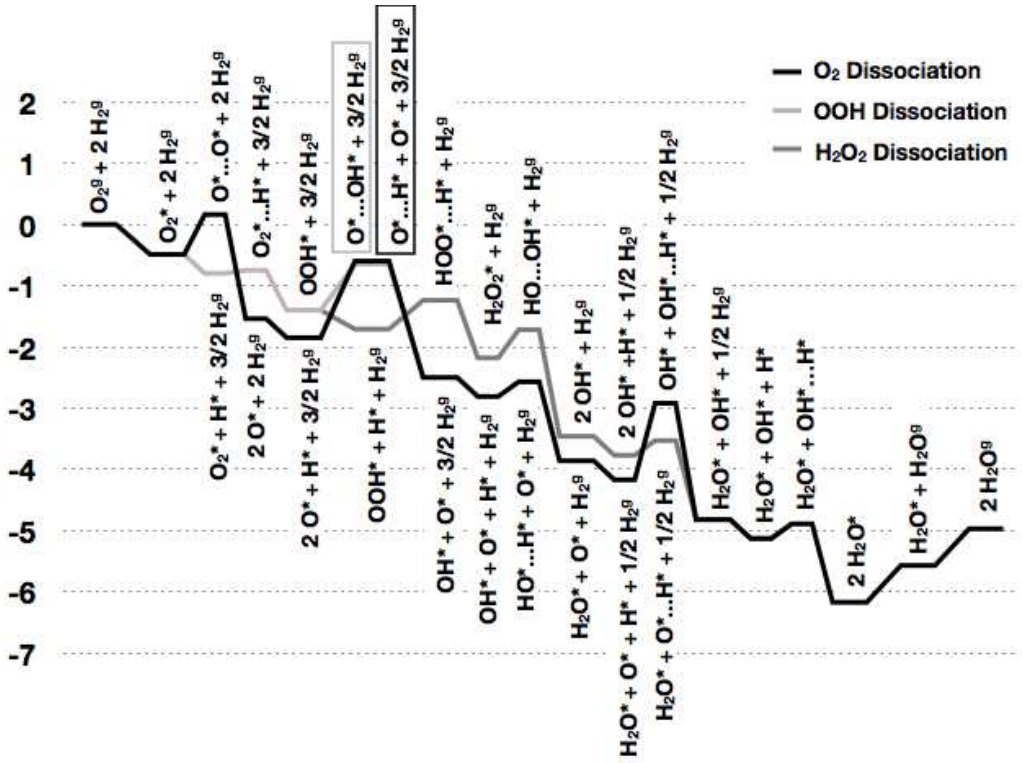
DFT - Simulation: Periodic boundary approach: H_2 oxidation over Pt(111)





J.A. Keith, J. Anton, T.Jacob. Chapter 1 in Modeling Heterogeneous Catalytic Reactions. O. Deutschmann (Ed.), 2011

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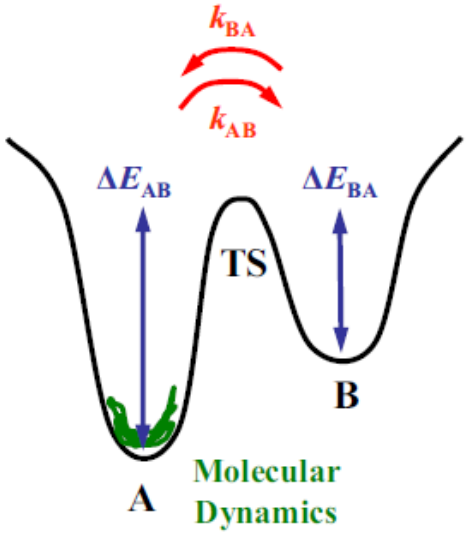
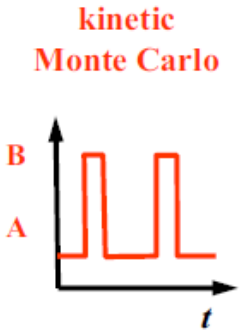
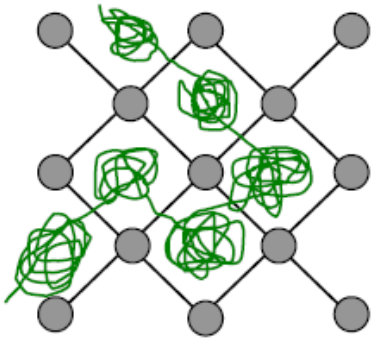
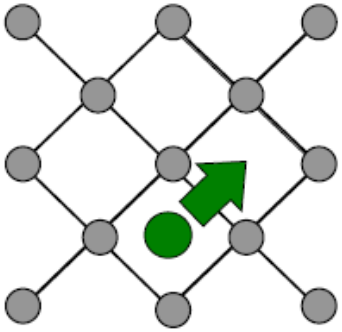
Molecular Dynamics vs. Monte Carlo Simulations





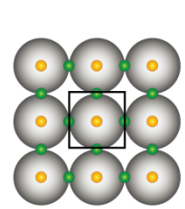


Molecular Dynamics: the whole trajectory

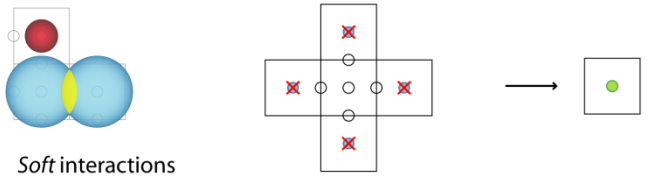


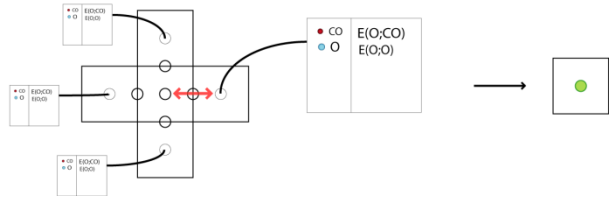
Kinetic Monte Carlo: coarse-grained hops

Formulation of reaction scheme



ontop
bridged





CO
O
hard sphere interaction
empty Place

K. Reuter. Chapter 2 (left) and L. Kunz et al., Chapter 4 (right) in Modeling Heterogeneous Catalytic Reactions. O. Deutschmann (Ed.), 2011

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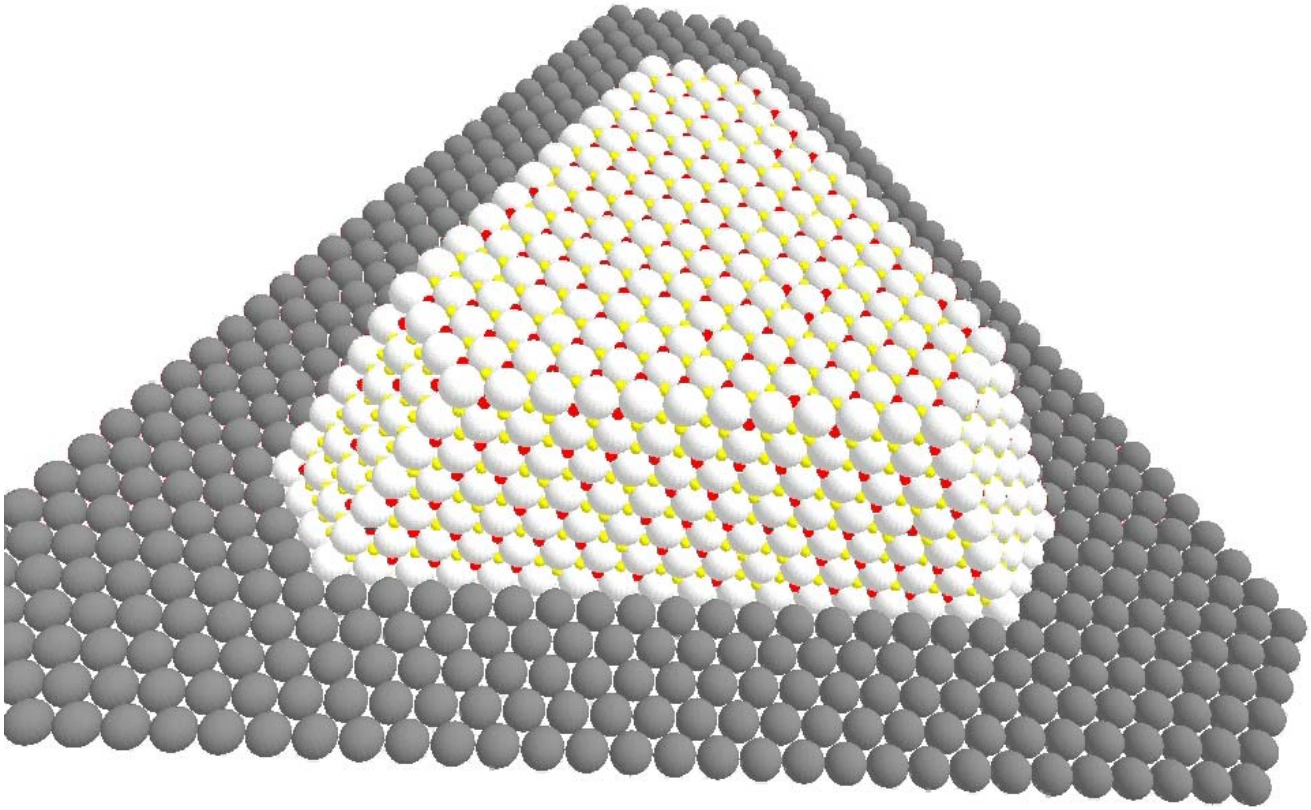
Kinetic Monte Carlo Simulation of surface reactions and diffusion: CO oxidation on Pt nanoperticle



$2\ CO + O_2 \rightarrow 2\ CO_2$
CO: blue O: red
Catalyst atom (Pt): white
Washcoat molecule (Al_2O_3): grey
Adsorption sites: yellow

L. Kunz et al., Chapter 4 in Modeling Heterogeneous Catalytic Reactions. O. Deutschmann (Ed.), 2011

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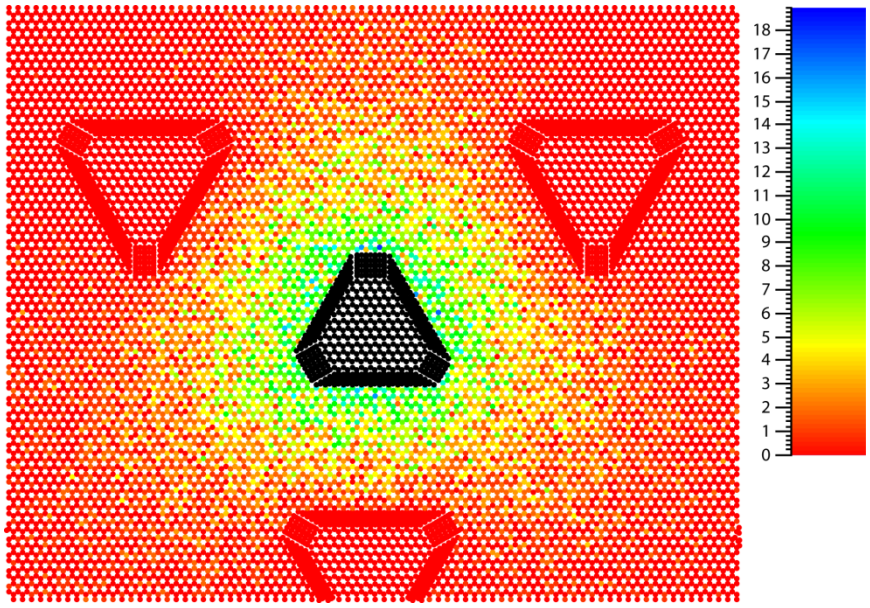
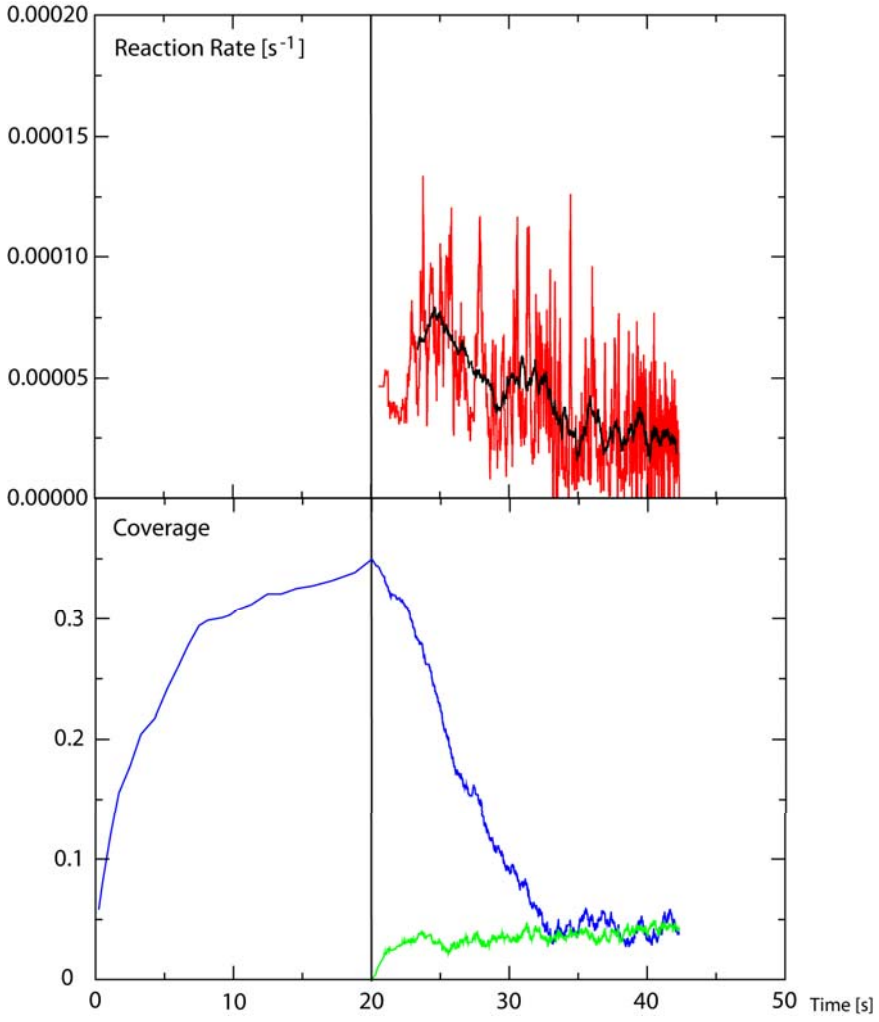
Kinetic Monte Carlo Simulation of surface reactions and diffusion: CO oxidation on Pt nanoperticle

Results of simulations:

- coverages over time on each facet
- reaction rates of each process
- number of times each process was used





L. Kunz et al., Chapter 4 in Modeling Heterogeneous Catalytic Reactions. O. Deutschmann (Ed.), 2011

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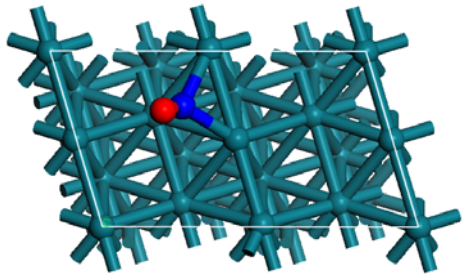
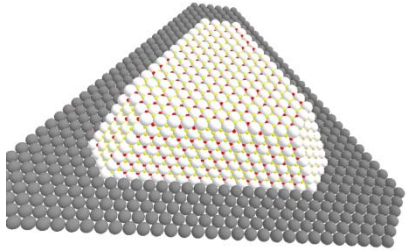
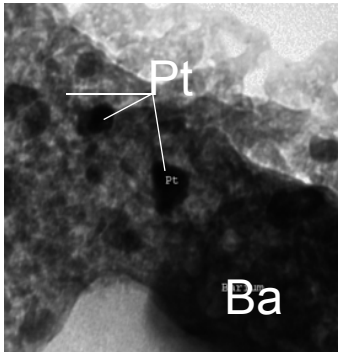
Modeling heterogeneous reactions: Molecular picture leads to mechanistic model







Surface coverage

$$\Theta_i = \frac{c_i \sigma_i}{\Gamma} \qquad \frac{\partial \Theta_i}{\partial t} = \frac{\dot{s}_i M_i}{\Gamma}$$

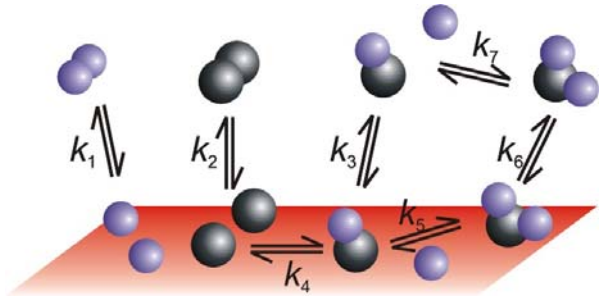
Surface reaction rate

$$\dot{s}_i = \sum_{k \in \mathbf{R}} \nu_{ik} k_{f_k} \prod_{j \in \mathbf{S}} c_j^{\nu'_{jk}}$$

Rate expression

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{a_k}}{RT}\right] \prod_{i=1}^{N_s} \Theta_i^{\mu_{ik}} \exp\left[\frac{\varepsilon_{i_k} \Theta_i}{RT}\right]$$

Locally resolved reaction rates depending on gas-phase concentration and surface coverages



O. Deutschmann. Chapter 6.6 in Handbook of Heterogeneous Catalysis, 2007

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Proposed surface reaction mechanism for three-way catalyst: Mean field approximation

	A (mole, cm, s)	E_a (kJ/mol)
Adsorption/desorption reactions		
$C_3H_6 + Pt(s) + Pt(s) \rightarrow C_3H_6(s)$	$S^0 = 0.98$	
$C_3H_6(s) \rightarrow Pt(s) + Pt(s) + C_3H_6$	3.7×10^{12}	74.4
$C_3H_6 + Pt(s) + O(s) \rightarrow C_3H_5(s) + OH(s)$	$S^0 = 0.05$ $\mu(\Theta_{Pt(s)}) = -0.9$	
$C_3H_5(s) + OH(s) \rightarrow O(s) + Pt(s) + C_3H_6$	3.7×10^{21}	31.0
$CH_4 + Pt(s) + Pt(s) \rightarrow CH_3(s) + H(s)$	$S^0 = 0.01$	
$O_2 + Pt(s) + Pt(s) \rightarrow O(s) + O(s)$	$S^0 = 0.07$	
$O(s) + O(s) \rightarrow Pt(s) + Pt(s) + O_2$	3.2×10^{21}	224.7 $-120\Theta_{O(s)}$
$H_2 + Pt(s) + Pt(s) \rightarrow H(s) + H(s)$	$S^0 = 0.046$ $\mu(\Theta_{Pt(s)}) = -1$	
$H(s) + H(s) \rightarrow Pt(s) + Pt(s) + H_2$	2.1×10^{21}	69.1 $-6\Theta_{H(s)}$
$H_2O + Pt(s) \rightarrow H_2O(s)$	$S^0 = 0.75$	
$H_2O(s) \rightarrow Pt(s) + H_2O$	5.0×10^{13}	49.2
$CO_2 + Pt(s) \rightarrow CO_2(s)$	$S^0 = 0.005$	
$CO_2(s) \rightarrow Pt(s) + CO_2$	3.6×10^{10}	23.7
$CO + Pt(s) \rightarrow CO(s)$	$S^0 = 0.84$	
$CO(s) \rightarrow Pt(s) + CO$	2.1×10^{13}	136.2 $-33\Theta_{CO(s)}$
$NO + Pt(s) \rightarrow NO(s)$	$S^0 = 0.85$	
$NO(s) \rightarrow Pt(s) + NO$	2.1×10^{12}	80.7
$NO_2 + Pt(s) \rightarrow NO_2(s)$	$S^0 = 0.9$	
$NO_2(s) \rightarrow Pt(s) + NO_2$	1.4×10^{13}	61.0
$N_2O + Pt(s) \rightarrow N_2O(s)$	$S^0 = 0.025$	
$N_2O(s) \rightarrow Pt(s) + N_2O$	1.2×10^{10}	0.7
$N(s) + N(s) \rightarrow Pt(s) + Pt(s) + N_2$	3.7×10^{21}	113.9 $-75\Theta_{CO(s)}$
Surface reactions		
Propylene oxidation		
$C_3H_6(s) \rightarrow C_3H_5(s) + H(s)$	1.0×10^{13}	75.4
$C_3H_5(s) + H(s) \rightarrow C_3H_6(s)$	3.7×10^{21}	48.8
$C_3H_5(s) + Pt(s) \rightarrow C_2H_3(s) + CH_2(s)$	3.7×10^{21}	108.2
$C_2H_3(s) + CH_2(s) \rightarrow C_3H_5(s) + Pt(s)$	3.7×10^{21}	3.3
$C_2H_3(s) + Pt(s) \rightarrow CH_3(s) + C(s)$	3.7×10^{21}	46.0
$CH_3(s) + C(s) \rightarrow C_2H_3(s) + Pt(s)$	3.7×10^{21}	46.5
$CH_3(s) + Pt(s) \rightarrow CH_2(s) + H(s)$	1.3×10^{22}	70.4
$CH_2(s) + H(s) \rightarrow CH_3(s) + Pt(s)$	2.9×10^{22}	0.4
$CH_2(s) + Pt(s) \rightarrow CH(s) + H(s)$	7.0×10^{22}	59.2
$CH(s) + H(s) \rightarrow CH_2(s) + Pt(s)$	8.1×10^{21}	0.7
$CH(s) + Pt(s) \rightarrow C(s) + H(s)$	3.1×10^{22}	0.0
$C(s) + H(s) \rightarrow CH(s) + Pt(s)$	5.8×10^{21}	128.9
$C_3H_5(s) + O(s) \rightarrow C_3H_4(s) + OH(s)$	5.0×10^{21}	70.0
$C_3H_4(s) + 4\,O(s) + 2\,Pt(s) \rightarrow 3\,C(s) + 4\,OH(s)$	2.6×10^{64}	0.0 [a]
$C_2H_3(s) + O(s) \rightarrow CH_3CO(s) + Pt(s)$	3.7×10^{19}	62.3
$CH_3CO(s) + Pt(s) \rightarrow C_2H_3(s) + O(s)$	7.9×10^{20}	191.4 $+60\Theta_{O(s)}$
$CH_3(s) + CO(s) \rightarrow CH_3CO(s) + Pt(s)$	3.7×10^{21}	82.9
$CH_3CO(s) + Pt(s) \rightarrow CH_3(s) + CO(s)$	1.8×10^{23}	6.1 $+33\Theta_{CO(s)}$
$CH_3(s) + O(s) \rightarrow OH(s) + CH_2(s)$	3.7×10^{21}	36.6
$OH(s) + CH_2(s) \rightarrow CH_3(s) + O(s)$	2.3×10^{22}	26.0
$CH_2(s) + O(s) \rightarrow OH(s) + CH(s)$	3.7×10^{21}	25.1
$OH(s) + CH(s) \rightarrow CH_2(s) + O(s)$	1.2×10^{21}	26.8
$CH(s) + O(s) \rightarrow OH(s) + C(s)$	3.7×10^{21}	25.1
$OH(s) + C(s) \rightarrow CH(s) + O(s)$	1.9×10^{21}	214.2
Carbon monoxide oxidation		
$CO(s) + O(s) \rightarrow CO_2(s) + Pt(s)$	3.7×10^{21}	48.2
	2.5×10^{20}	38.2
	3.7×10^{21}	94.2
$CO_2(s) + Pt(s) \rightarrow CO(s) + O(s)$	1.3×10^{21}	0.9
	3.7×10^{21}	0.0
$C(s) + O(s) \rightarrow CO(s) + Pt(s)$	2.8×10^{21}	151.1
	3.7×10^{21}	0.0
$CO(s) + Pt(s) \rightarrow C(s) + O(s)$	2.8×10^{21}	90.1
Reactions of hydroxyl species		
$H(s) + O(s) \rightarrow OH(s) + Pt(s)$		
$OH(s) + Pt(s) \rightarrow H(s) + O(s)$		
$OH(s) + H(s) \rightarrow H_2O(s) + Pt(s)$		
$H_2O(s) + Pt(s) \rightarrow OH(s) + H(s)$		
$OH(s) + OH(s) \rightarrow H_2O(s) + O(s)$		
$H_2O(s) + O(s) \rightarrow OH(s) + OH(s)$		
$CO(s) + OH(s) \rightarrow HCOO(s) + Pt(s)$		
$HCOO(s) + Pt(s) \rightarrow CO(s) + OH(s)$		
$HCOO(s) + O(s) \rightarrow OH(s) + CO_2(s)$		
$OH(s) + CO_2(s) \rightarrow HCOO(s) + O(s)$		
$HCOO(s) + Pt(s) \rightarrow H(s) + CO_2(s)$		
$H(s) + CO_2(s) \rightarrow HCOO(s) + Pt(s)$		
Reactions of NO and NO_2		
$NO(s) + Pt(s) \rightarrow N(s) + O(s)$	5.0×10^{20}	107.8 $+33\Theta_{CO(s)}$
$N(s) + O(s) \rightarrow NO(s) + Pt(s)$	1.0×10^{21}	122.6 $-60\Theta_{O(s)}$
$O(s) + NO \rightarrow NO_2(s)$	2.0×10^{13}	111.3 $+75\Theta_{CO(s)}$ $-60\Theta_{O(s)}$
$NO_2(s) \rightarrow O(s) + NO$	3.3×10^{14}	115.5
$N(s) + NO(s) \rightarrow N_2O(s) + Pt(s)$	1.0×10^{21}	90.9
$N_2O(s) + Pt(s) \rightarrow N(s) + NO(s)$	2.9×10^{24}	133.1
$O(s) + NO(s) \rightarrow NO_2(s) + Pt(s)$	1.3×10^{17}	133.0 $+75\Theta_{CO(s)}$
$NO_2(s) + Pt(s) \rightarrow O(s) + NO(s)$	8.1×10^{18}	58.0
$H(s) + NO(s) \rightarrow OH(s) + N(s)$	1.2×10^{21}	25.0 $+80\Theta_{CO(s)}$
$OH(s) + N(s) \rightarrow H(s) + NO(s)$	6.4×10^{21}	99.9
$NO_2(s) + H(s) \rightarrow OH(s) + NO(s)$	3.9×10^{21}	20.0
$OH(s) + NO(s) \rightarrow NO_2(s) + H(s)$	6.1×10^{22}	175.3

D. Chatterjee, O. Deutschmann, J. Warnatz. Faraday Discuss. 119 (2001) 371
J. Koop, O. Deutschmannn. Appl. Catal. B: Env. 91 (2009) 47

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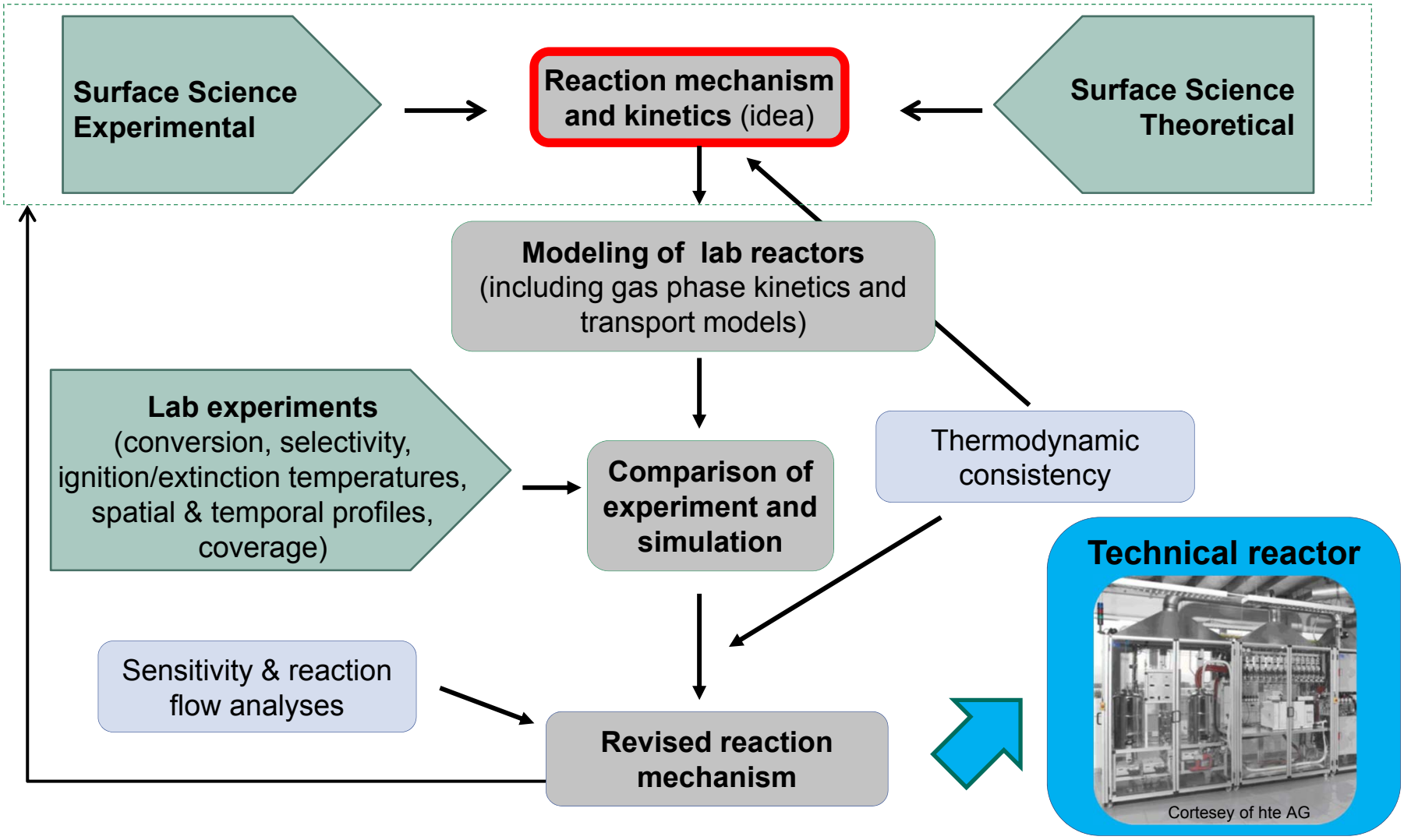
Development of micro kinetic models for simulations of catalytic reactors



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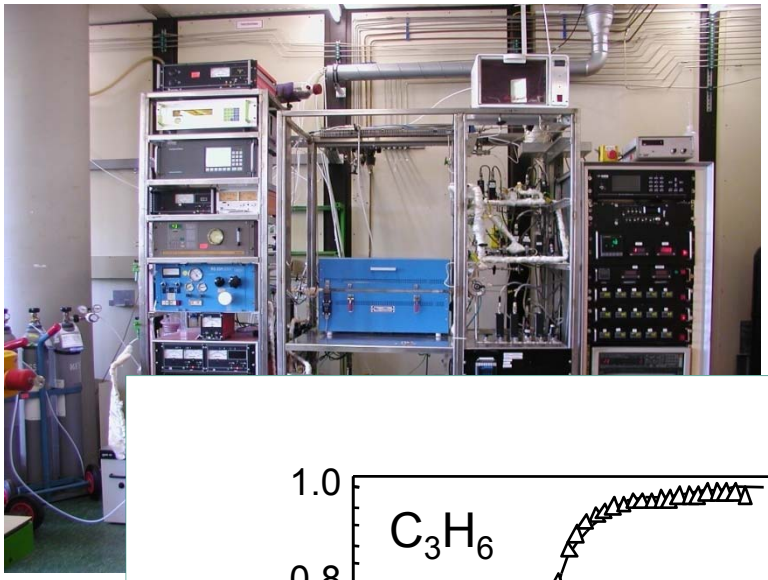
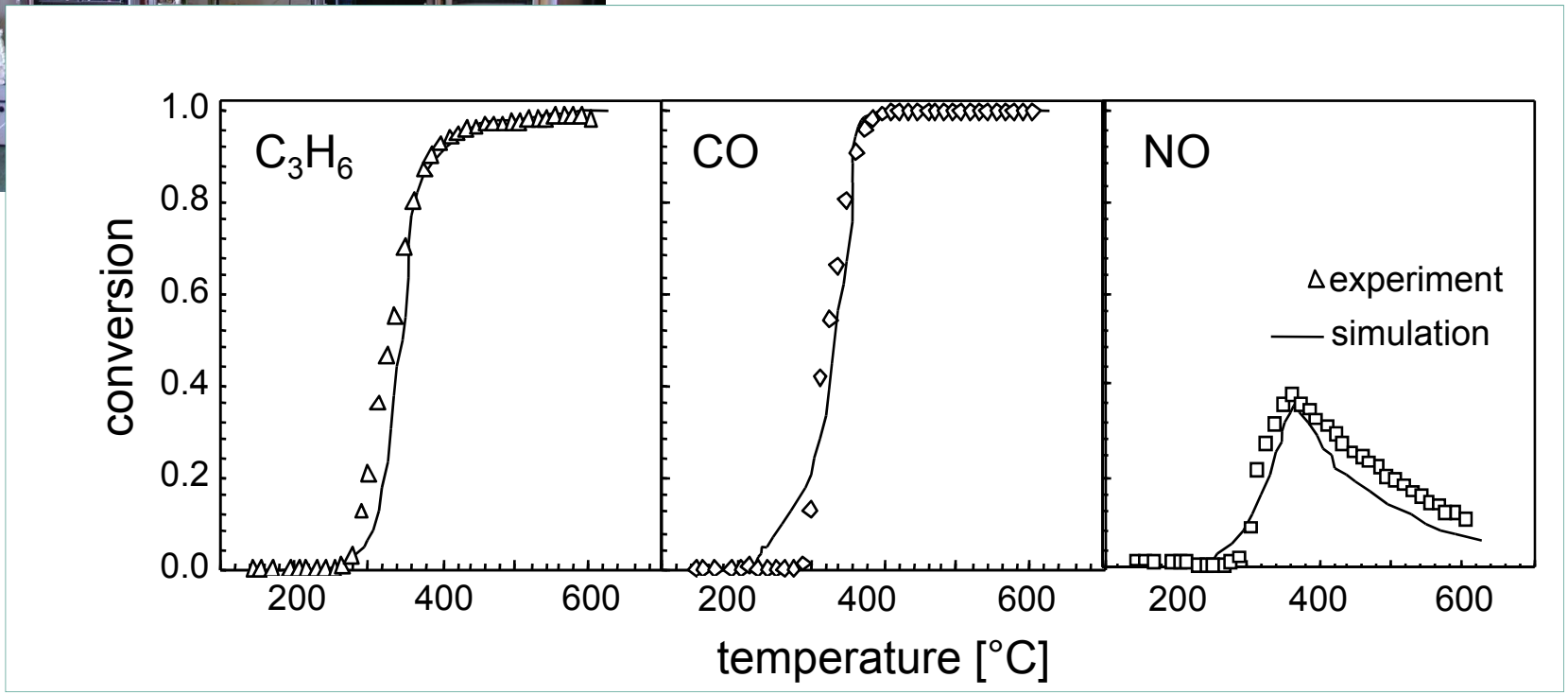
Conversion of a synthetic exhaust in a real three way catalyst: Steady-state conditions



Laboratory experiments at well-defined conditions, e.g. differentially operated reactors (no gradients),
are used for first model evaluation



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Kinetics – Interaction between Reaction, Mass and Heat Transfer: Outline

1. Microkinetics of reactions on the catalytic surface
2. **Transport and reactions in porous media (internal diffusion)**
3. Reactive flow and external diffusion
4. Gas-phase chemistry
5. Transient processes and heat transport

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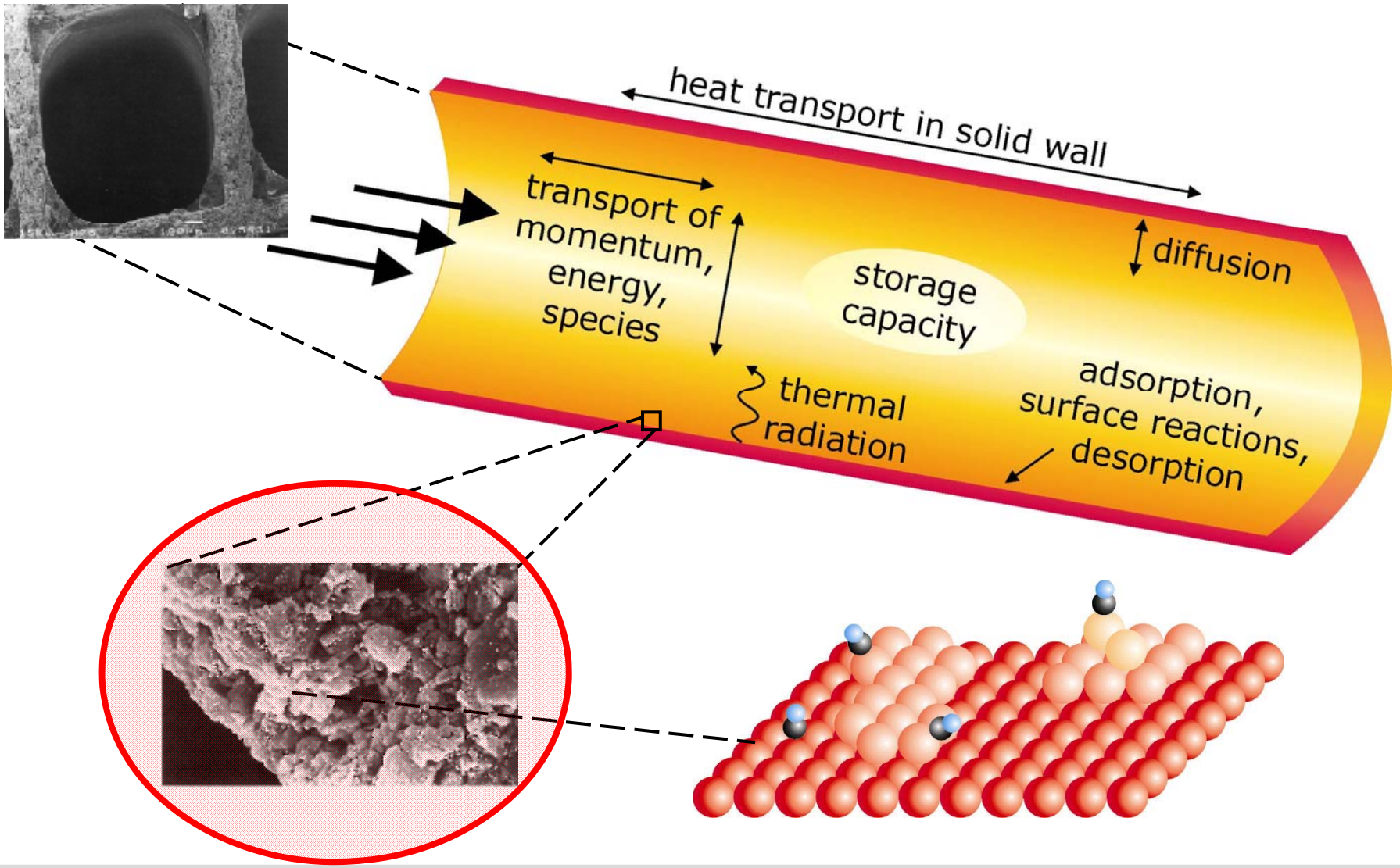
Coupling of internal diffusion and reaction



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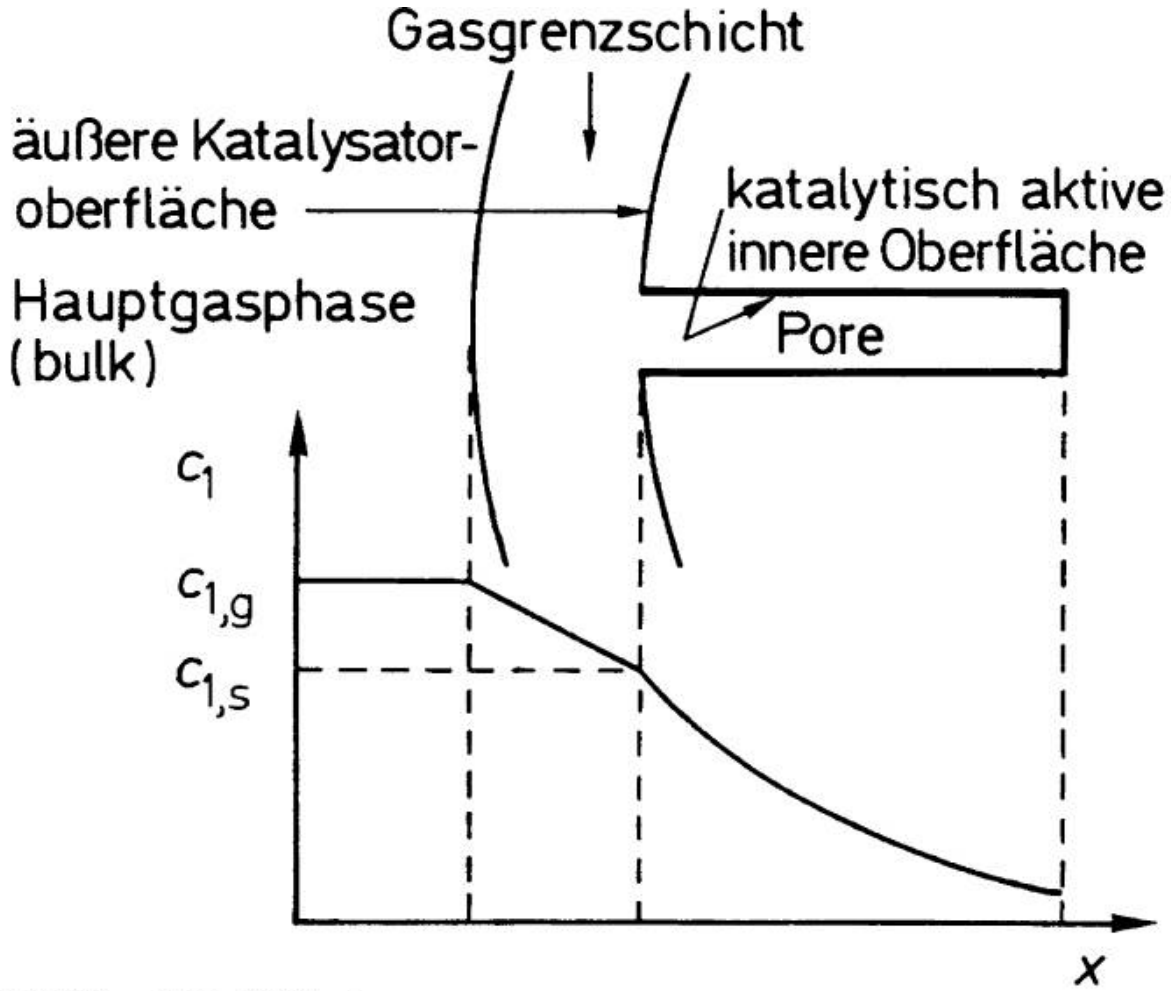
Stofftransporthemmung für einen porösen Katalysator



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ISBN: 3-527-31000-2 Abb-04-03-01

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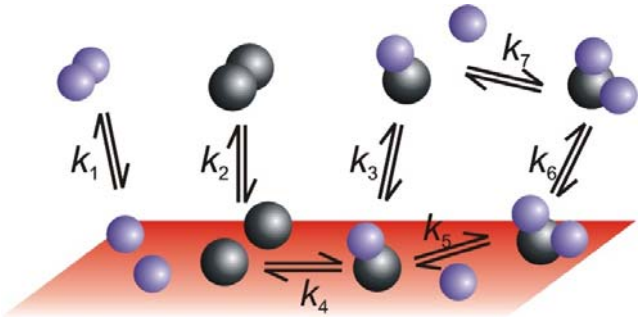
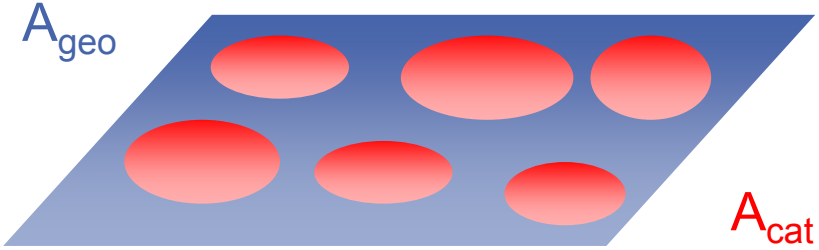
Coupling of surface reaction rate and flow field - Modeling transport limitation of reaction rate

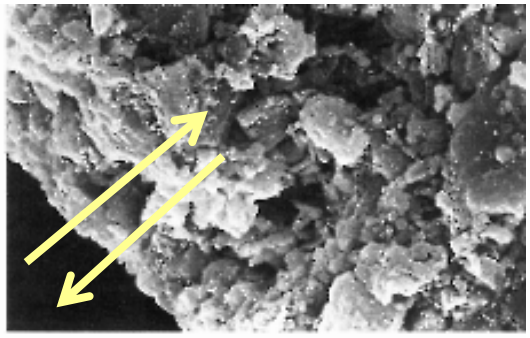


microscopic site density Γ



macroscopic catalyst area → $F_{cat/geo}$ = A_{cat} / A_{geo}

$$j_{i,s} = F_{\text{cat/geo}}\, \eta_i\, M_i\, \dot{s}_i$$



Effectiveness factor $\eta_i = \dfrac{\tanh(\Phi_i)}{\Phi_i}$

$$\Phi_i = L \sqrt{\frac{\dot{s}_i\, \gamma}{D_{\text{eff},i}\, c_{i,0}}}$$

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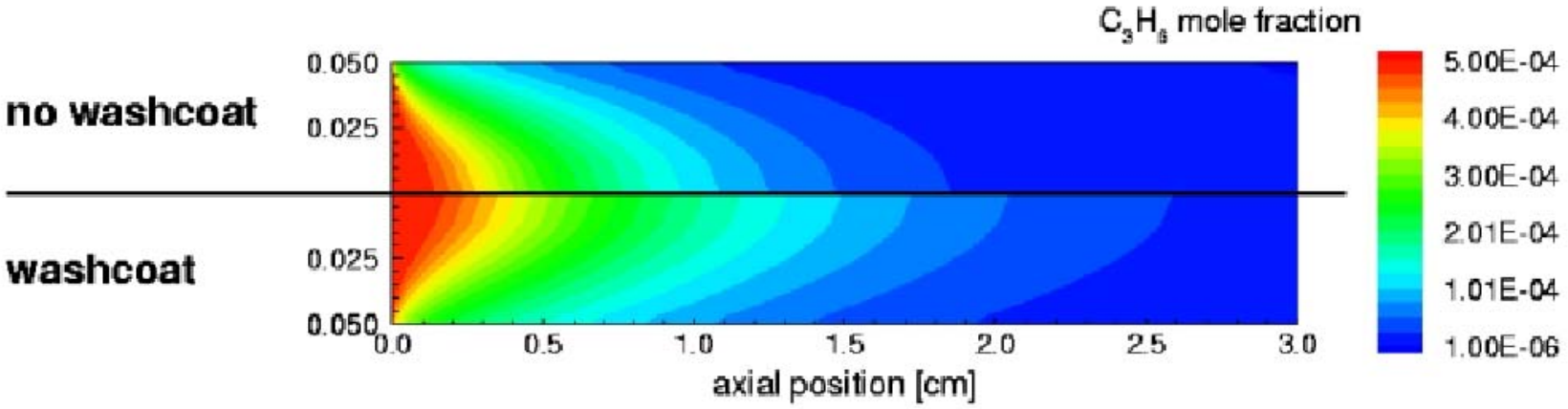
HC-SCR on Pt/Al_2O_3: Impact of washcoat transport limitation on conversion



Conditions:

500 ppm C_3H_6, 500 ppm NO, 5 Vol.-% O_2, in N_2, 6 slpm, u = 0.63 m/s; T = 570 K

D. Chatterjee, O. Deutschmann, 2000

Olaf Deutschmann
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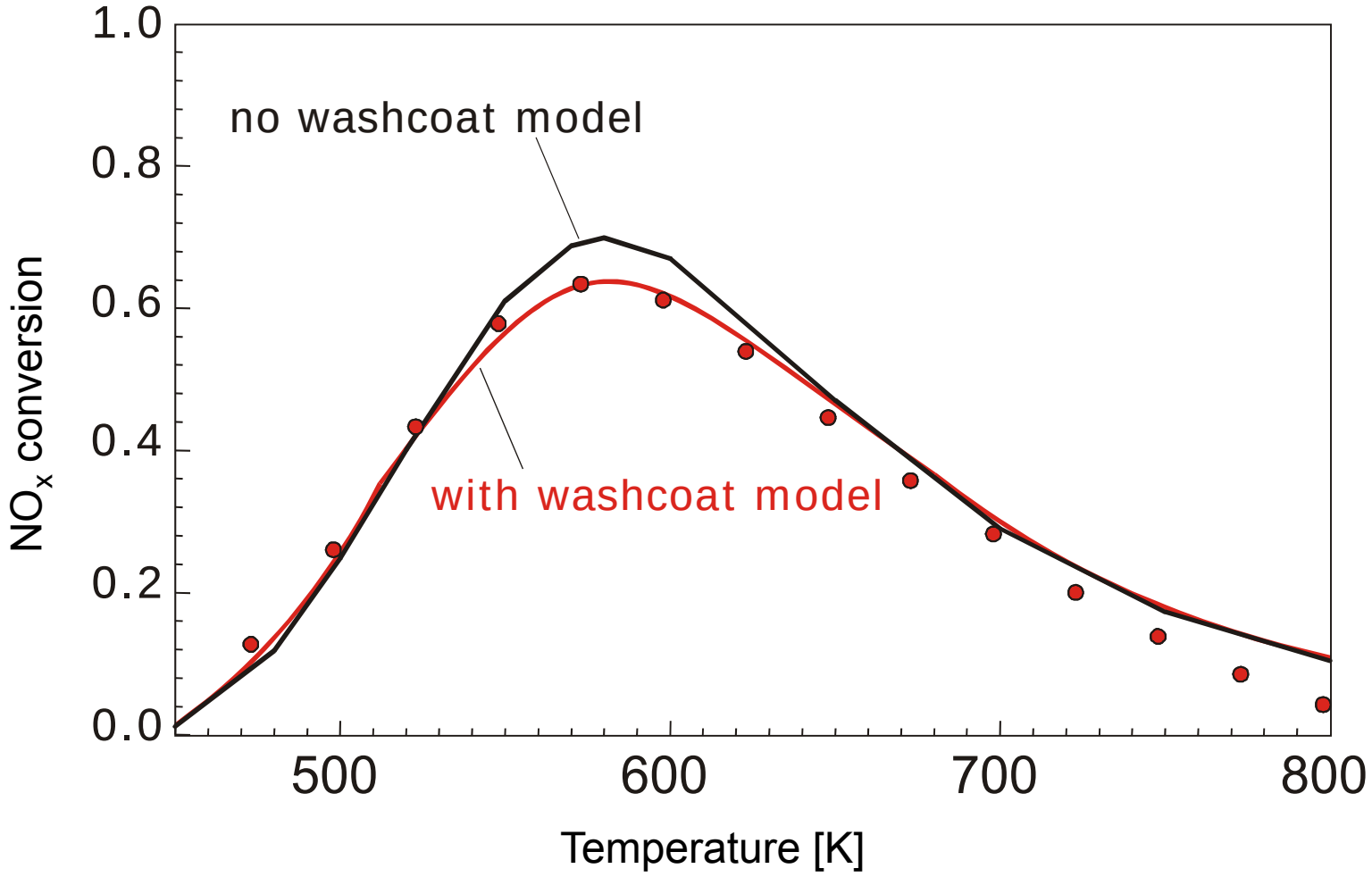
NO oxidation on Pt/Al_2O_3: Impact of washcoat transport limitation on conversion



Conditions: 500 ppm NO, 1 Vol.-% O_2 in N_2

D. Chatterjee, O. Deutschmann, 2000

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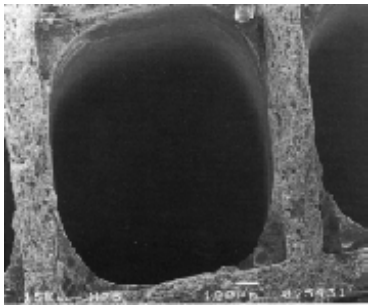
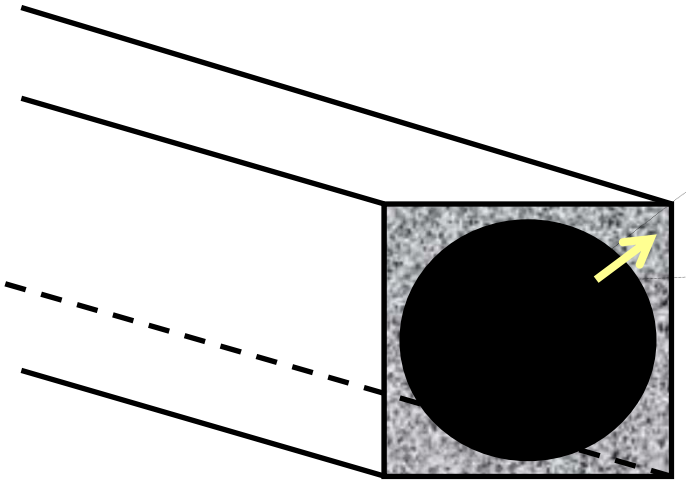
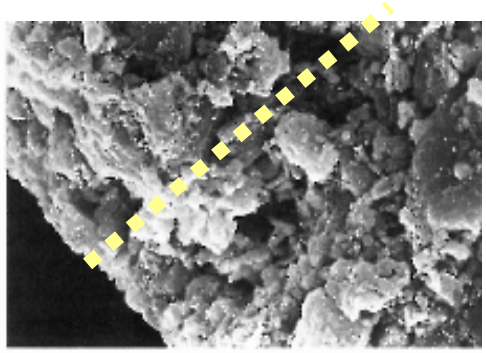
Modeling reaction and transport in porous media: 1d reaction-diffusion equations



Washcoat is treated as continuum





Discretization of the washcoat normal to the gas-phase-washcoat boundary at each radial and axial position

$$D_{\mathrm{eff},i}\frac{\partial c_i^{\mathrm{W}}}{\partial r}+\gamma\, M_i \dot{s}_i = 0 \qquad (i=1,\ldots,N_{\mathrm{g}})$$

$$\dot{s}_i = \sum_{k=1}^{K_s} \nu_{ik} k_{f_k} \prod_{j=1}^{N_g+N_s} c_j^{\nu'_{jk}}$$

$$\dot{s}_i = 0 \qquad (i=N_{\mathrm{g}}+1,\ldots,N_{\mathrm{g}}+N_{\mathrm{s}})$$

$$j_i^{\mathrm{surf}} = j_{r,i}^{\mathrm{W}}(r=0) = -D_{\mathrm{eff},i}\left.\frac{\partial c_i^{\mathrm{W}}}{\partial r}\right|_{r=0}$$

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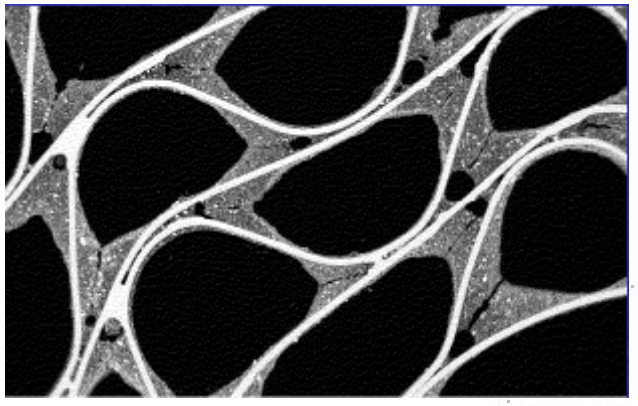
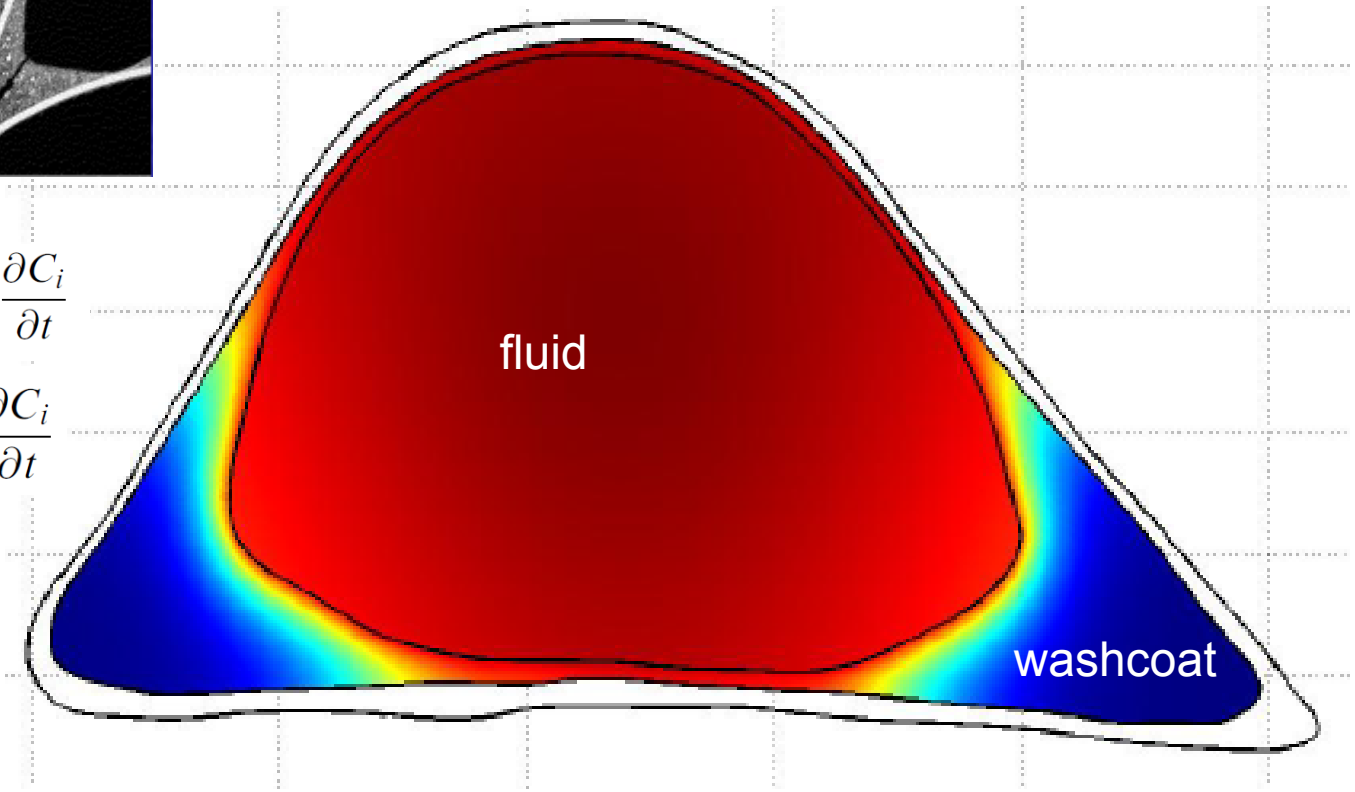
Understanding the interaction of diffusion and reaction: Potential for reduced catalyst costs by zone coating



Reactant concentration in a complex shaped channel

$$\nabla \cdot (D_i \nabla C_i) - \nabla \cdot (v C_i) = \frac{\partial C_i}{\partial t}$$

$$(D_{\text{eff}})_i \nabla^2 C_i - (-R_i) = \varepsilon \frac{\partial C_i}{\partial t}$$



R.E. Hayes, B. Liu, M. Votsmeier. Chem. Eng. Sci. 60 (2005) 2037.

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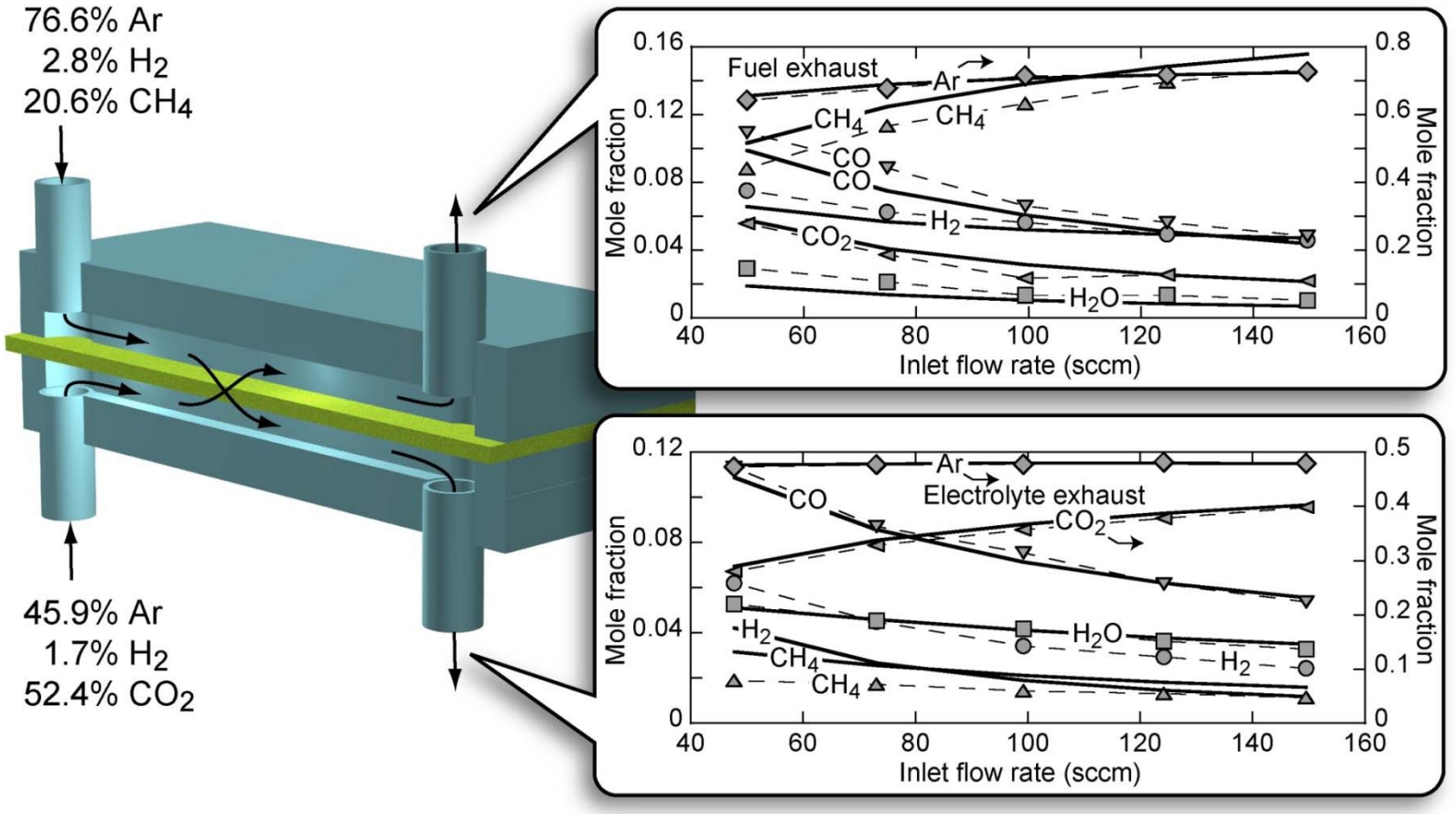
Experimental set-up for the evaluation of transport and reaction kinetics in a Ni/YSZ membrane: CH_4 dry reforming



E. Hecht, G.K. Gupta, H. Zhu. A.M. Dean, R.J. Kee, L. Maier, O. Deutschmann. Applied Catalysis A: General 295 (2005) 40–51

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Institute for Chemical Technology and Polymer Chemistry

Kinetics – Interaction between Reaction, Mass and Heat Transfer: Outline

1. Microkinetics of reactions on the catalytic surface
2. Transport and reactions in porous media (internal diffusion)
3. **Reactive flow and external diffusion**
4. Gas-phase chemistry
5. Transient processes and heat transport

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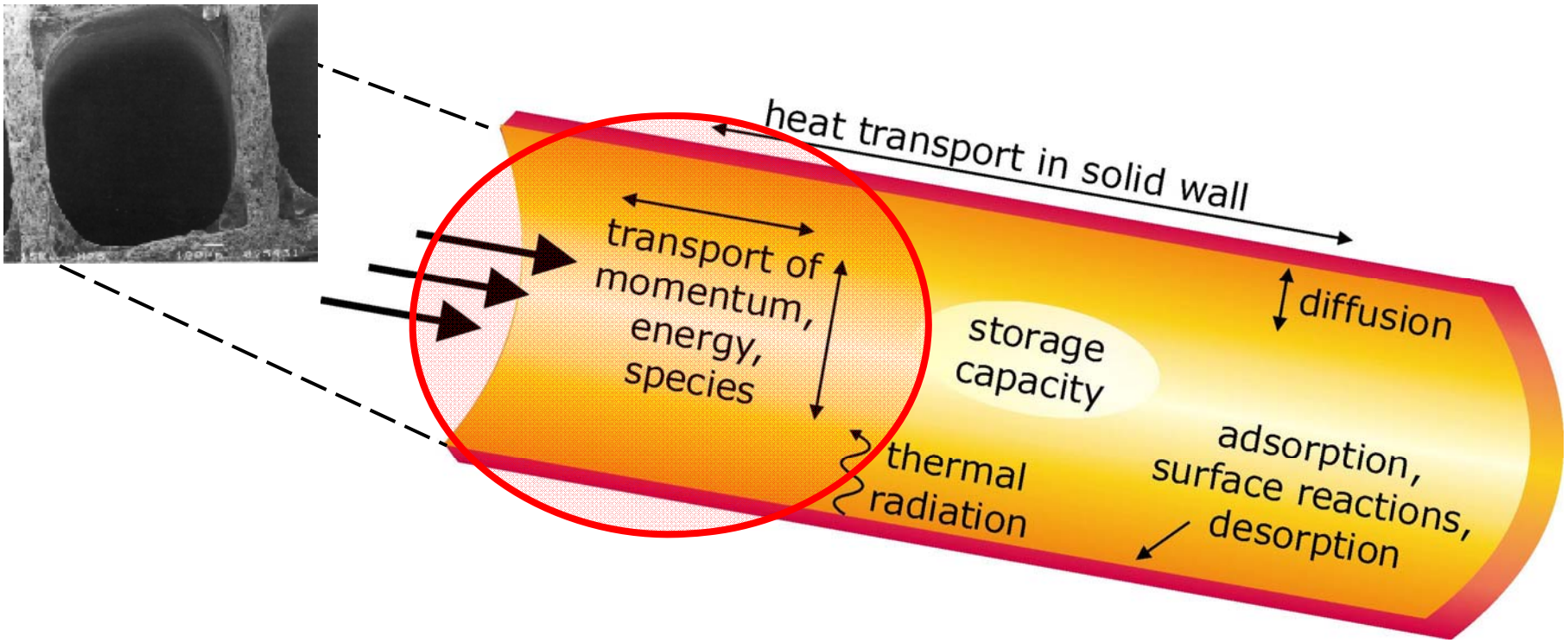
Modeling the flow in the channel



General:
Transient 3D Navier-Stokes equations + species mass balances + heat balances

Simplifying assumptions often made:
No direct transients, cylindrical channel, no axial (and radial) diffusion

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Most general approach for modeling laminar flow fields: Transient 3D Navier-Stokes equations

Karlsruhe Institute of Technology

Total mass

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho v_i)}{\partial x_i} = S_\mathrm{m}$$

Momentum

$$\frac{\partial (\rho v_i)}{\partial t} + \frac{\partial (\rho v_i v_j)}{\partial x_j} + \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} = \rho g_i$$

$$\tau_{ij} = -\mu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) + \left(\frac{2}{3}\mu - \kappa \right) \delta_{ij} \frac{\partial v_k}{\partial x_k}$$

Species' mass

$$\frac{\partial (\rho Y_i)}{\partial t} + \frac{\partial (\rho v_j Y_i)}{\partial x_j} + \frac{\partial (j_{i,j})}{\partial x_j} = R_i^\mathrm{hom}$$

$$j_{i,j} = -\rho \frac{Y_i}{X_i} D_i^\mathrm{M} \frac{\partial X_i}{\partial x_j} - \frac{D_i^\mathrm{T}}{T} \frac{\partial T}{\partial x_j}$$

Heat transport

$$\frac{\partial (\rho h)}{\partial t} + \frac{\partial (\rho v_j h)}{\partial x_j} + \frac{\partial j_{q,j}}{\partial x_j} = \frac{\partial p}{\partial t} + v_j \frac{\partial p}{\partial x_j} - \tau_{jk} \frac{\partial v_j}{\partial x_k} + S_\mathrm{h}$$

$$j_{q,j} = -\lambda \frac{\partial T}{\partial x_j} + \sum_{i=1}^{Ng} h_i j_{i,j}$$

solid phase

$$\frac{\partial (\rho h)}{\partial t} - \frac{\partial}{\partial x_j} \left(\lambda \frac{\partial T}{\partial x_j} \right) = S_\mathrm{h}$$

$$S_{h,\mathrm{ext\,rad}} = -\varepsilon \sigma \left(T_\mathrm{solid}^4 - T_\mathrm{ref}^4 \right) A$$

temperature

$$h = \sum_{i=1}^{Ng} Y_i h_i(T)$$

Equation of state (perfect gas)

$$p = \frac{\rho R T}{\sum_{i=1}^{N_g} X_i M_i}$$

$$X_i = \frac{1}{\sum_{j=1}^{Ng} Y_j / M_j} \frac{Y_i}{M_i}$$

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Model simplification by assuming a cylindrical channel and neglecting axial diffusion: Boundary-layer equations

Total mass flux

$$\frac{\partial(\rho u)}{\partial z} = -\frac{1}{r}\frac{\partial(r\rho v)}{\partial r}$$

Axial momentum flux

$$\frac{\partial(\rho u u)}{\partial z} = -\frac{1}{r}\frac{\partial(r\rho v u)}{\partial r} - \frac{\partial p}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}\left(\eta r \frac{\partial u}{\partial r}\right) + \rho g_z$$

Enthalpy flux

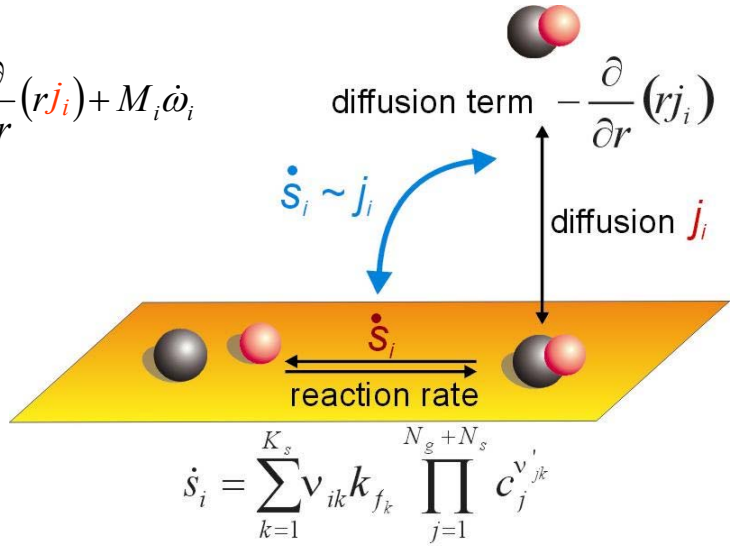
$$\frac{\partial(\rho u h)}{\partial z} = -\frac{1}{r}\frac{\partial(r\rho v h)}{\partial r} + u\frac{\partial p}{\partial z} - \frac{1}{r}\frac{\partial}{\partial r}(r q_r)$$

Species mass flux

$$\frac{\partial(\rho u Y_i)}{\partial z} = -\frac{1}{r}\frac{\partial(r\rho v Y_i)}{\partial r} - \frac{1}{r}\frac{\partial}{\partial r}(r j_i) + M_i \dot{\omega}_i$$

Coupling between surface reactions and flow field:

$$\dot{j}_{i,wall} = F_{\text{cat/geo}}\ \eta_i M_i\ \dot{s}_i$$



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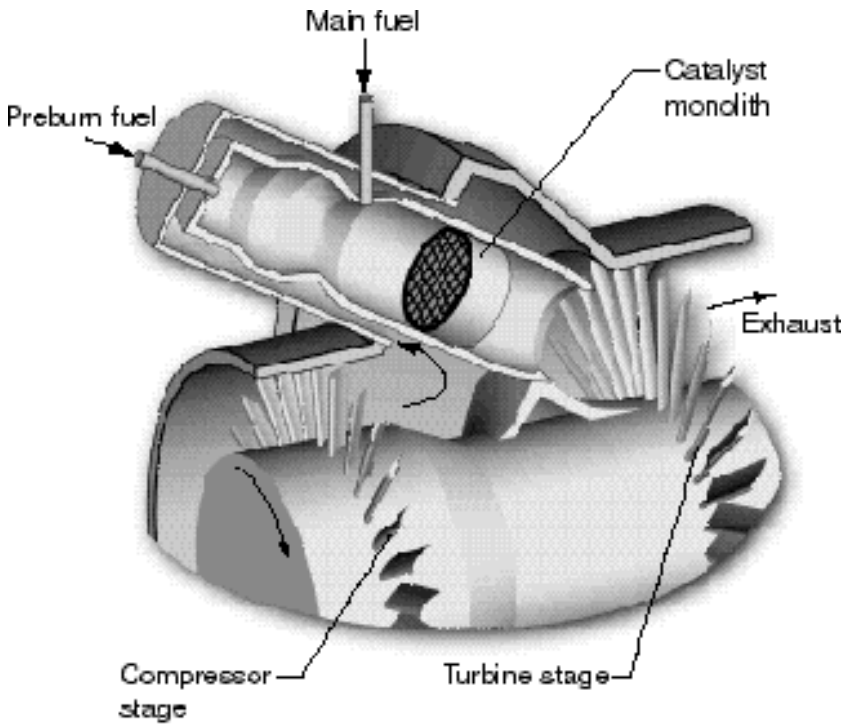
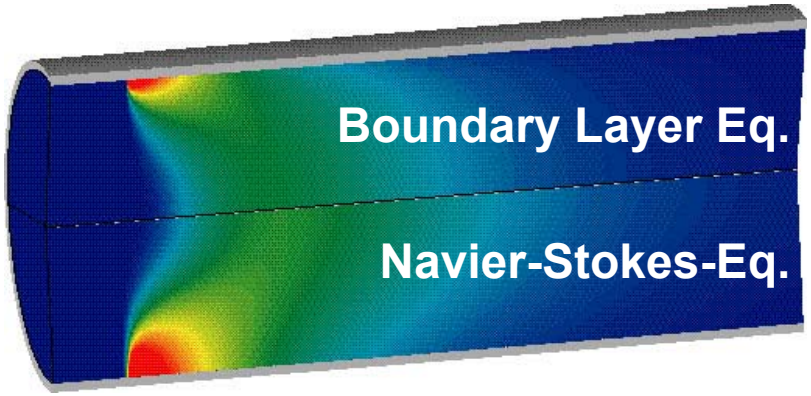
Catalytic combustion of natural gas in catalytic channel: 2D Navier-Stokes and 2D Boundary layer approach

$$CH_4 + 2\,O_2 \xrightarrow{Pt/Pd} CO_2 + 2\,H_2O$$



Picture: Courtesy of Robert J. Kee, Colorado School of Mines



L. L. Raja, R. J. Kee, O. Deutschmann, J. Warnatz, L. D. Schmidt. Catalysis Today 59 (2000) 47-60.

Computed CO concentrations in single monolith channel

⇒ No significant differences

⇒ Axial diffusion can be neglected

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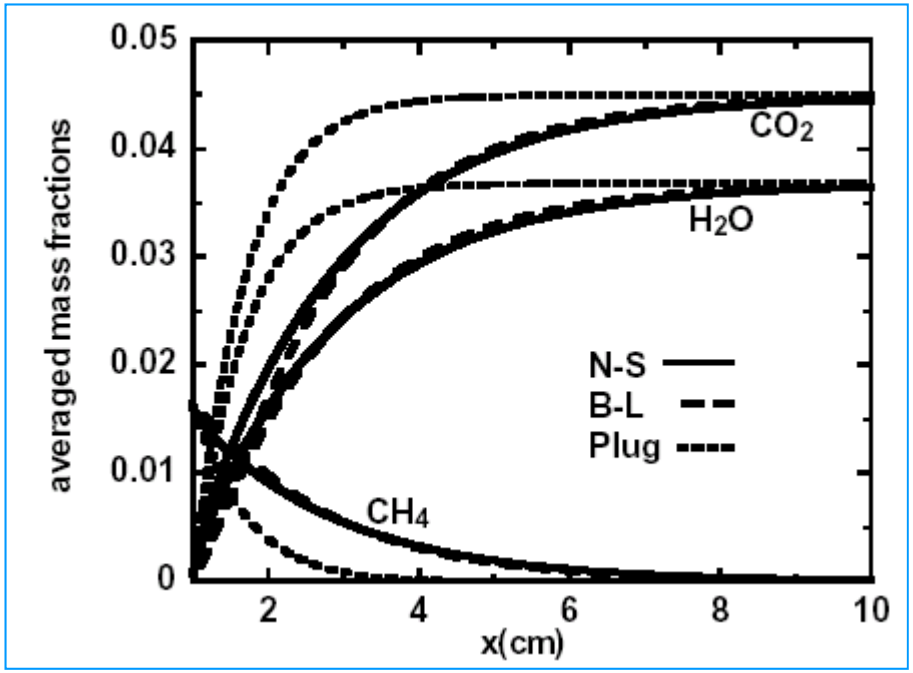
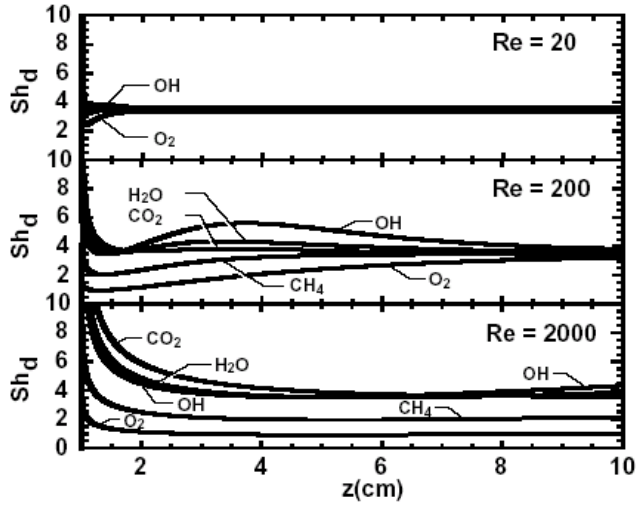
Catalytic combustion of natural gas in catalytic channel: 2D Navier-Stokes, 2D Boundary layer, and 1d Plug flow approach

1D – Plug-Flow-Model over estimates conversion





Use of mass transfer coefficient is difficult due to large reaction rate causing strong variation oif the Sherwood number

L. L. Raja, R. J. Kee, O. Deutschmann, J. Warnatz, L. D. Schmidt. Catalysis Today 59 (2000) 47-60.

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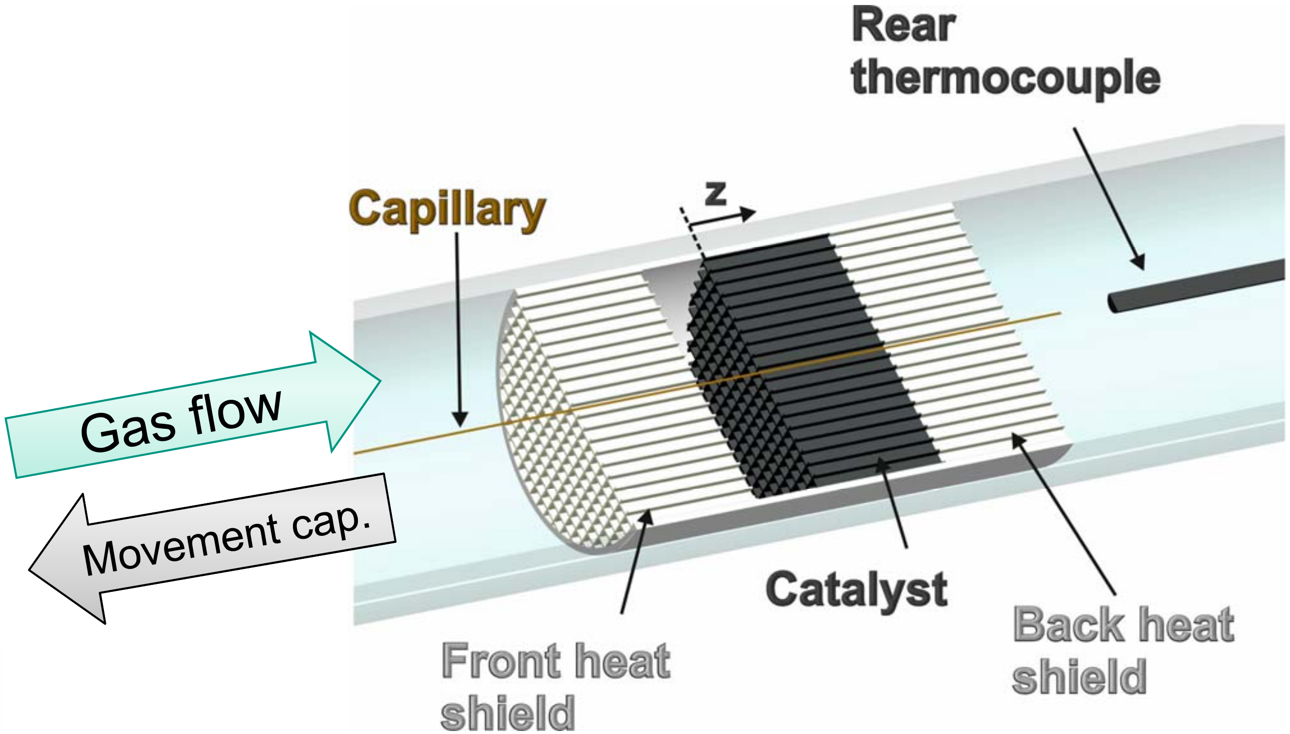
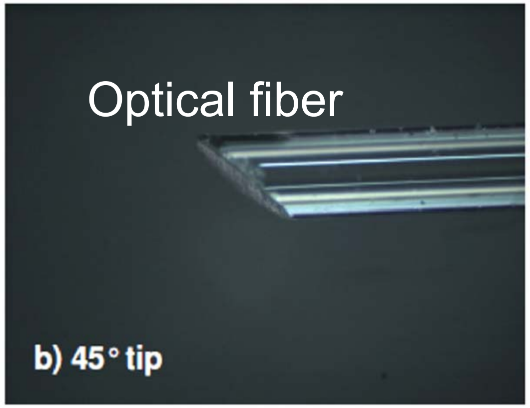
In-Situ Sampling Technique





$\frac{\ }{A_{\text{channel}}} = 2{,}96\%$

A. Donazzi, D. Livio, A. Beretta, G. Groppi, P. Forzatti, Applied Catalysis A: General, 402 (2011) 41.

- Movement of capillary: with motorized linear stage
- Concentration profiles:
- Temperature profiles:
  - Resolution: 0.25 mm
  - Gas samples sucked from catalyst channel with capillary (outer diameter = 170 µm)
  - capillary (outer diameter = 660 µm)
  - Gas-phase temperature: Thermocouple
  - Surface temperature: Optical fiber connected to pyrometer
  - Analysis of gas samples: FT-IR, MS

R. Horn, K.A. Williams, N.J. Degenstein, L.D. Schmidt, J. Catal., 242 (2006) 92.
D. Livio, C. Diehm, A. Donazzi, A. Beretta, G. Groppi, O. Deutschmann, Appl. Catal. A 467 (2013) 530.

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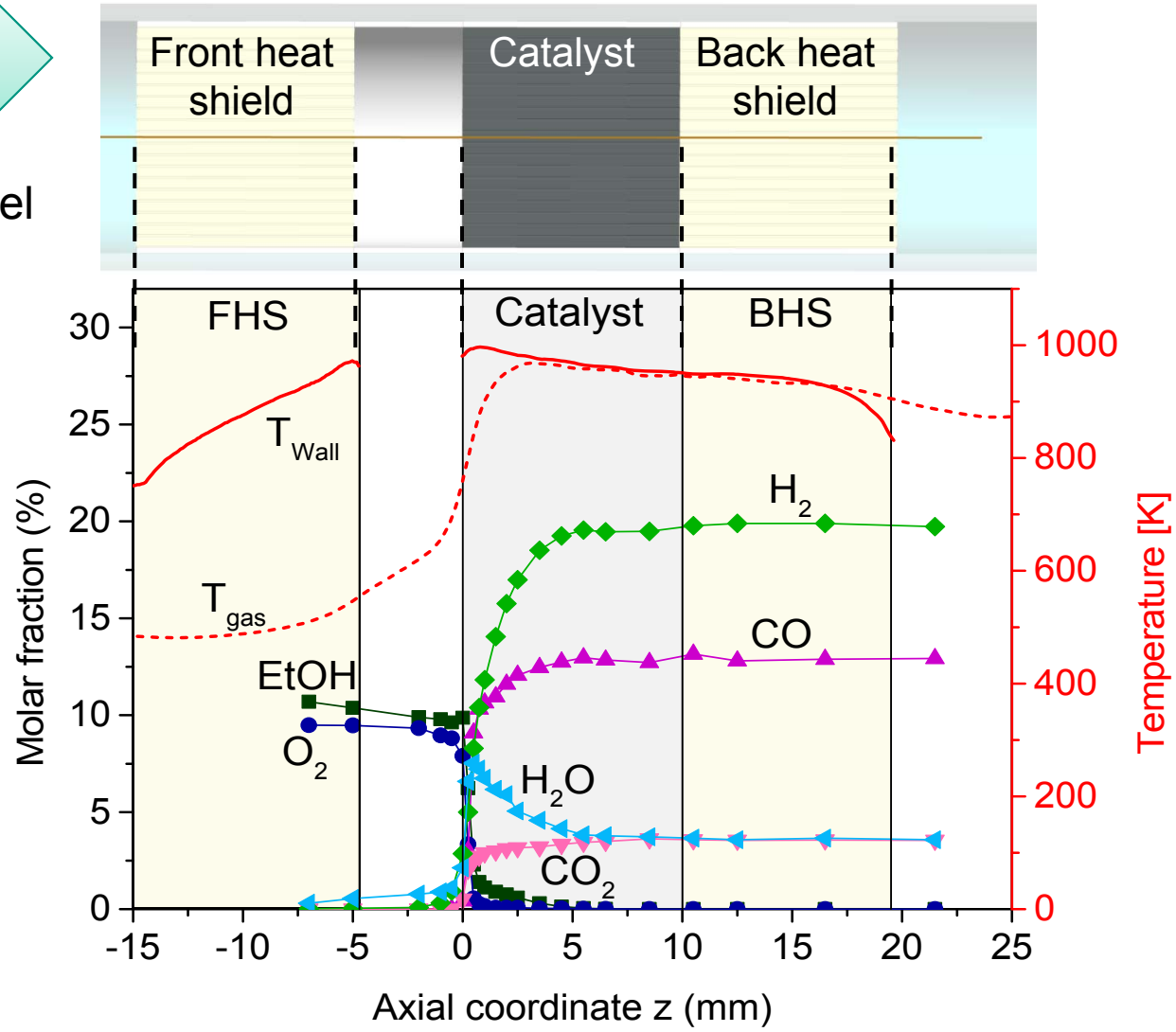
Partial oxidation of ethanol over Rh/Al_2O_3
Concentration and temperature profiles in axial direction

Gas flow

C/O = 0.75
Central channel



D. Livio, C. Diehm, A. Donazzi, A. Beretta, G. Groppi, O. Deutschmann, Appl. Catal. A 467 (2013) 530

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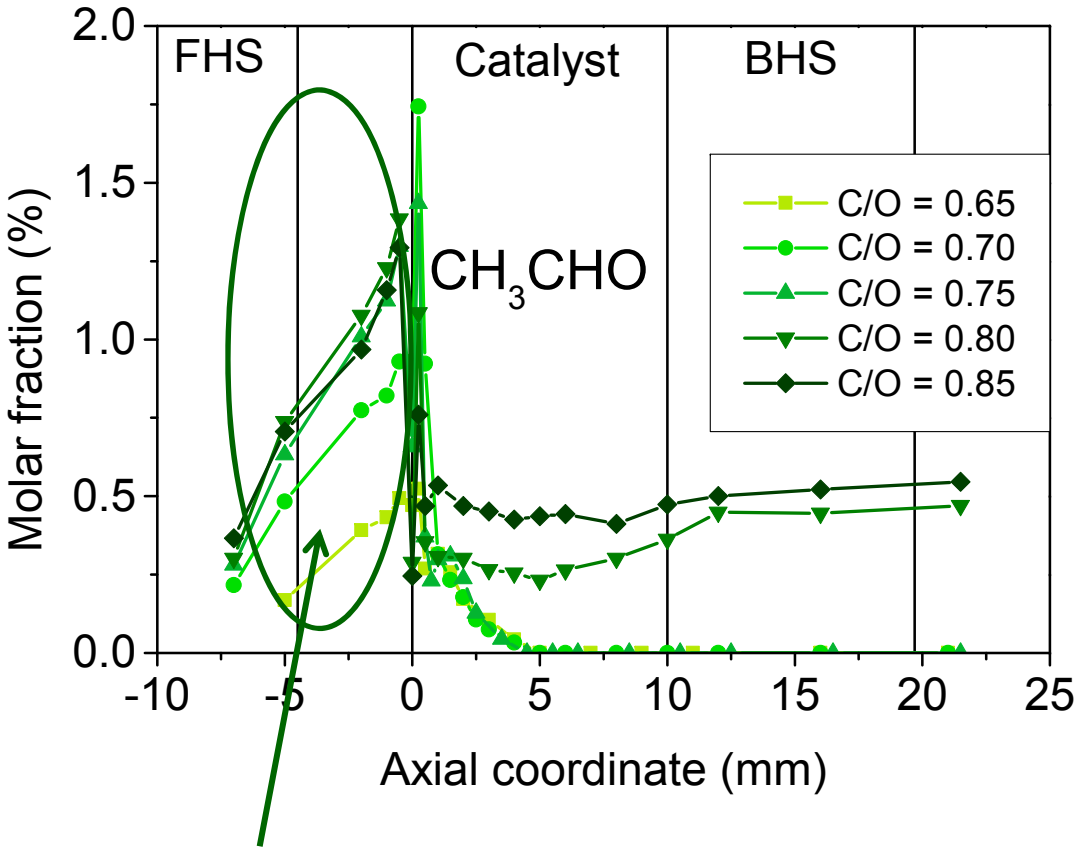
Partial oxidation of ethanol over Rh/Al_2O_3
Formation of acetaldehyde in the gas phase



Increasing formation of acetaldehyde with rising ethanol concentration in feed

D. Livio, C. Diehm, A. Donazzi, A. Beretta, G. Groppi, O. Deutschmann, Appl. Catal. A 467 (2013) 530

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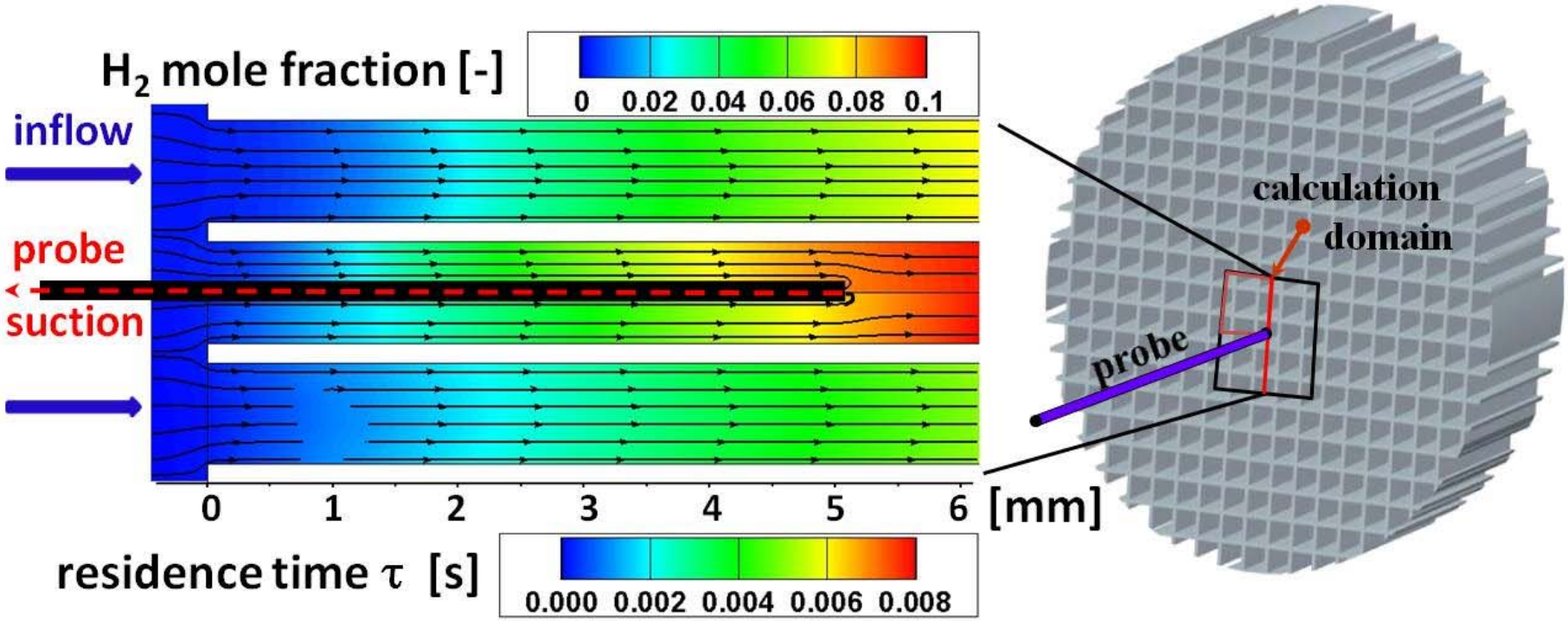
CFD simulations of impact of capillary on profiles: Hydrogen profile and residence time



CPOX of CH_4 over Rh/Al_2O_3
C/O = 1
Probe tip at *z* = 5 mm

M. Hettel, C. Diehm, B. Torkashvand, O. Deutschmann, Catalysis Today 216 (2013) 2.

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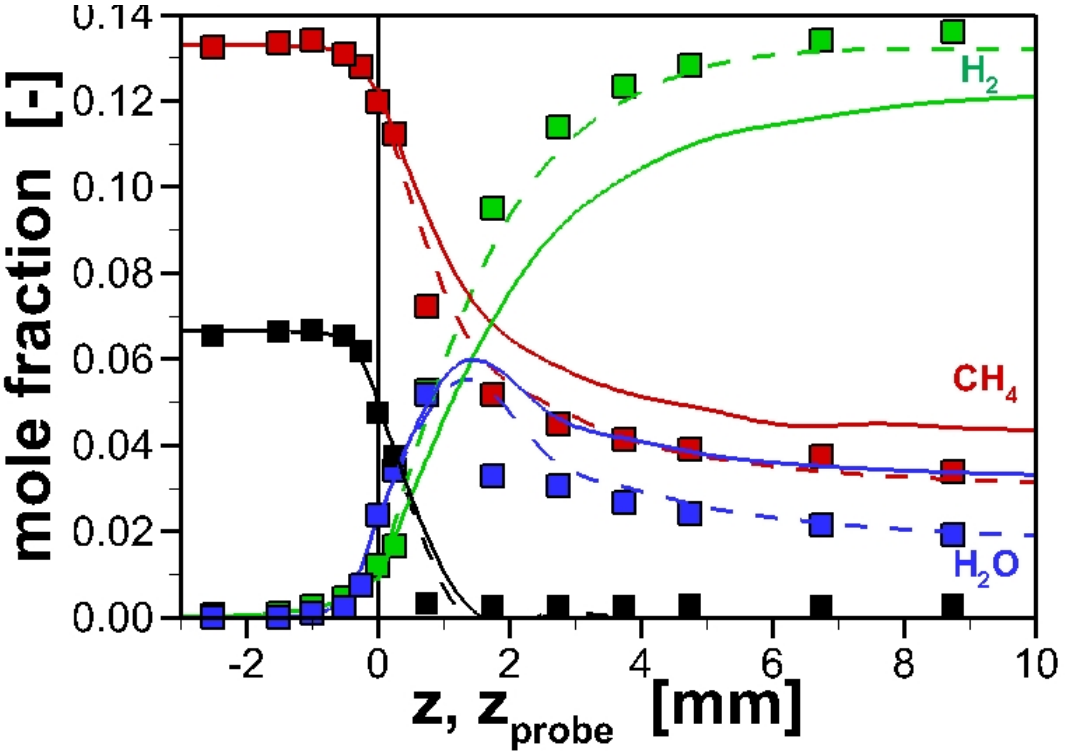
Institute for Chemical Technology and Polymer Chemistry

Impact of capillary on spatial profiles
Comparison of measured and modeled data



CPOX of CH_4
C/O = 1.0

	channel$_{ref}$	channel$_{probe}$	experiment
CH_4	———	- - - -	■
H_2	———	- - - -	■
H_2O	———	- - - -	■
O_2	———	- - - -	■

- Decrease of reactant concentrations upstream of catalyst both in simulation and experiment

  ➡ Diffusion due to high temperature and high concentration gradients

M. Hettel, C. Diehm, B. Torkashvand, O. Deutschmann, Catalysis Today, 2013

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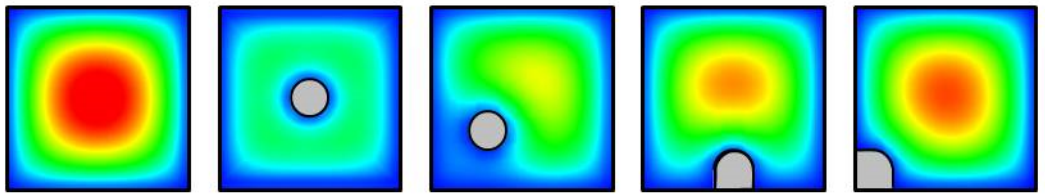
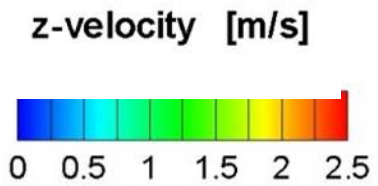
Impact of axial and radial position of capillary on volumetric flux though probe channel

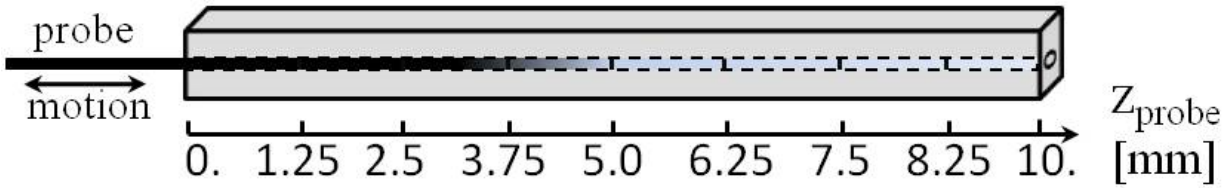
Impact of radial position of capillary on axial velocity and volumetric flux





$\frac{\dot{V}_{channel,probe}}{\dot{V}_{channel,ref}}$	Ref.	A	B	C	D
	1.00	0.46	0.62	0.79	0.91

Impact of axial position of the tip for central location on volumetric flux



$\frac{\dot{V}_{channel,probe}}{\dot{V}_{channel,ref}}$				
0.96	0.75	0.62	0.52	0.46

M. Hettel, C. Diehm, B. Torkashvand, O. Deutschmann, Catalysis Today 216 (2013) 2.

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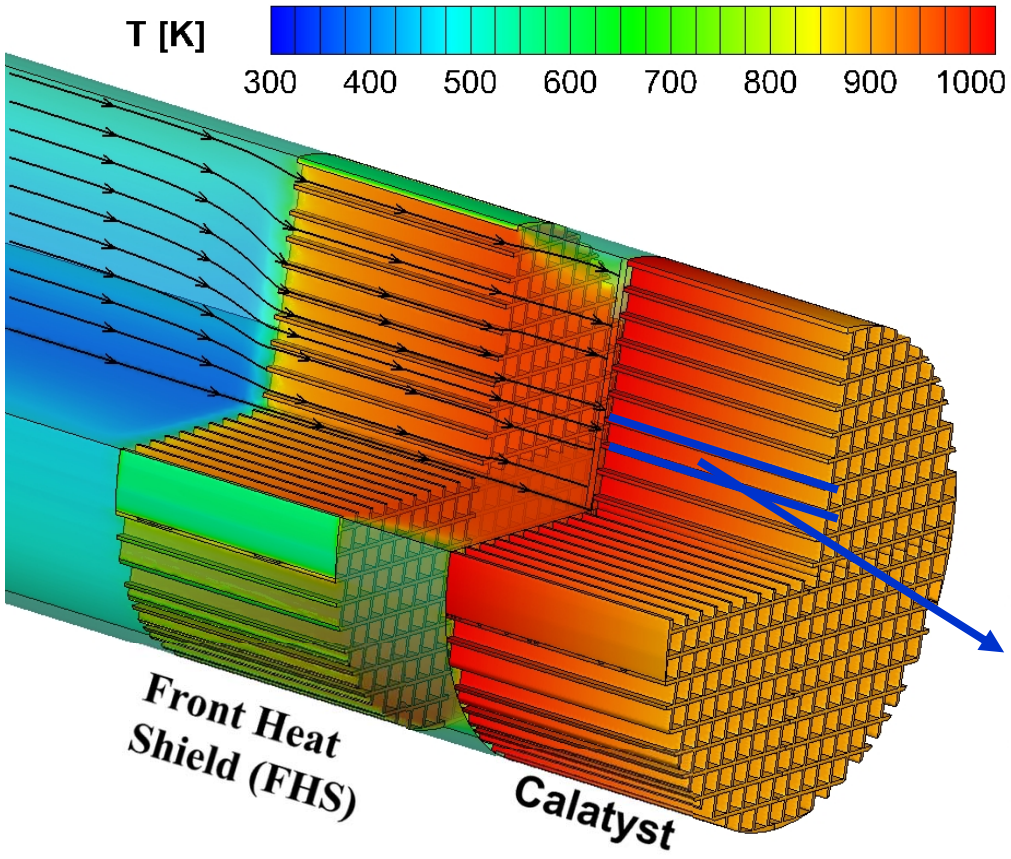
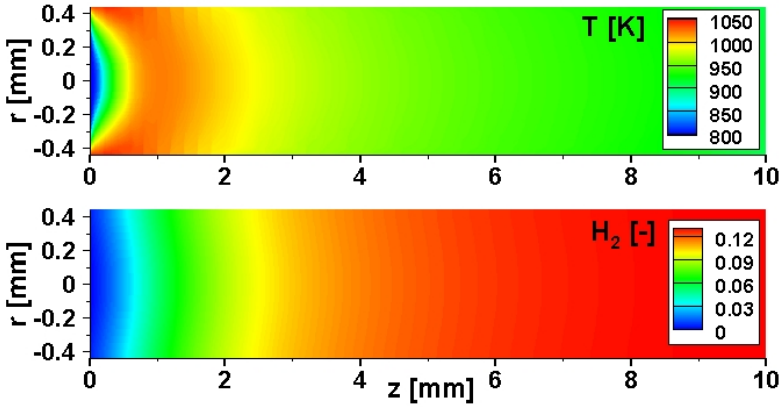
Syngas Formation in CPOX of CH_4 on Rh: CFD simulation using OpenFoam and DETCHEM



CH_4+O_2 in N_2
C/O = 1.0
Rh (10 mm)

Surface mechanism for
CPOX of CH_4 on Rh
(38 reactions, 6 gas-phase species,
11 adsorbed species)



M. Hettel, C. Diehm, O. Deutschmann, 2014

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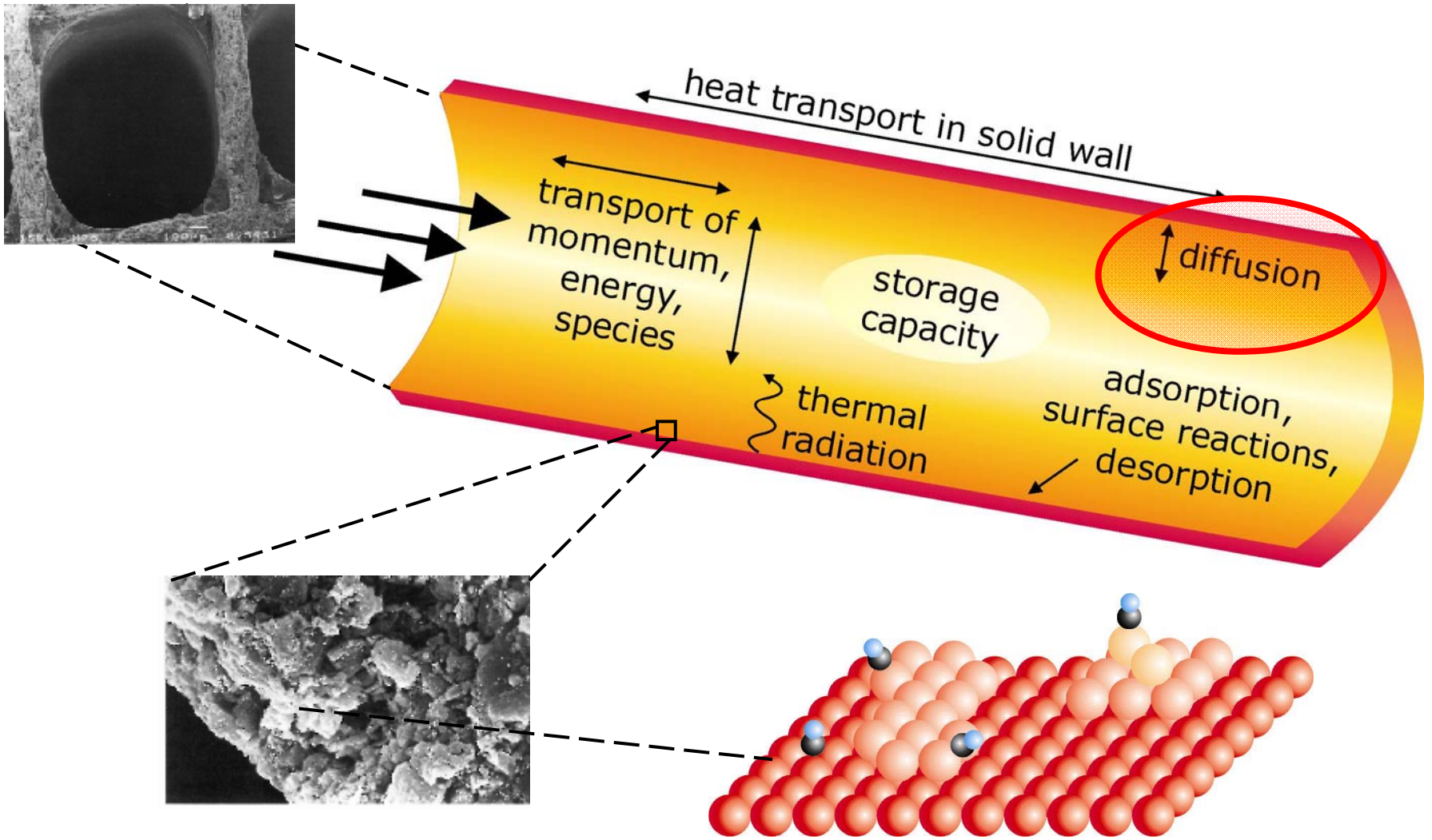
Coupling of external diffusion and reaction



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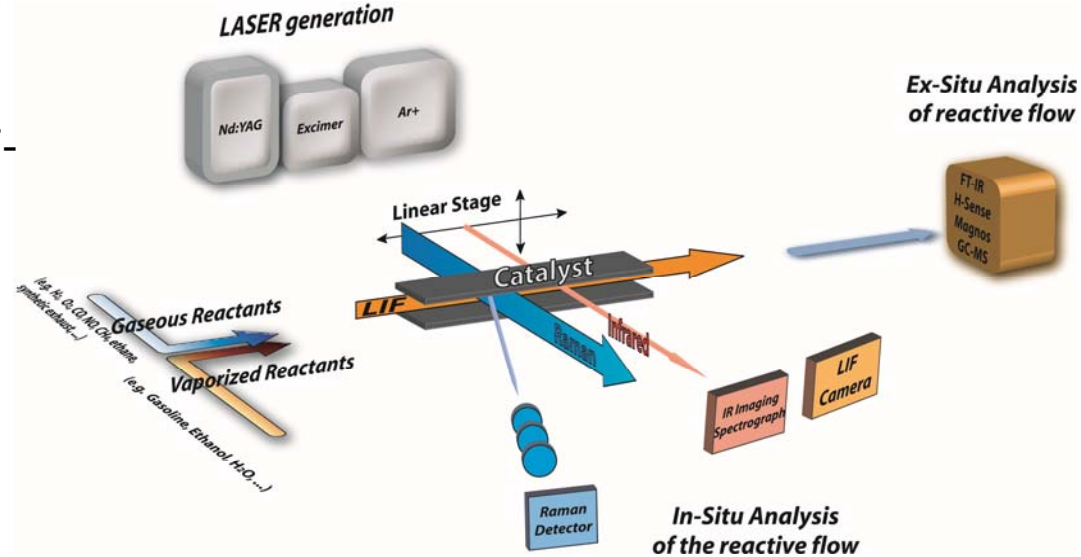
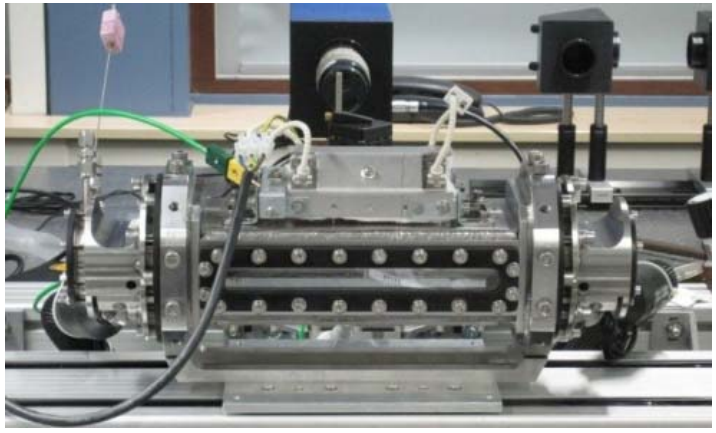
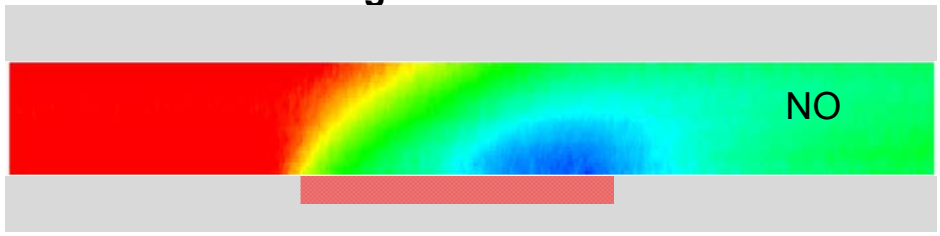
Labor CATHLEN:
Optical diagnostics of catalytic reactors

In-situ analysis of spatial and temporal profiles of species concentration and temperature in the gas phase above a catalytic surface using Raman and LIF-spectroscopy





NO LIF profile during reduction by H_2 to NH_3 in Pt/Al_2O_3 one-side-coated single channel of a DOC



A. Zellner, R. Suntz, O. Deutschmann, Chemie Ingenieur Technik 86 (2014) 538.

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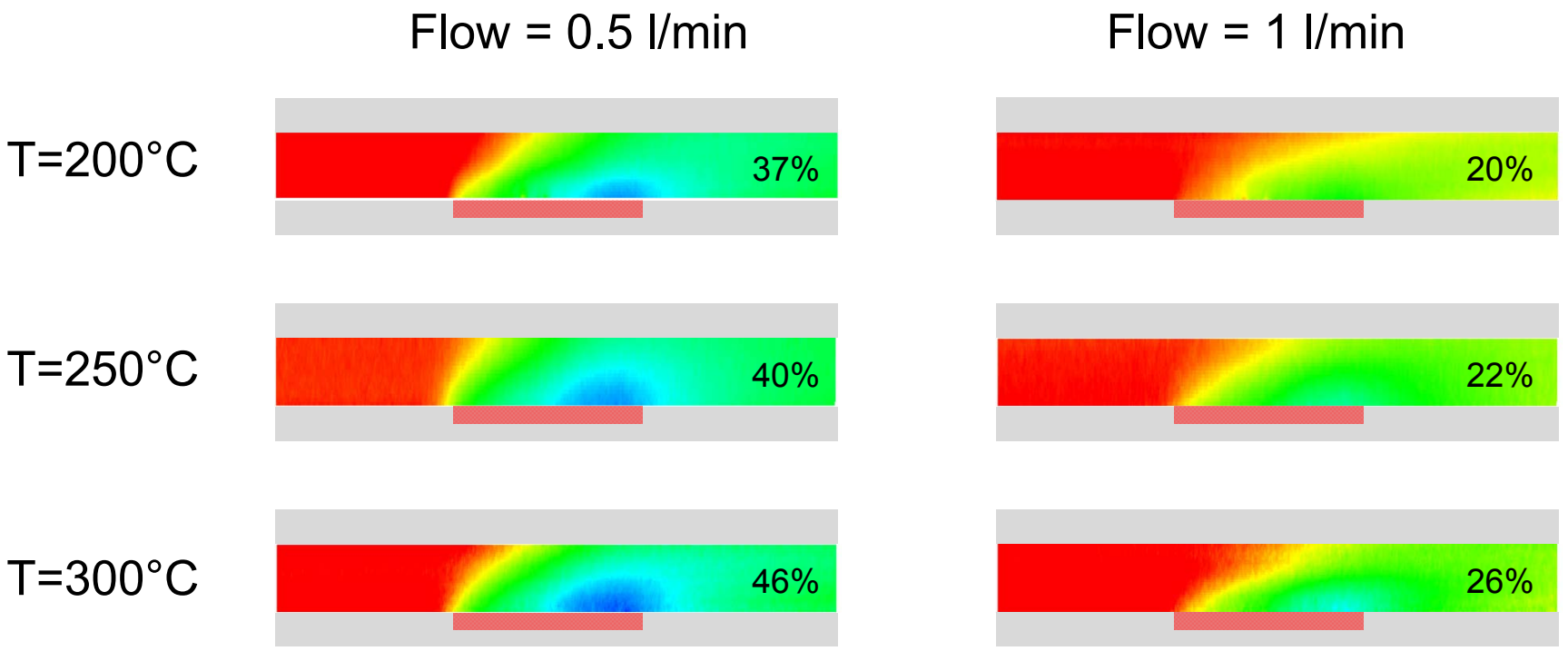
NO reduction by H_2 to NH_3 over Pt - DOC catalyst: LIF monitored NO conversion



T = 200 – 300°C
p = 1 atm
Flow = 0.5 - 1 l/min
NO = 100 pmm
H_2 = 1.000 ppm

A. Zellner, R. Suntz, O. Deutschmann, Angew. Chem., subm.

Olaf Deutschmann
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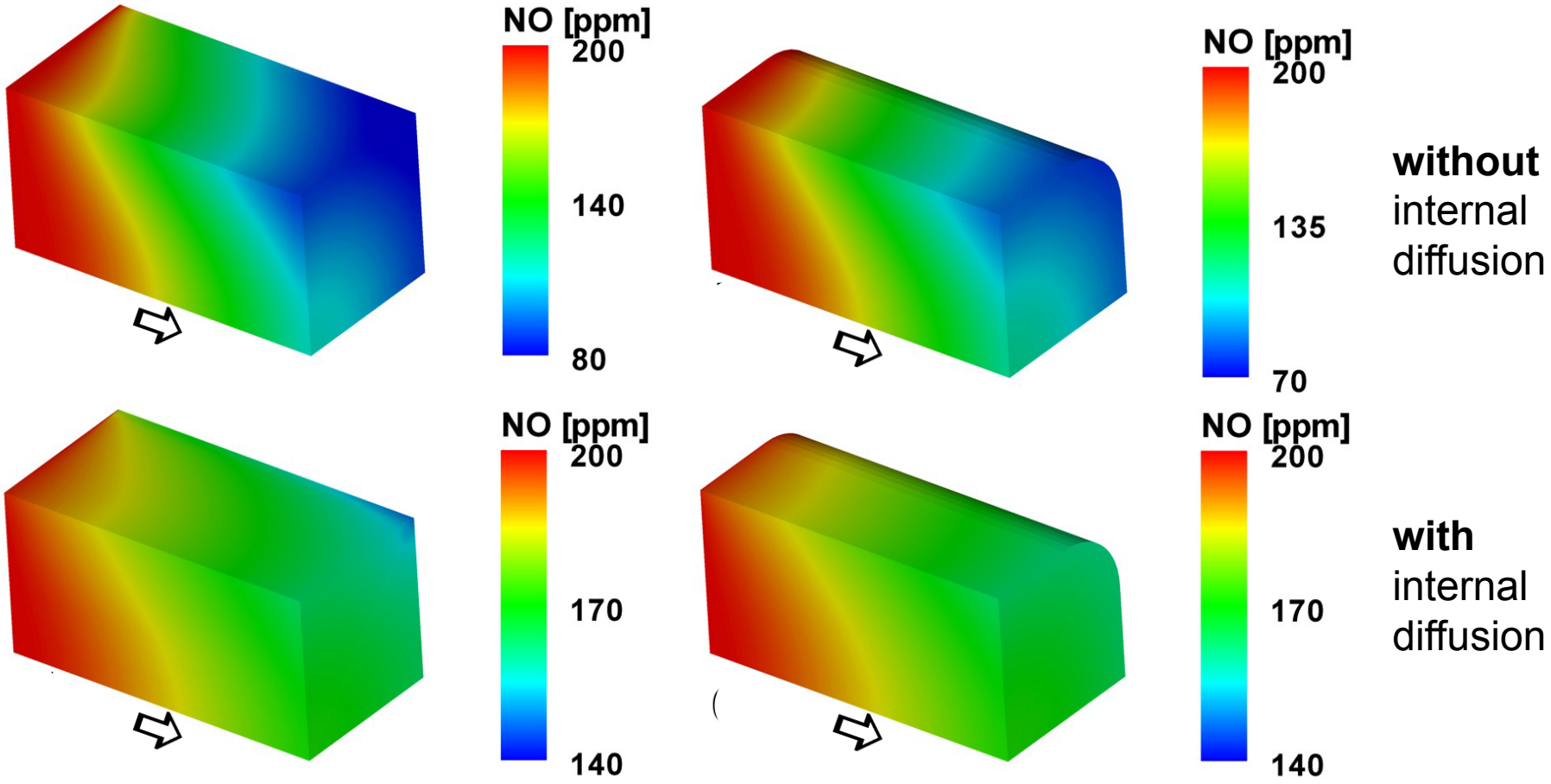
Impact of models for channel shape and washcoat diffusion on NO profiles in a DOC



NO profiles at lean conditions at 250°C (steady-state operation)
CFD code: Fluent + DETCHEM

N. Mladenov, J. Koop, S. Tischer, O. Deutschmann. Chem. Eng. Sci. 65 (2010) 812

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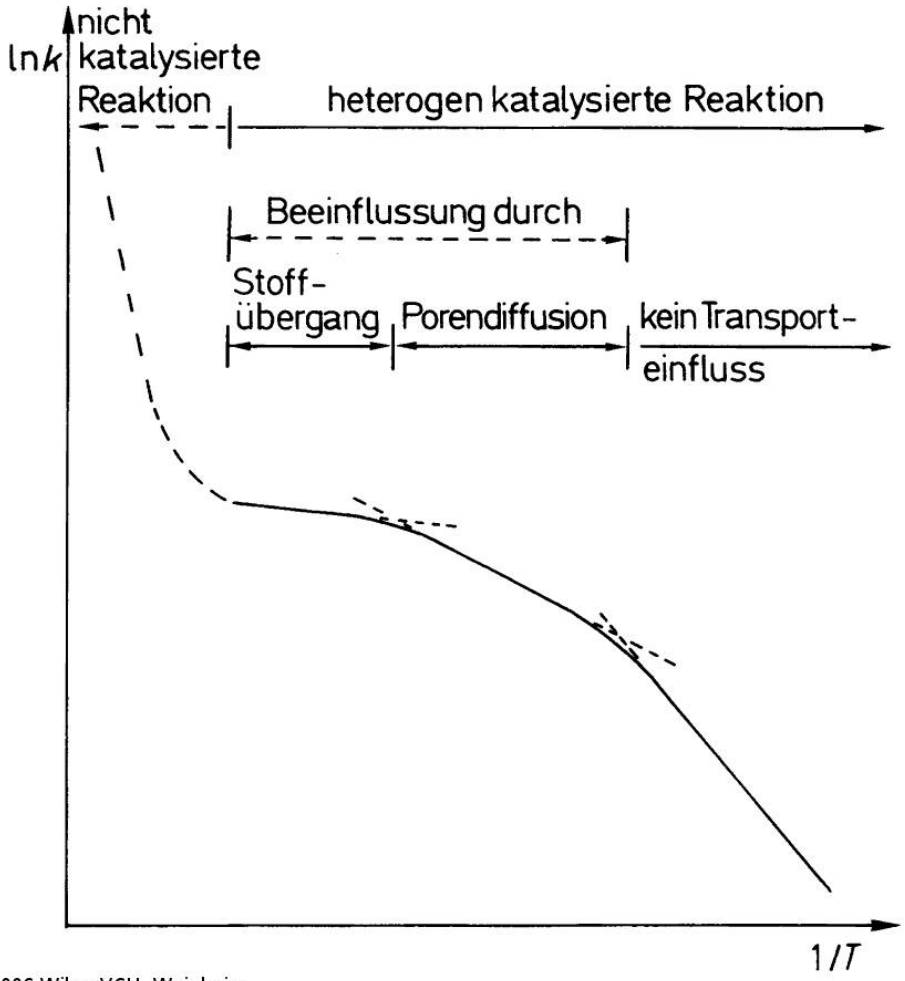
Institute for Chemical Technology and Polymer Chemistry

Zusammenspiel von äußerem und innerem Stofftransport: Temperaturabhängigkeit der effektiven Reaktionsgeschwindigkeit



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Kinetics – Interaction between Reaction, Mass and Heat Transfer: Outline

1. Microkinetics of reactions on the catalytic surface
2. Transport and reactions in porous media (internal diffusion)
3. Reactive flow and external diffusion
4. **Gas-phase chemistry**
5. Transient processes and heat transport

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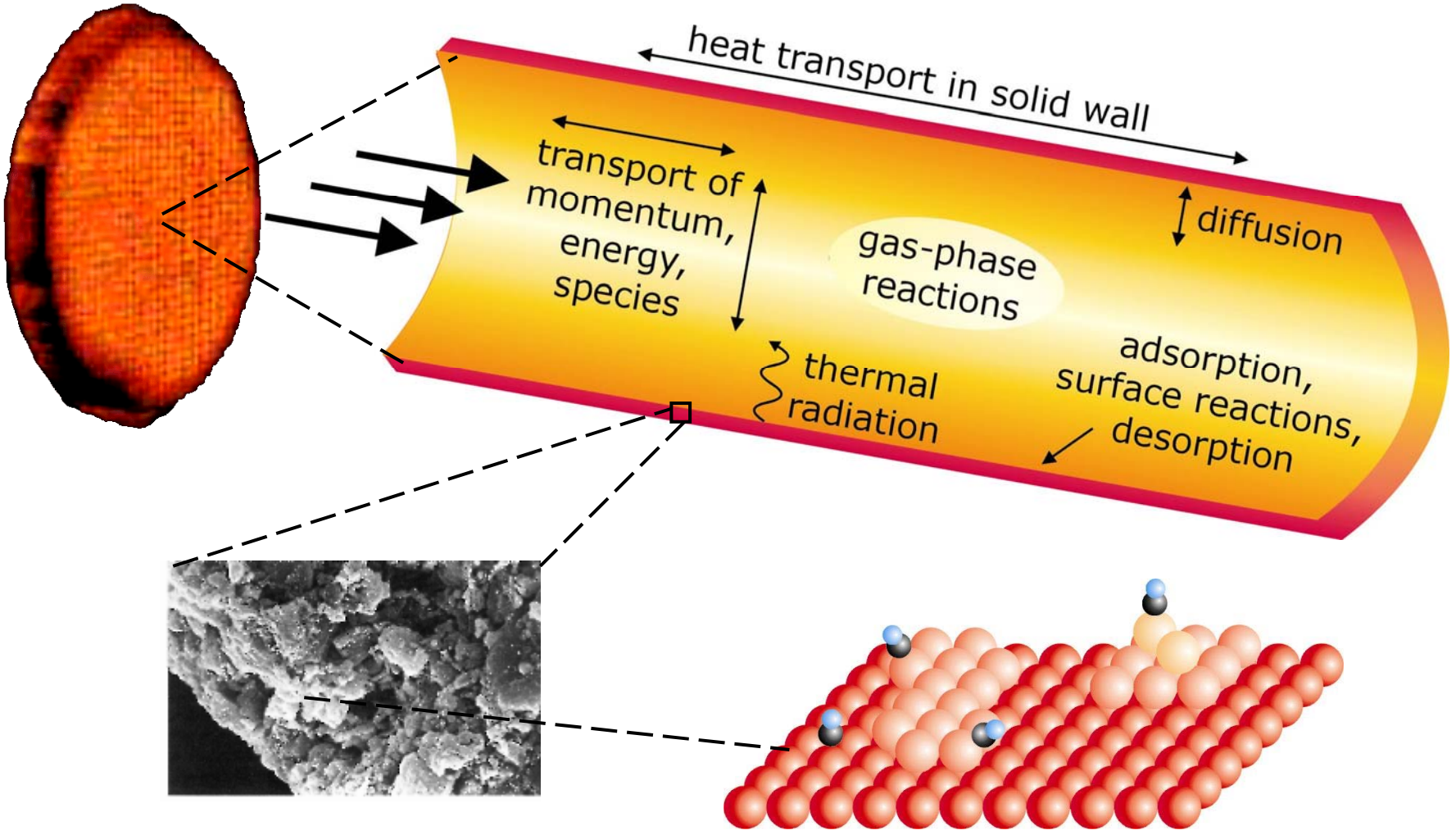
Impact of gas-phase reactions



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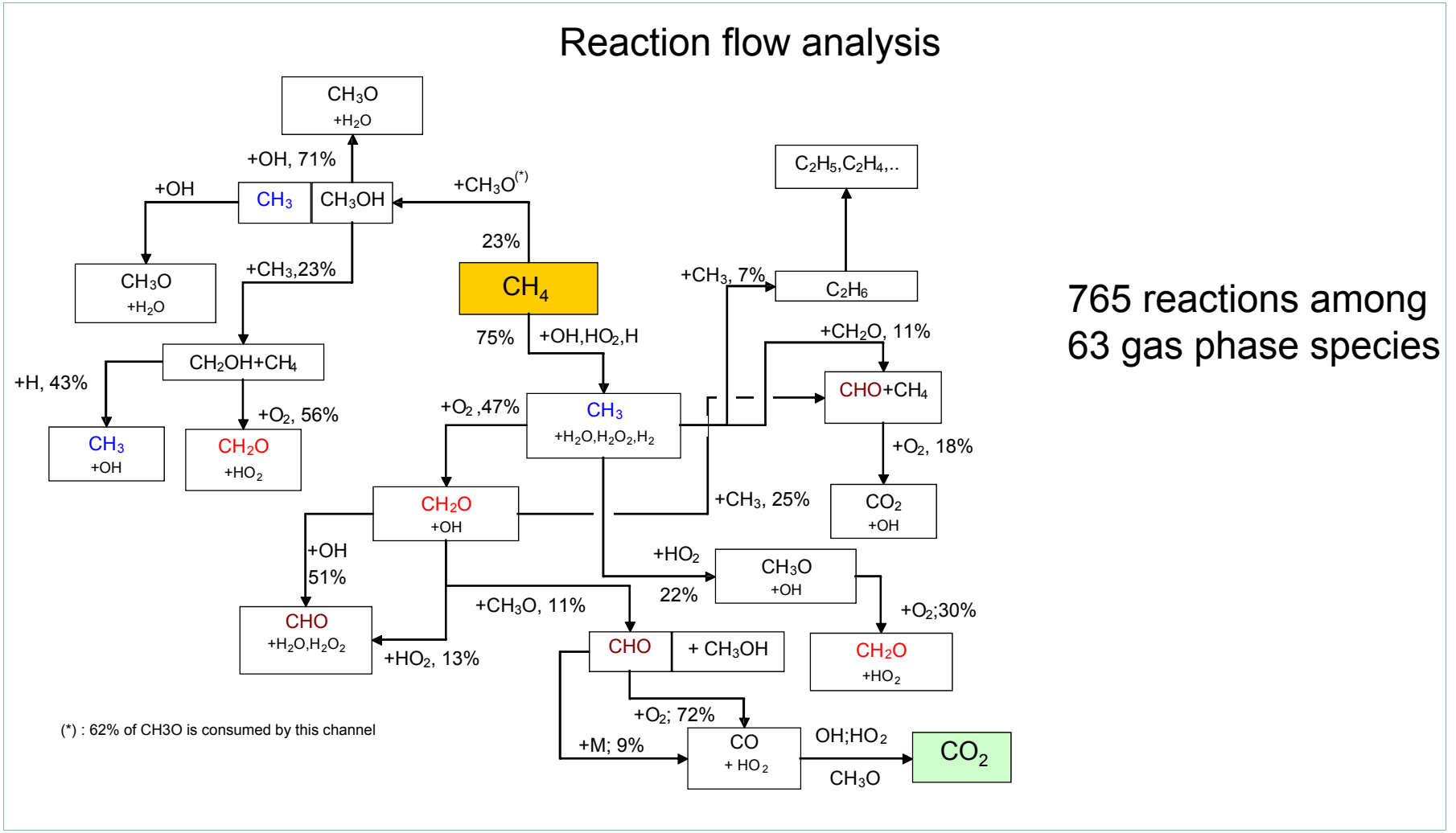
Gas-phase reactions: Complex schemes even for simple fuels - CH_4 partial oxidation



765 reactions among
63 gas phase species

R. Quiceno, J. Perez-Ramirez, J. Warnatz, O. Deutschmann. Appl. Catal. A: General 303 (2006) 166–176

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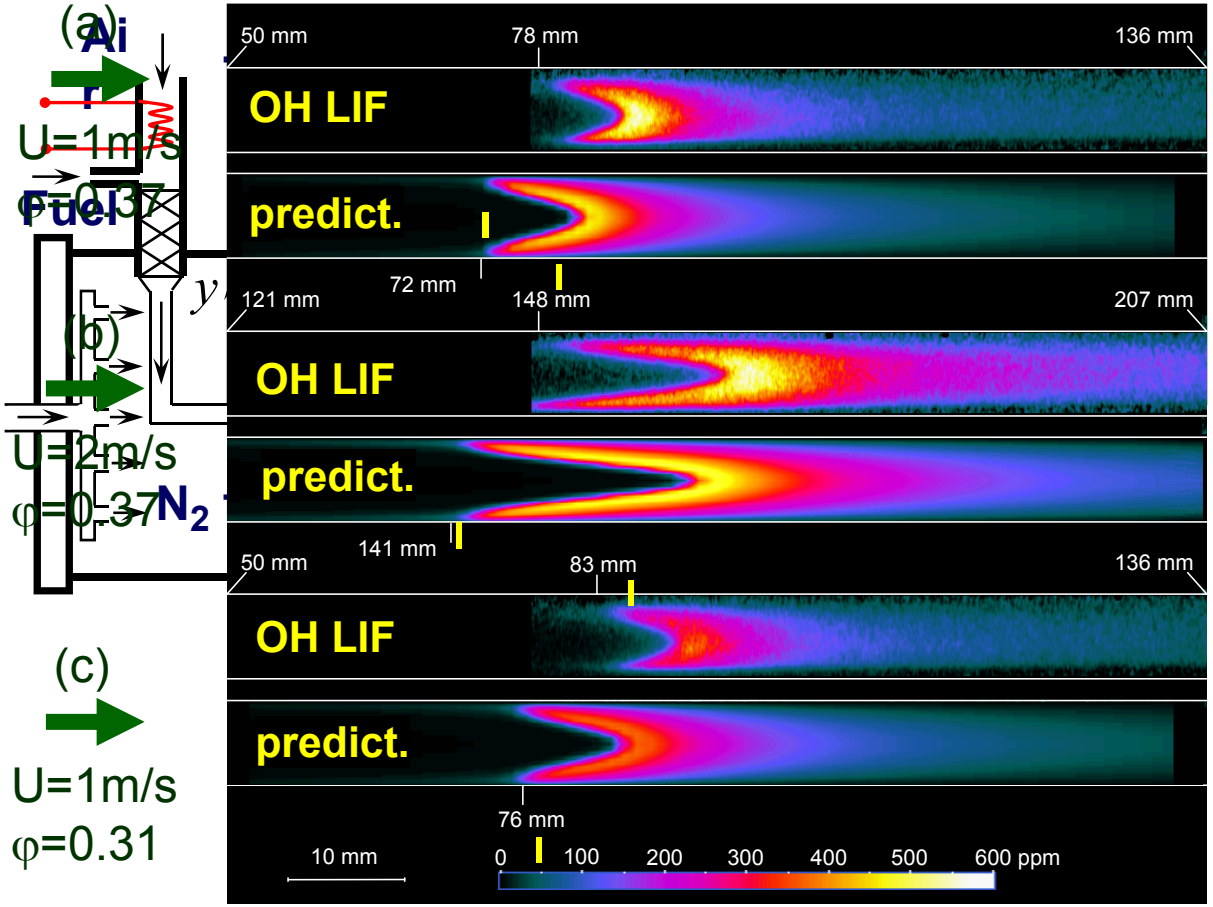
Homogeneous ignition in catalytic combustion of methane/air mixtures over platinum

Comparison of experimentally observed (PLIF) and numerically predicted (2D NS model with detailed gas phase and surface kinetics) OH profiles in a laminar plane channel flow



U. Dogwiler, J. Mantzaras, C. Appel, P. Benz, B. Kaeppeli, R. Bombach, A. Arnold. Proc. Combust. Inst. 27 (1998) 2275

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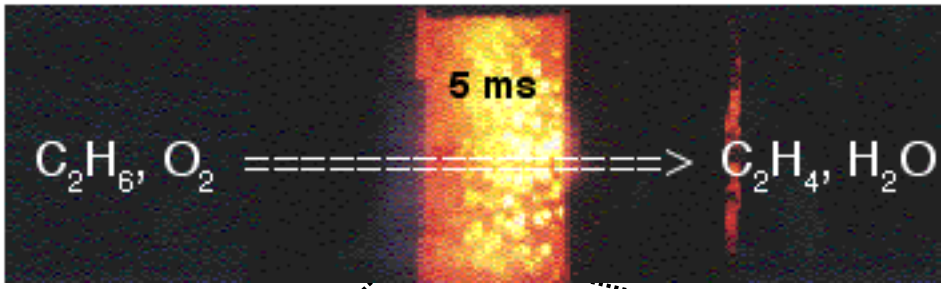
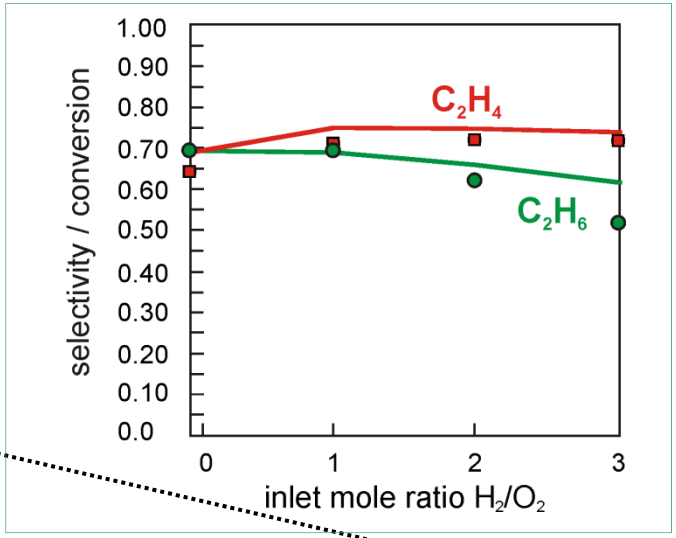
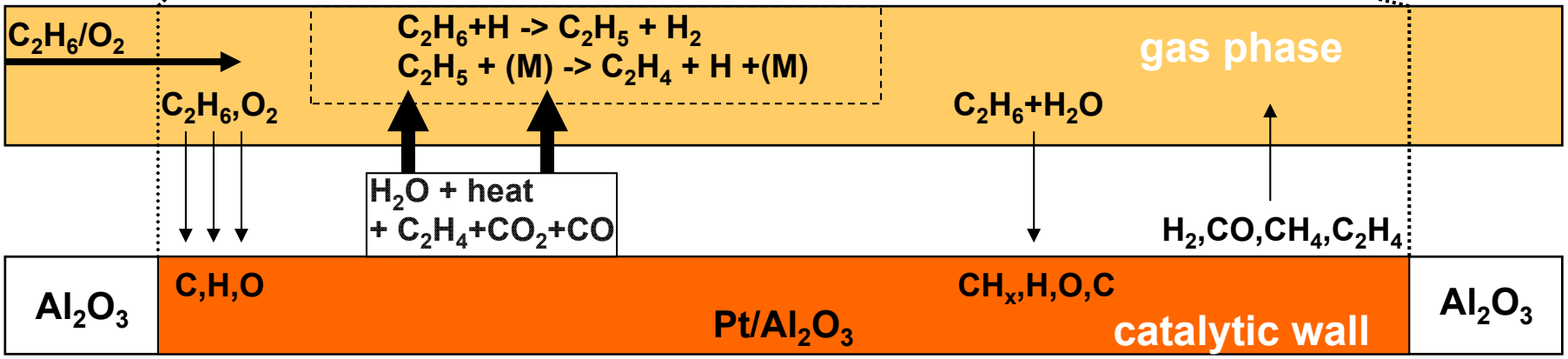
Oxidative dehydrogenation of ethane to ethylene on platinum at short contact times







A. Bodke, L.D. Schmidt, J. Catal. 191 (2000) 62
D. K. Zerkle, M. D. Allendorf, M. Wolf, O. Deutschmann. J. Catal.196 (2000) 18
A. Beretta, E. Ranzi, P. Forzatti, Chem. Eng. Sci. 56 (2001) 779

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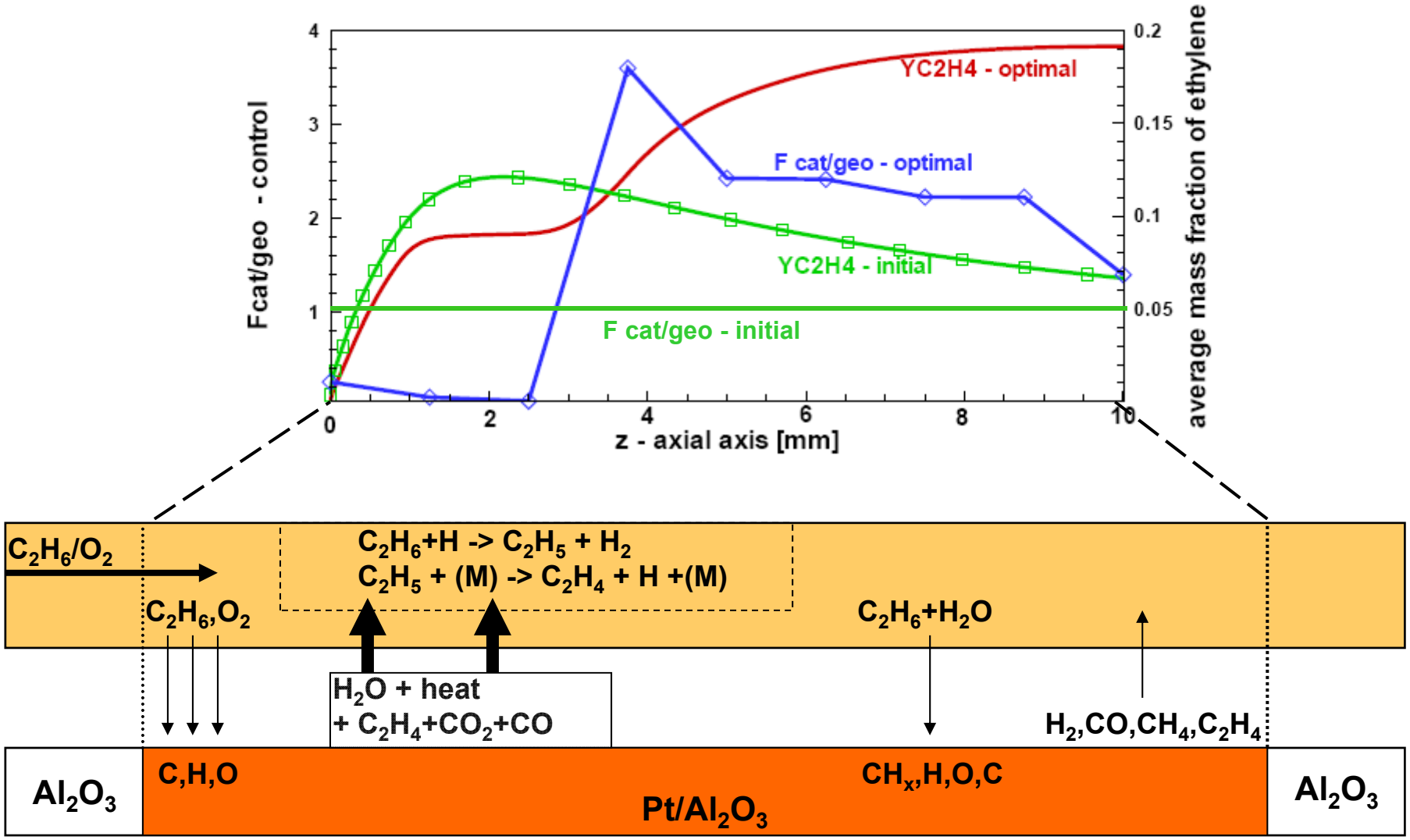
Mathematical optimization of catalyst loading: Oxy-dehydrogenation of ethane to ethylene over Pt



H.D. Minh, S. Tischer, H.G. Bock, O. Deutschmann, AIChE J. 54 (2008) 2432.

Olaf Deutschmann
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More efficient technology for auxiliary power supply in automobile vehicles needed

Idling long-haul trucks consumes 1 billion gallons of diesel fuel annually in the USA
→11 million tons CO_2, 180,000 tons NO_x, 5000 tons particulates!

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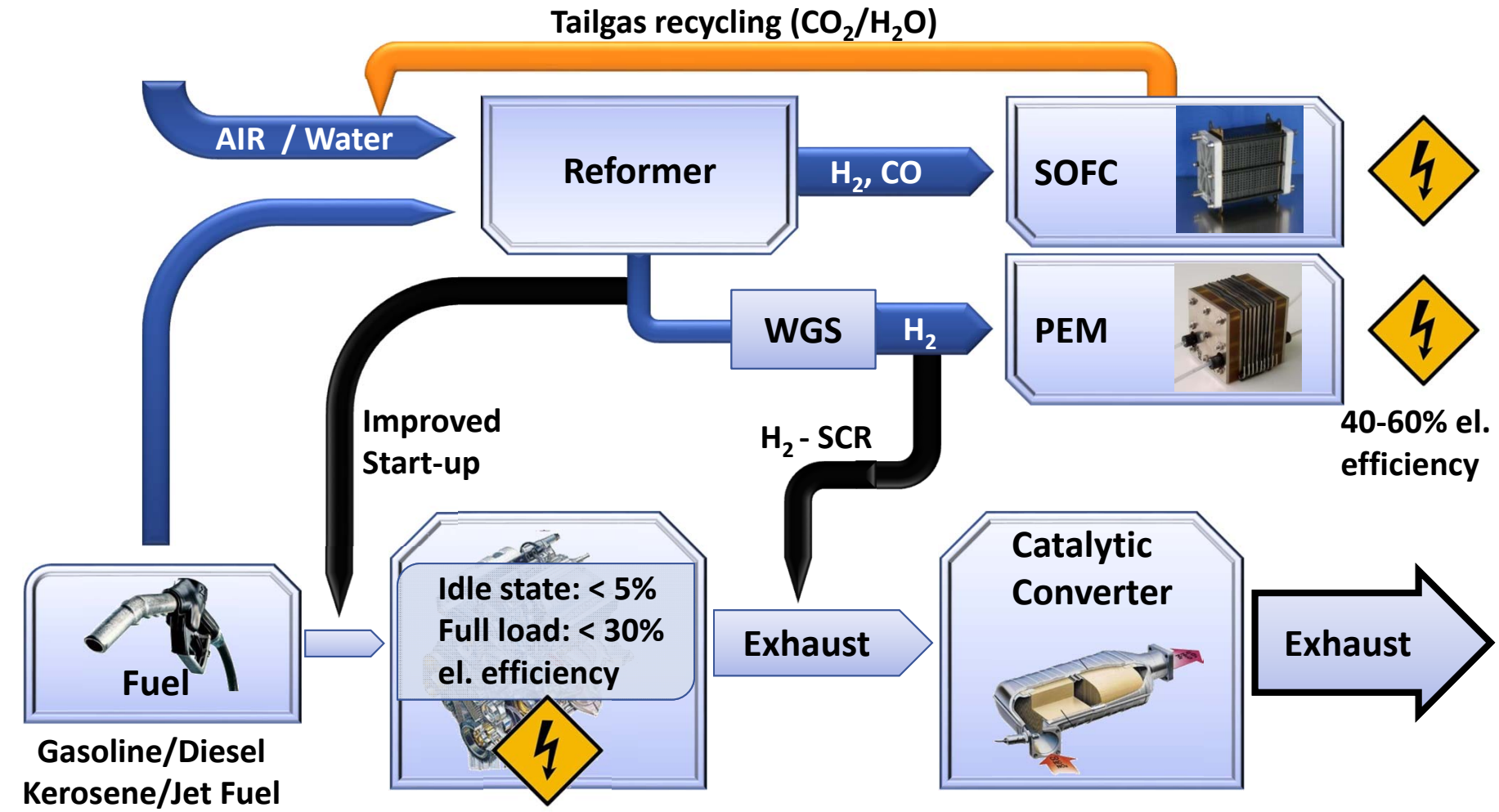
Conversion of logistic fuels provides electricity and reduces fuel consumption, pollutant emissions, and noise



O. Deutschmann. Chemie Ingenieur Technik 83 (2011) 1954
T. Kaltschmitt, C. Diehm, O. Deutschmann. Ind.& Eng. Chemi. Res. 51 (2012) 7536

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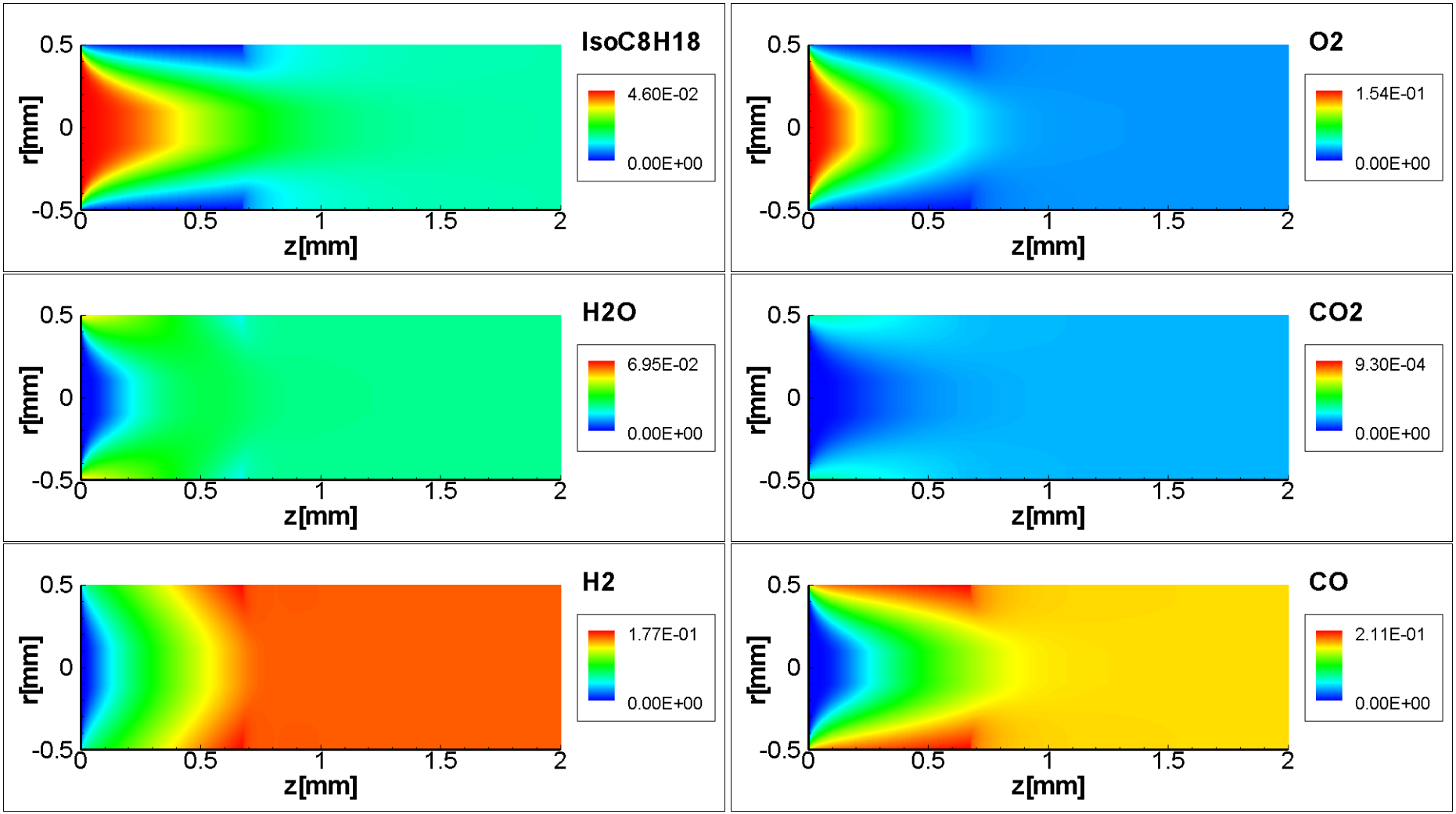
CPOX of iso-octane in catalytic channel: Numerically predicted 2D species profiles in gas-phase



C/O = 1.2, 800°C

M. Hartmann, L. Maier, O. Deutschmann, Combust. Flame 157 (2010) 1771

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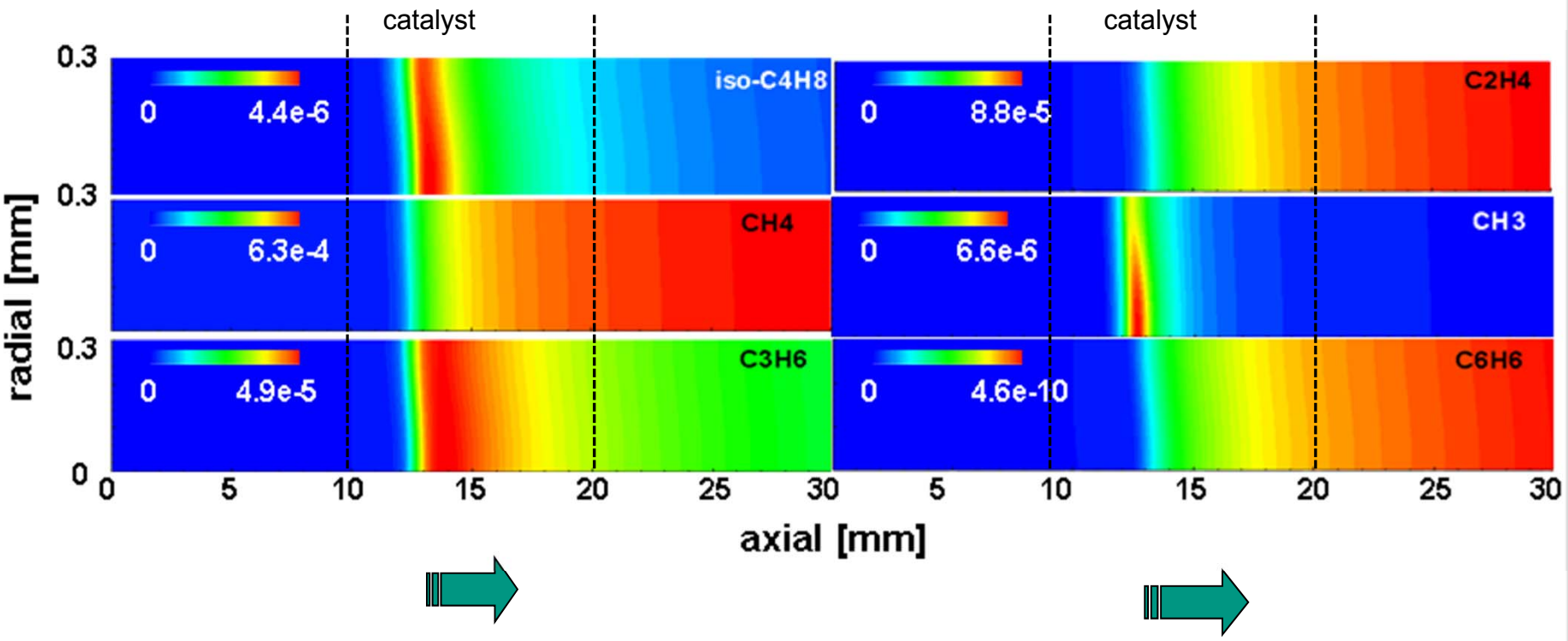
Institute for Chemical Technology and Polymer Chemistry

CPOX of i-octane: Coke precursors are formed in the gas phase in the catalytic zone and downstream



C/O = 1.0 5 slpm

L. Maier, M. Hartmann, O. Deutschmann, Combust. Flame 158 (2011) 796–808.

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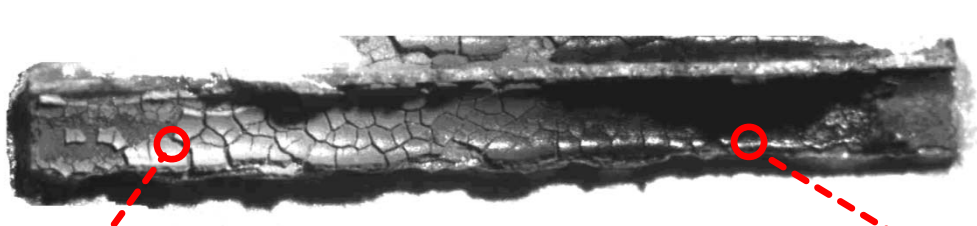
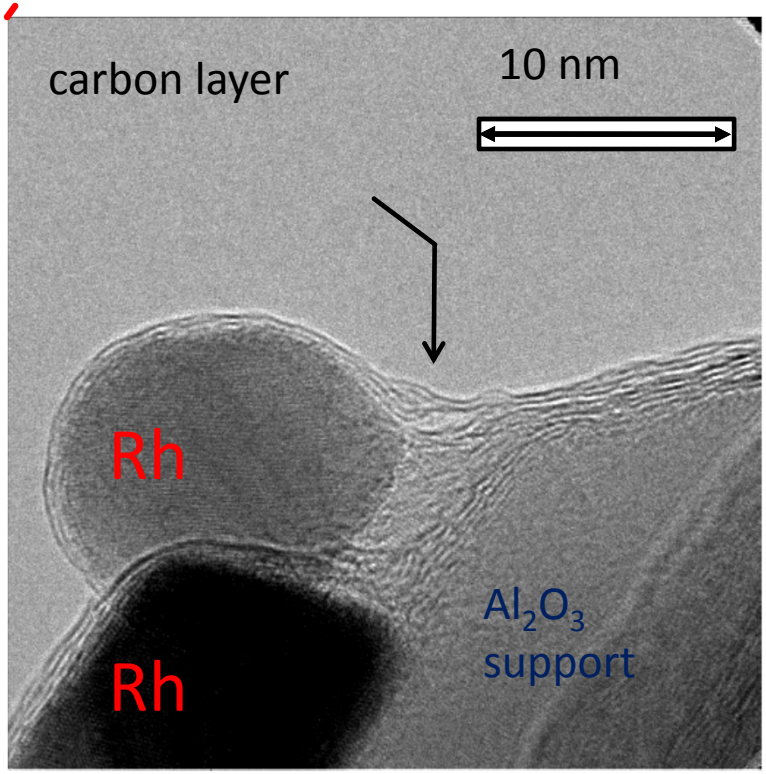
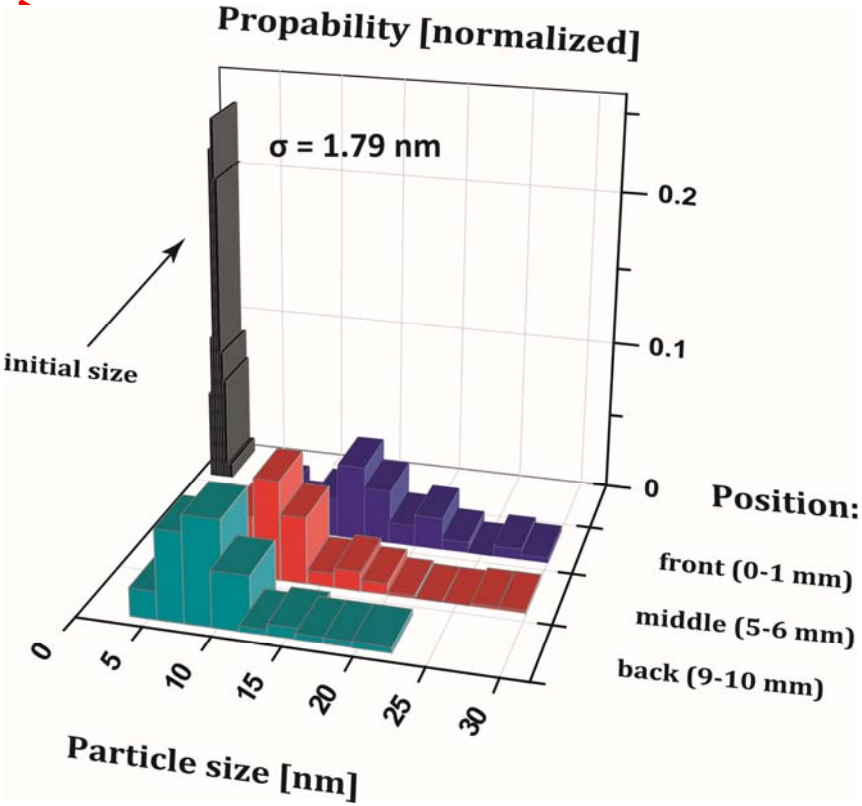
Institute for Chemical Technology and Polymer Chemistry

Catalyst deactivation by coking: TEM-Images of the Rh particles



d = 0.6 mm

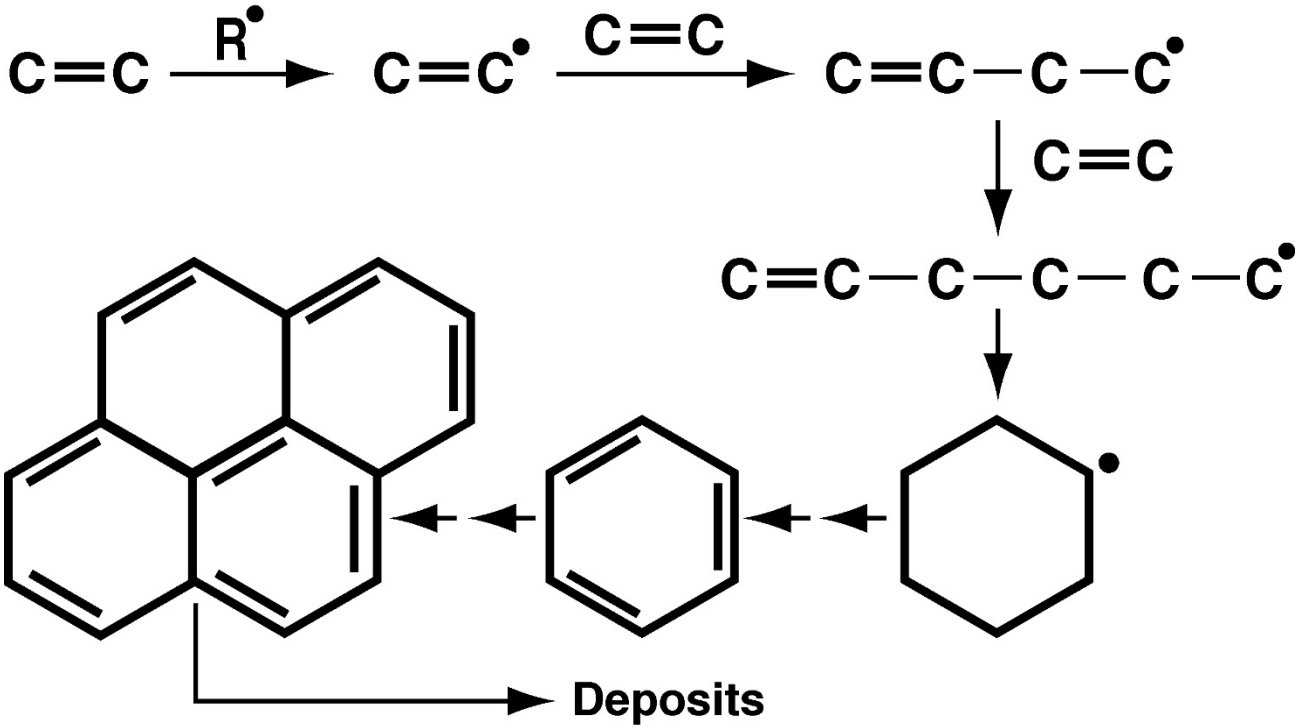




M. Hartmann, B. Reznik, O. Deutschmann, 2010, to be published

Olaf Deutschmann
Institute for Chemical Technology and Polymer Chemistry

Small olefins in reformate gas can lead to gas-phase molecular-weight growth and carbon deposits



A. Dean, Colorado School of Mines

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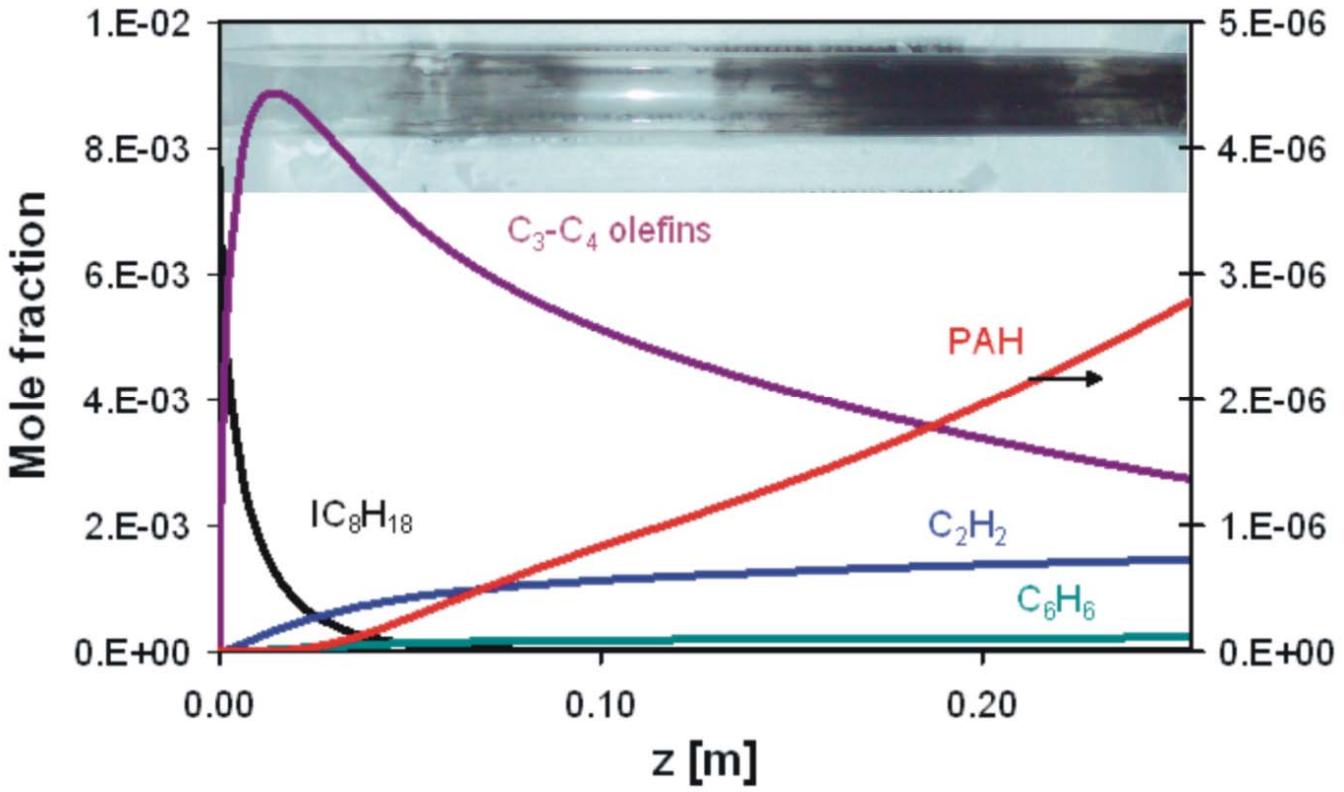
Institute for Chemical Technology and Polymer Chemistry

Coke formation in partial oxidation of iso-octane: Carbon distribution along the reactor (w/o catalyst)



C/O = 1.6, 1108 K, 6 SLPM. C_3-C_4 olefins contain 1,2-propadiene, propene, propyne, n-butene (1-buten, 2-butene), iso-butene, 1,3-butadiene; PAH contains naphthalene, anthracene, pyrene. Embedded photo shows the tubular quartz reactor after operation.

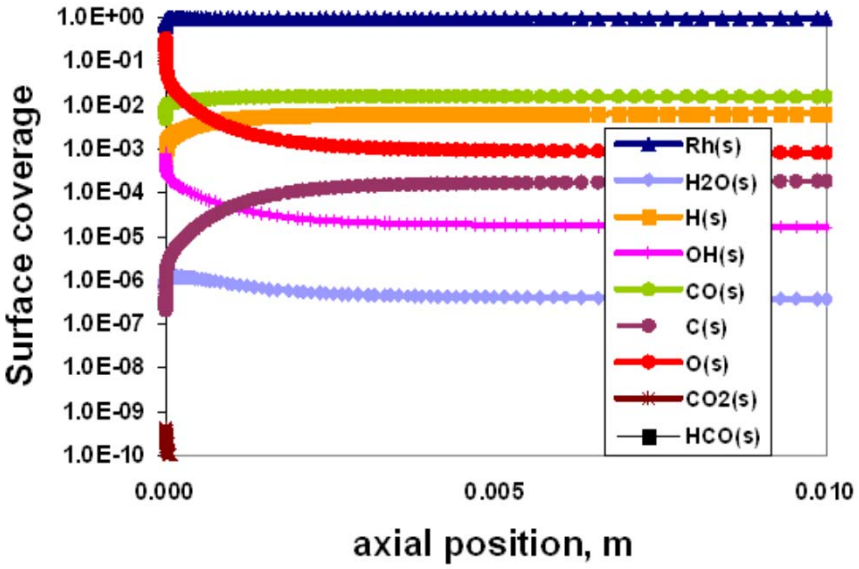
T. Kaltschmitt, L. Maier, O. Deutschmann. Proceedings of the Combustion Institute 33 (2011) 3177

Olaf Deutschmann
Institute for Chemical Technology and Polymer Chemistry

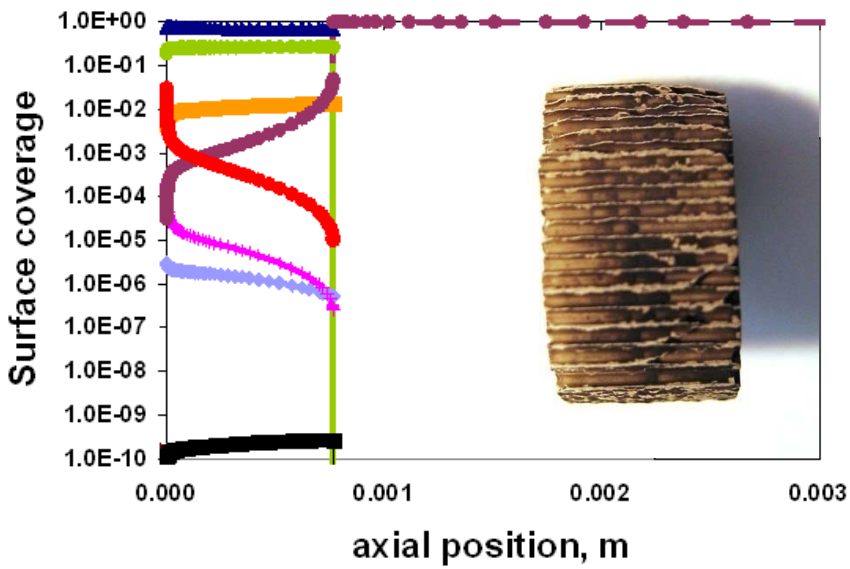
CPOX of i-octane: Coke formation on the downstream section of the catalyst at rich conditions

Numerically predicted surface coverage along the monolithic catalyst

C/O = 0.8



C/O = 1.2



M. Hartmann, L. Maier, O. Deutschmann, Combust. Flame 157 (2010) 1771

Olaf Deutschmann
Institute for Chemical Technology and Polymer Chemistry

Kinetics – Interaction between Reaction, Mass and Heat Transfer: Outline

1. Microkinetics of reactions on the catalytic surface
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4. Gas-phase chemistry
5. **Transient processes and heat transport**

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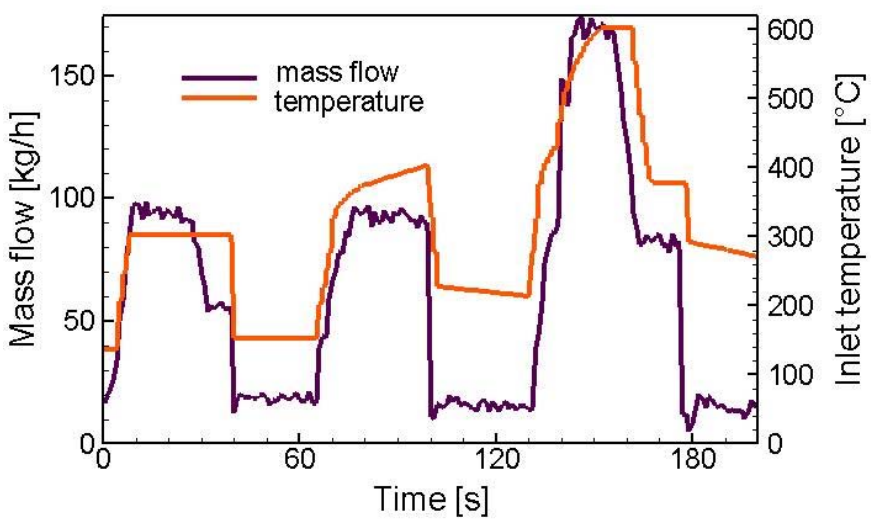
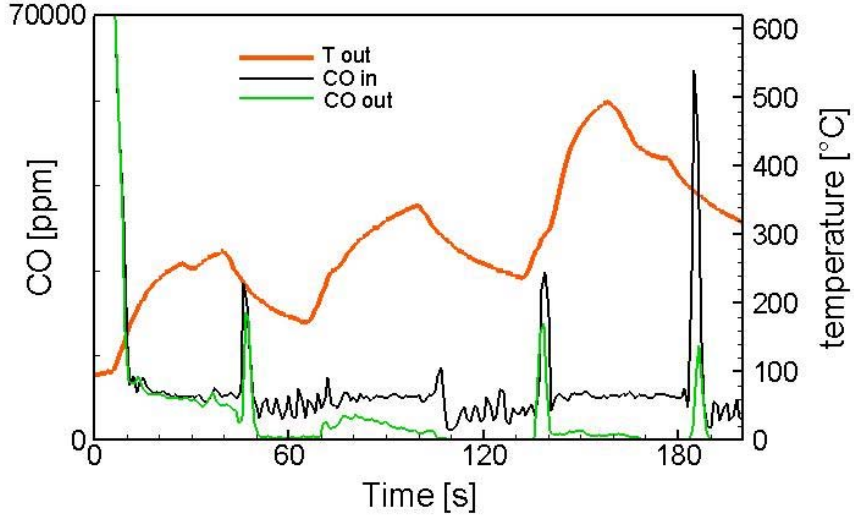
Institute for Chemical Technology and Polymer Chemistry

Simulation at real driving conditions is very challenging: Continuous variation of all inlet variables





J. Braun, T. Hauber, H. Többen, J. Windmann, P. Zacke, D. Chatterjee, C. Correa, O. Deutschmann, L. Maier, S.Tischer, J. Warnatz, SAE paper 2002-01-0065

Olaf Deutschmann
Institute for Chemical Technology and Polymer Chemistry

DETCHEM^{MONOLITH}: Computer program for the numerical simulation of transients in catalytic monoliths

Karlsruhe Institute of Technology

MONOLITH
Temperature of the solid structure incl. canning
by a 2D / 3D heat balance

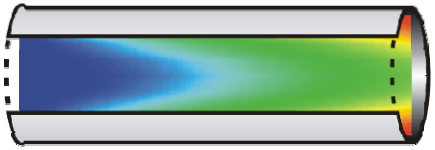
transient
quasi-steady-state

temperature profile
at the wall

heat source term

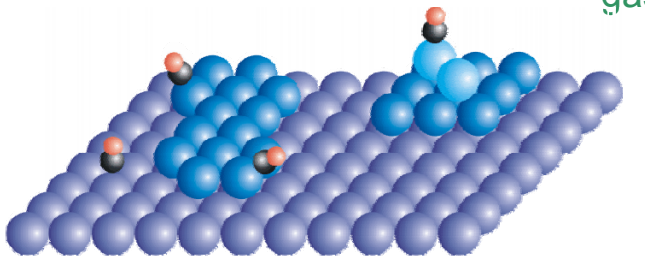
time scale ~ 1 s
residence time < 100 ms

CHANNEL or PLUG
1D or 2D-flow field simulations for a representative number of channels using boundary layer or plug flow equations



gas phase concentrations
temperature

chemical source term
transport coefficients



DETCHEM - Library
Thermodynamic and transport properties
Detailed reaction mechanisms for gas-phase & surface

S. Tischer, O. Deutschmann, Catal. Today 105 (2005) 407, www.detchem.de

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Institute for Chemical Technology and Polymer Chemistry

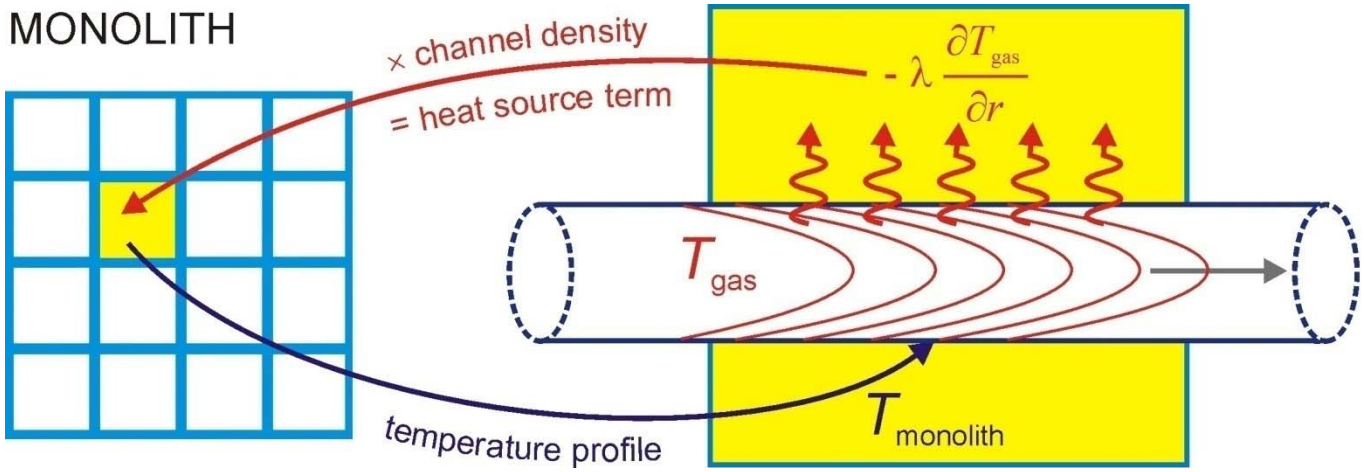
Modeling the temperature of the solid phase of the monolith: Transient three-dimensional heat balance

Temperature

$$\frac{\partial T_{\text{monolith}}}{\partial t} = \nabla^2 \left(\frac{\lambda T_{\text{monolith}}}{\rho c_p} \right) + \frac{q}{\rho c_p}$$

Heat source term

$$q = -\sigma \cdot 2\pi r \, \lambda \frac{\partial T_{\text{gas}}}{\partial r}\bigg|_{\text{surface}}$$



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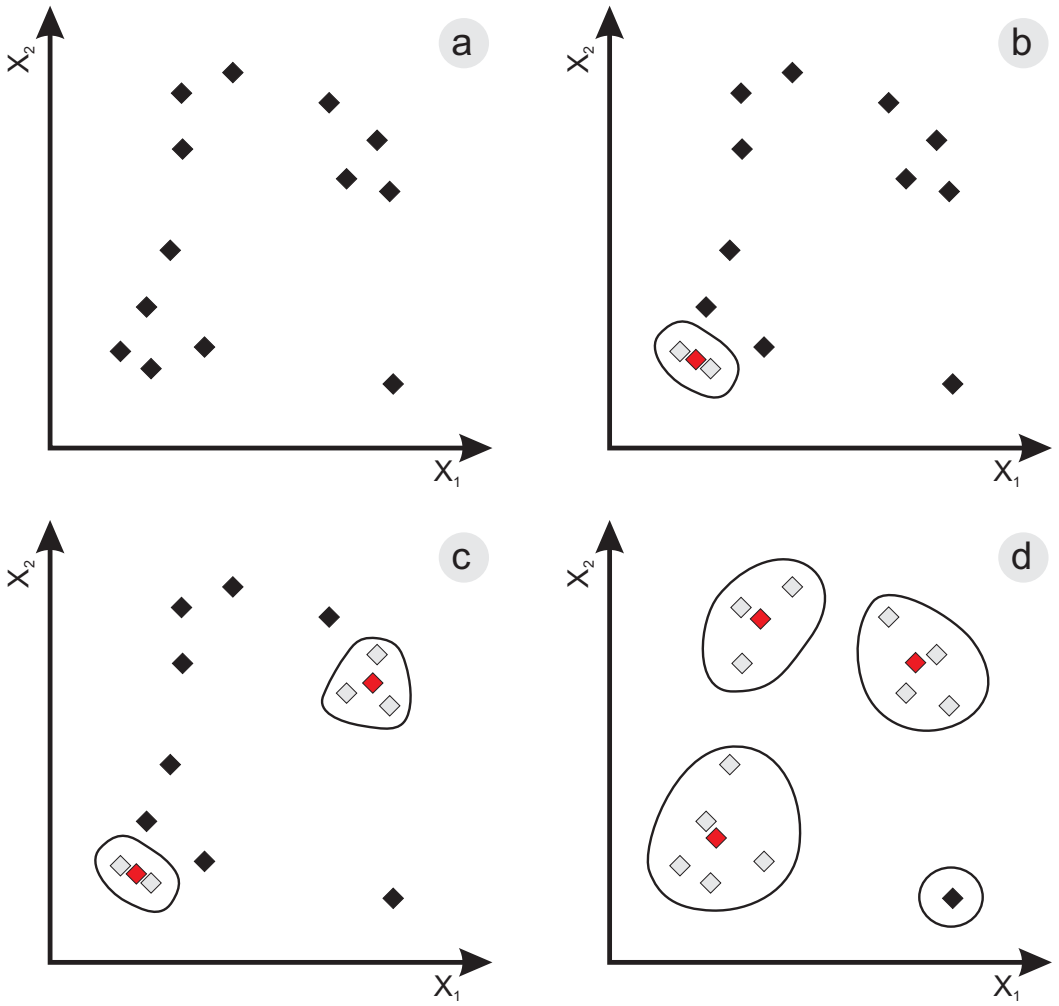
DETCHEM^{MONOLITH}
Selecting representative channels

- Cluster-Agglomeration:
- channels may differ in:
  wall temperature profile
  inlet conditions
- ➔ discrete vectors
- $x=(x_1,x_2,..)$

Clustering of „similair“ vectors

Vectors in one cluster are represented by an averaged vector



S. Tischer, O. Deutschmann. Catalysis Today 105 (2005) 407-413

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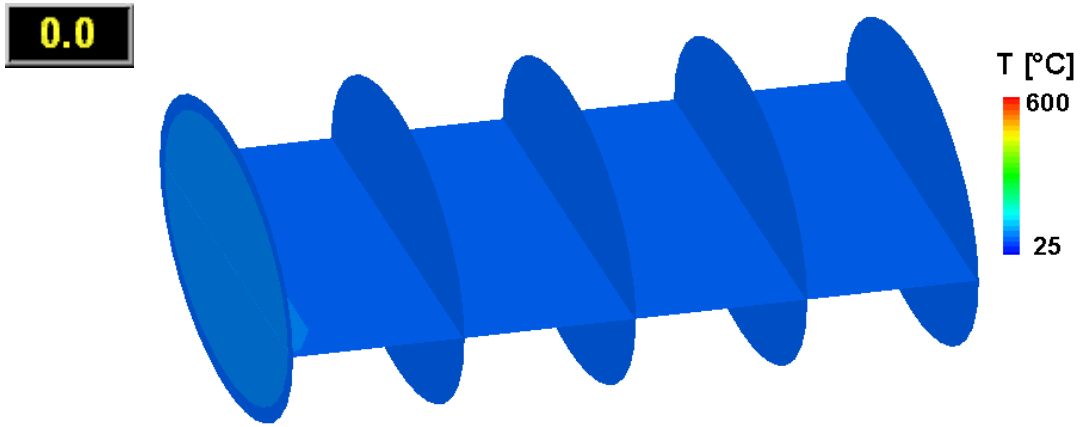
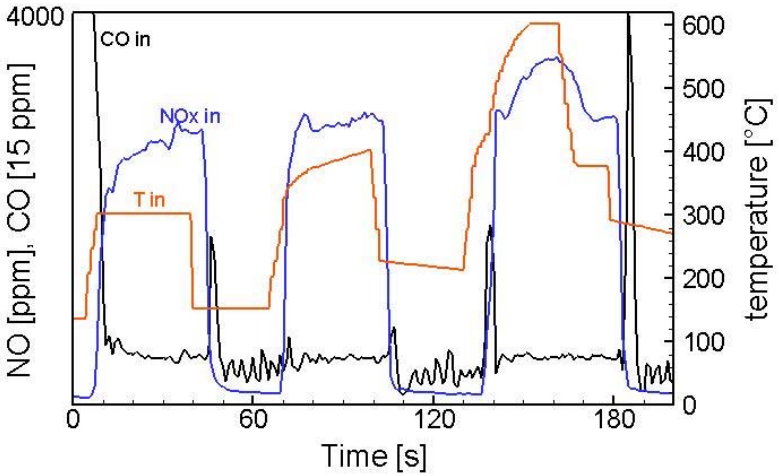
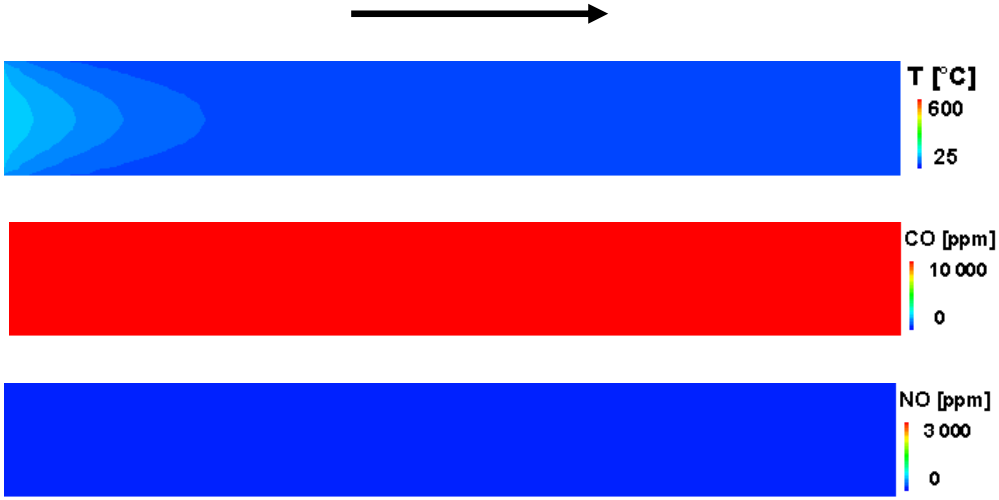
Pollutant reduction in a three-way catalyst during cold start-up: Simulation of a driving cycle







J. Braun, T. Hauber, H. Többen, J. Windmann, P. Zacke, D. Chatterjee, C. Correa, O. Deutschmann, L. Maier, S.Tischer, J. Warnatz, SAE paper 2002-01-0065

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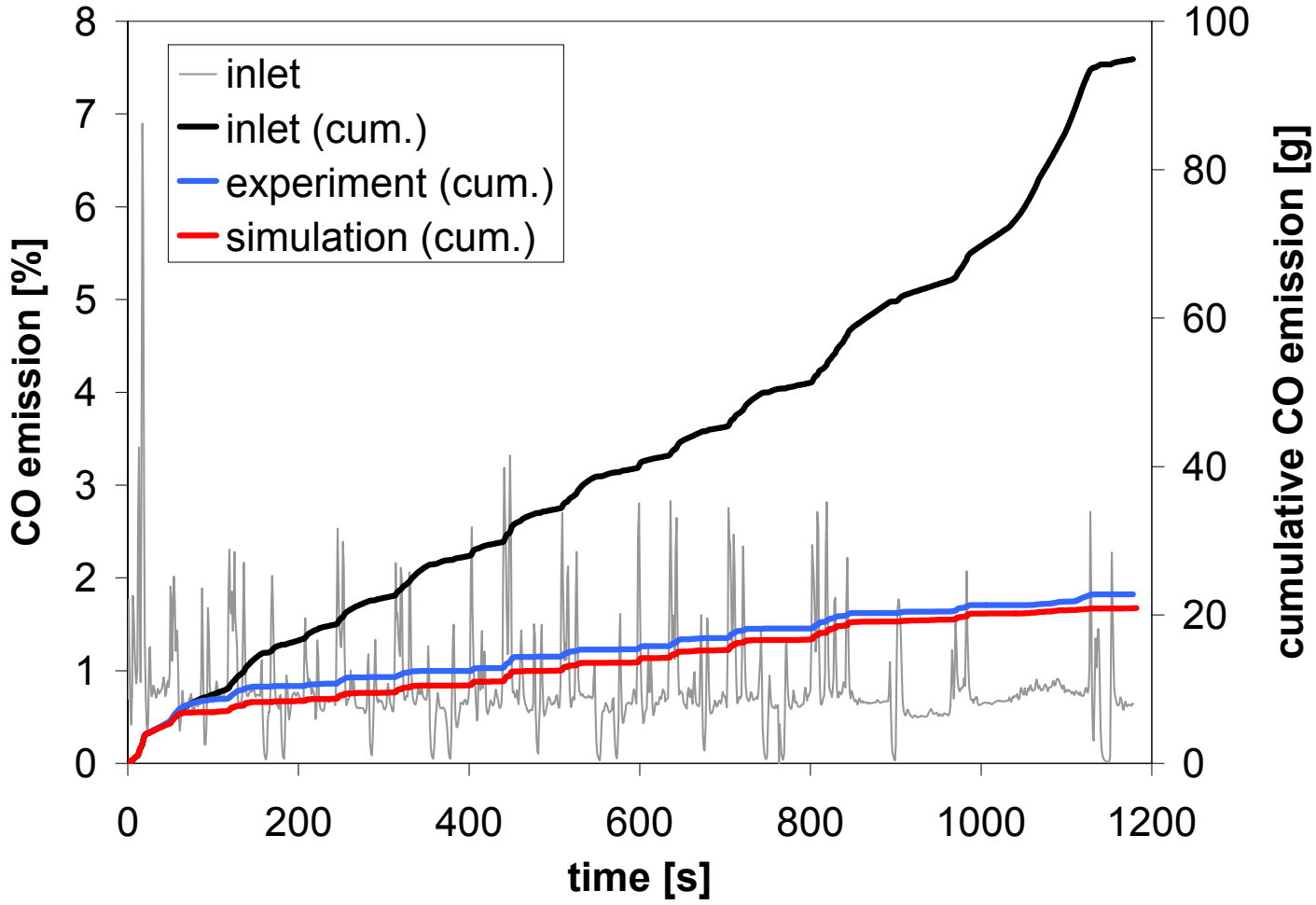
Cumulative CO emission in MEVG cycle: Experiment vs. simulation



Funded by Corning, 2006-2009

Tischer et al. SAE Technical paper 2007-01-1072 2007

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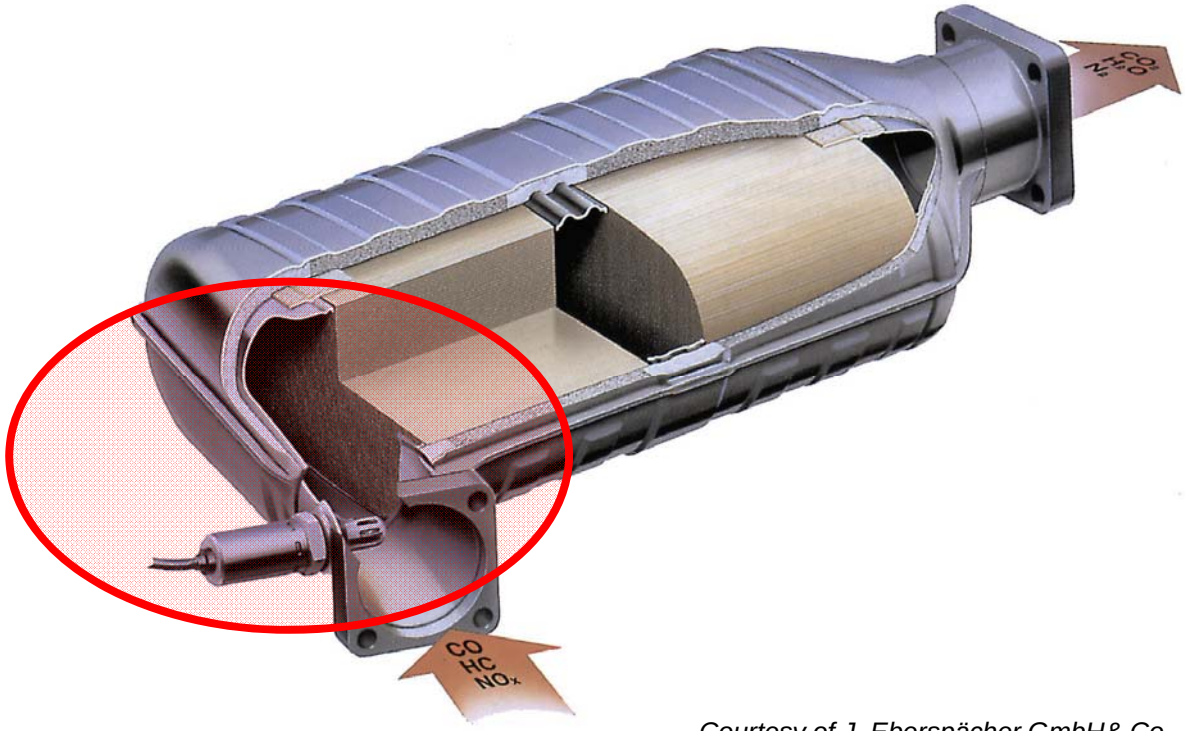
Spatially non-uniform inlet conditions: Non-efficient use of catalyst materials



Courtesy of J. Eberspächer GmbH& Co

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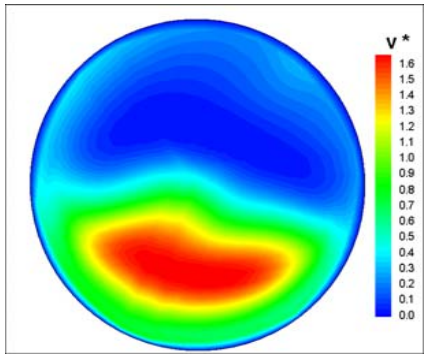
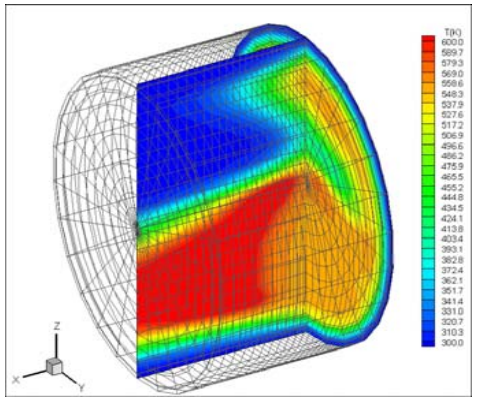
Simulation reveals consequences of design restrictions: Spatial non-uniformity increases pollution emissions

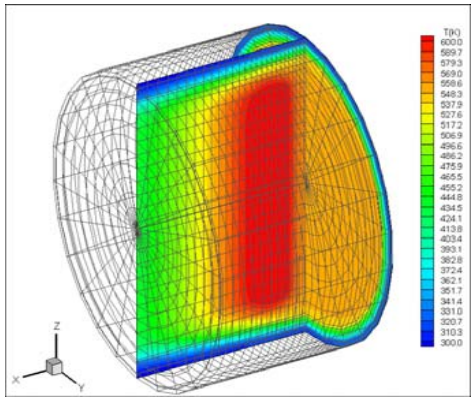
Non-uniform flow distribution at converter front face

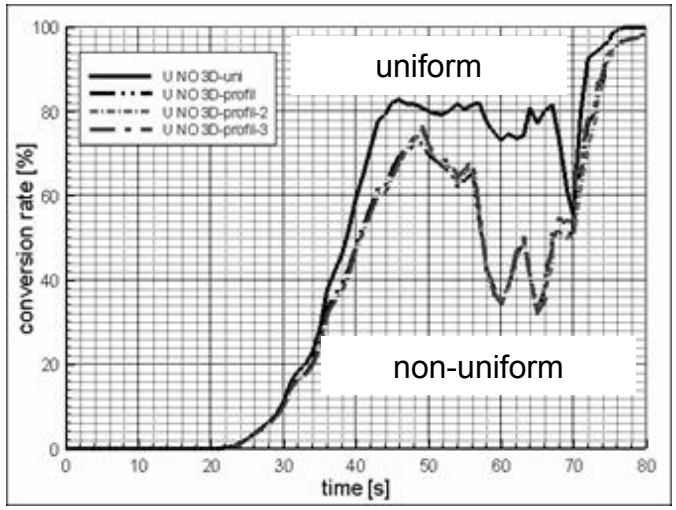


Temperature after 40 s Non-uniform flow distribution



Temperature after 40 s Uniform flow distribution





J. Windmann, P. Zacke, S.Tischer, O. Deutschmann, J. Warnatz, SAE paper 2003-01-0937 (2003)

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Institute for Chemical Technology and Polymer Chemistry

Natural gas → Liquid fuels

Syngas production by partial oxidation over Rh

Collaboration with Conoco Inc., 2002

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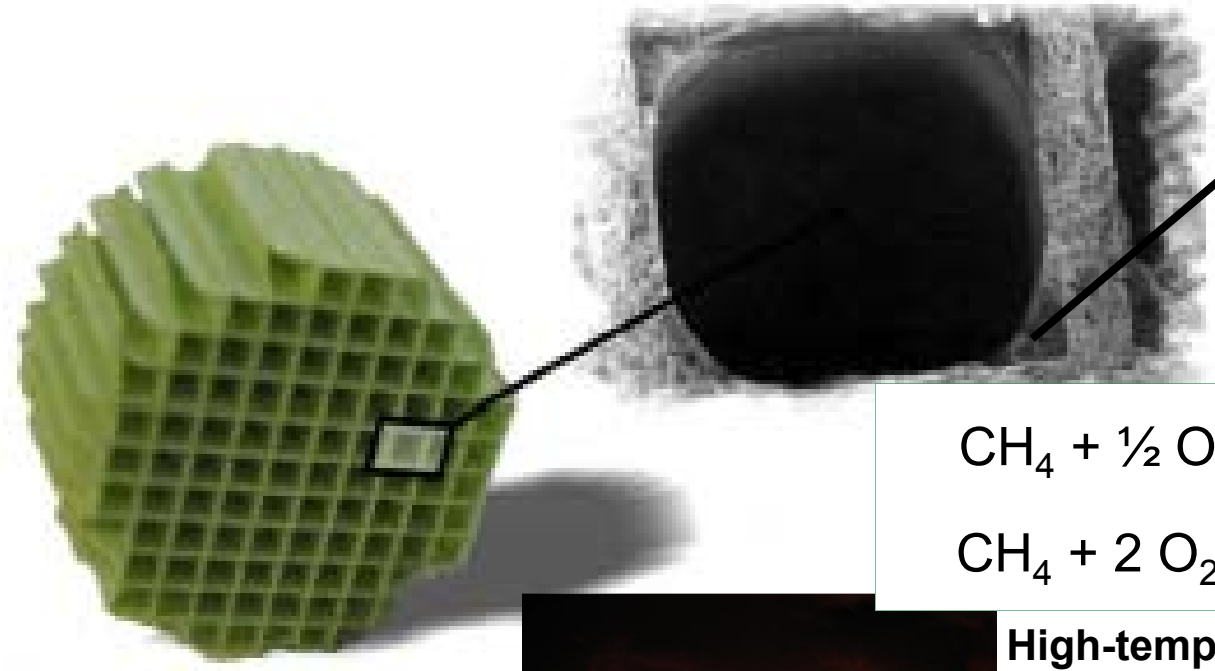
High-temperature catalysis: Compact and autothermal production of hydrogen in few milliseconds



5-50 μm thick oxide layer containing catalyst particles (Pt, Rh) of nm-size

$$CH_4 + ½\ O_2 \longrightarrow CO + 2\ H_2$$

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

High-temperature (1000°C) Rh catalyst converting natural gas into CO and H_2 in less than 5 ms without any additional energy supply

D.A. Hickman, L.D. Schmidt, Science 259 (1993) 343

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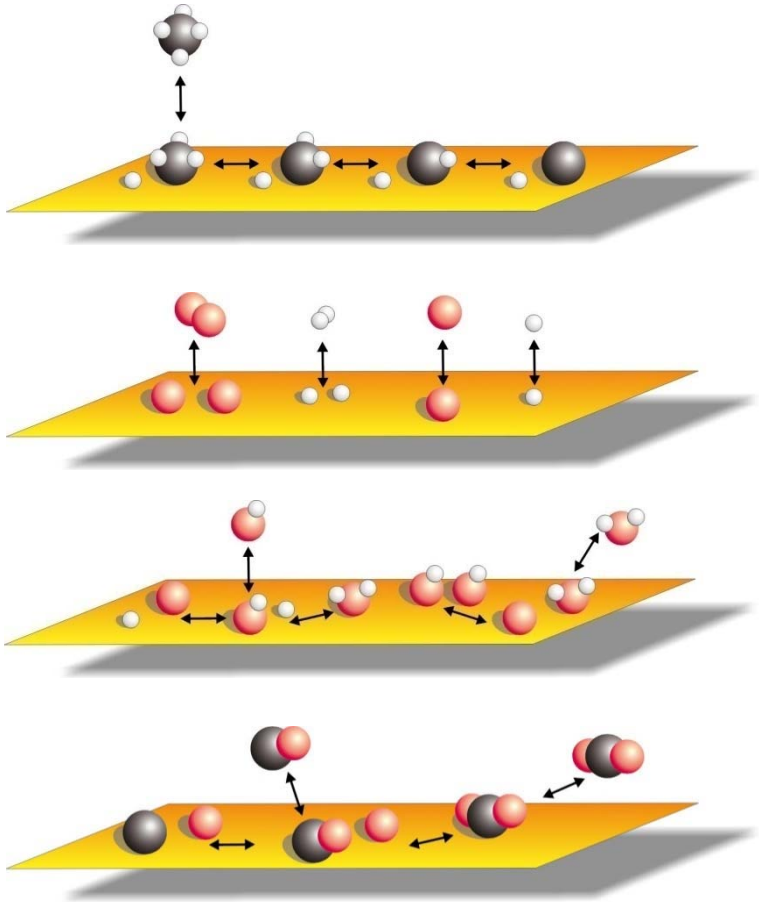
Surface reaction mechanisms: Scheme of partial oxidation of CH_4 over Rh



R. Schwiedernoch, S. Tischer, C. Correa, O. Deutschmann, Chem. Eng. Sci. 58 (2003) 633

Reaction					A/[cm, mol, s]	E_a/[kJ/mol]
H_2	+ Rh(s) + Rh(s)	→ H(s)	+ H(s)		$1.000 \cdot 10^{-02}$	s.c.
O_2	+ Rh(s) + Rh(s)	→ O(s)	+ O(s)		$1.000 \cdot 10^{-02}$	s.c.
CH_4	+ Rh(s)	→ CH_4(s)			$8.000 \cdot 10^{-03}$	s.c.
H_2O	+ Rh(s)	→ H_2O(s)			$1.000 \cdot 10^{-01}$	s.c.
CO_2	+ Rh(s)	→ CO_2(s)			$1.000 \cdot 10^{-05}$	s.c.
CO	+ Rh(s)	→ CO(s)			$5.000 \cdot 10^{-01}$	s.c.
H(s)	+ H(s)	→ Rh(s)	+ Rh(s)	+H_2	$3.000 \cdot 10^{+21}$	77.8
O(s)	+ O(s)	→ Rh(s)	+ Rh(s)	+O_2	$1.300 \cdot 10^{+22}$	355.2-280Θ_O
H_2O(s)		→ H_2O	+ Rh(s)		$3.000 \cdot 10^{+13}$	45.0
CO(s)		→ CO	+ Rh(s)		$1.330 \cdot 10^{+14}$	135.2-15Θ_{CO}
CO_2(s)		→ CO_2	+ Rh(s)		$1.000 \cdot 10^{+13}$	21.7
CH_4(s)		→ CH_4	+ Rh(s)		$1.000 \cdot 10^{+13}$	25.1
H(s)	+ O(s)	→ OH(s)	+ Rh(s)		$5.000 \cdot 10^{+22}$	83.7
OH(s)	+ Rh(s)	→ H(s)	+ O(s)		$3.000 \cdot 10^{+20}$	37.7
H(s)	+ OH(s)	→ H_2O(s)	+ Rh(s)		$3.000 \cdot 10^{+20}$	33.5
H_2O(s)	+ Rh(s)	→ H(s)	+ OH(s)		$5.000 \cdot 10^{+22}$	104.7
OH(s)	+ OH(s)	→ H_2O(s)	+ O(s)		$3.000 \cdot 10^{+21}$	100.8
H_2O(s)	+ O(s)	→ OH(s)	+ OH(s)		$3.000 \cdot 10^{+21}$	171.8
C(s)	+ O(s)	→ CO(s)	+ Rh(s)		$3.000 \cdot 10^{+22}$	97.9
CO(s)	+ Rh(s)	→ C(s)	+ O(s)		$2.500 \cdot 10^{+21}$	169.0
CO(s)	+ O(s)	→ CO_2(s)	+Rh(s)		$1.400 \cdot 10^{+20}$	121.6
CO_2(s)	+ Rh(s)	→ CO(s)	+ O(s)		$3.000 \cdot 10^{+21}$	115.3
CH_4(s)	+ Rh(s)	→ CH_3(s)	+ H(s)		$3.700 \cdot 10^{+21}$	61.0
CH_3(s)	+ H(s)	→ CH_4(s)	+ Rh(s)		$3.700 \cdot 10^{+21}$	51.0
CH_3(s)	+ Rh(s)	→ CH_2(s)	+ H(s)		$3.700 \cdot 10^{+24}$	103.0
CH_2(s)	+ H(s)	→ CH_3(s)	+ Rh(s)		$3.700 \cdot 10^{+21}$	44.0
CH_2(s)	+ Rh(s)	→ CH(s)	+ H(s)		$3.700 \cdot 10^{+24}$	100.0
CH(s)	+ H(s)	→ CH_2(s)	+ Rh(s)		$3.700 \cdot 10^{+21}$	68.0
CH(s)	+ Rh(s)	→ C(s)	+ H(s)		$3.700 \cdot 10^{+21}$	21.0
C(s)	+ H(s)	→ CH(s)	+ Rh(s)		$3.700 \cdot 10^{+21}$	172.0
CH_4(s)	+ O(s)	→ CH_3(s)	+ OH(s)		$3.700 \cdot 10^{+21}$	20.0
CH_3(s)	+ OH(s)	→ CH_4(s)	+ O(s)		$3.700 \cdot 10^{+21}$	24.3
CH_3(s)	+ O(s)	→ CH_2(s)	+ OH(s)		$3.700 \cdot 10^{+24}$	120.3
CH_2(s)	+ OH(s)	→ CH_3(s)	+ O(s)		$3.700 \cdot 10^{+21}$	15.1
CH_2(s)	+ O(s)	→ CH(s)	+ OH(s)		$3.700 \cdot 10^{+24}$	158.4
CH(s)	+ OH(s)	→ CH_2(s)	+ O(s)		$3.700 \cdot 10^{+21}$	36.8
CH(s)	+ O(s)	→ C(s)	+ OH(s)		$3.700 \cdot 10^{+21}$	30.1
C(s)	+ OH(s)	→ CH(s)	+ O(s)		$3.700 \cdot 10^{+21}$	145.5

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2\ H_2$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

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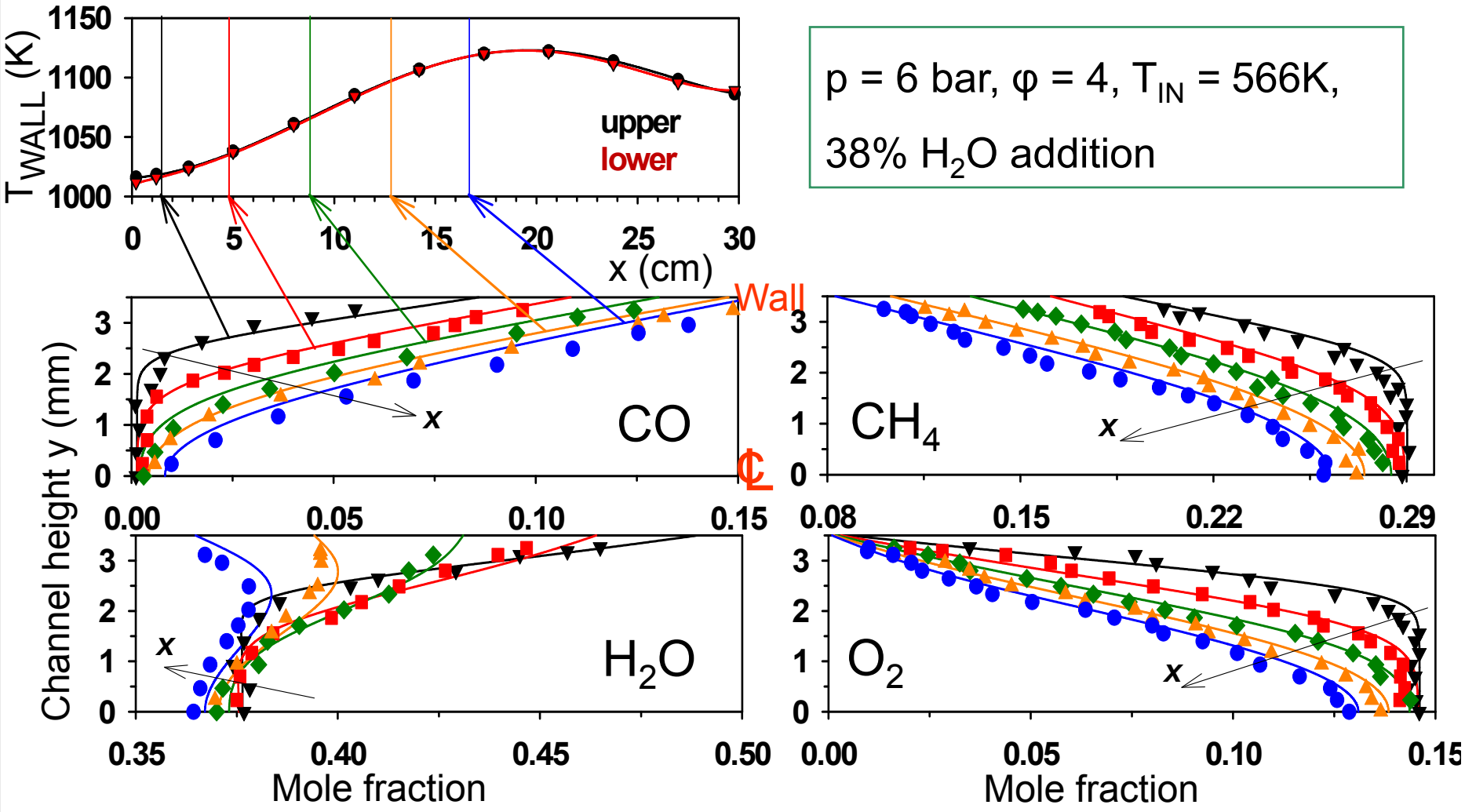
CPOX of CH_4 on Rh in single channel at steady state: 2d Raman profiles vs. computation (Mantzaras et al.)



p = 6 bar, φ = 4, T_{IN} = 566K,

38% H_2O addition

A. Schneider, J. Mantzaras, P. Jansohn et al. Proc. Comb. Inst. 31 (2007)

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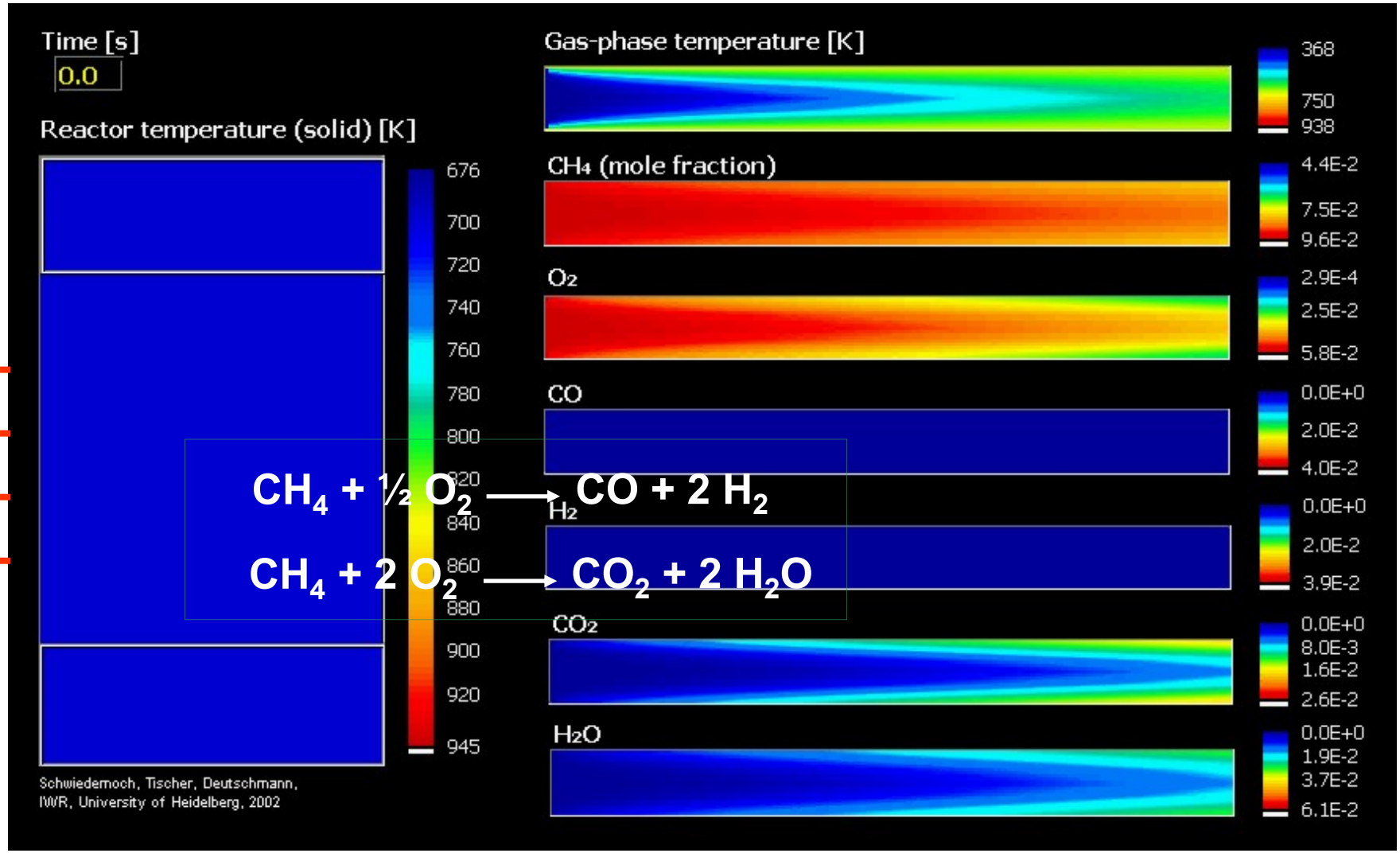
Partial oxidation of CH_4 on Rh at 1 bar: Computed temperature and concentration profiles during light-off



R. Schwiedernoch, S. Tischer, C. Correa, O. Deutschmann, Chem. Eng. Sci., 58 (2003) 633-642

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More efficient technology for auxiliary power supply in automobile vehicles needed

Idling long-haul trucks consumes 1 billion gallons of diesel fuel annually in the USA
→11 million tons CO_2, 180,000 tons NO_x, 5000 tons particulates!

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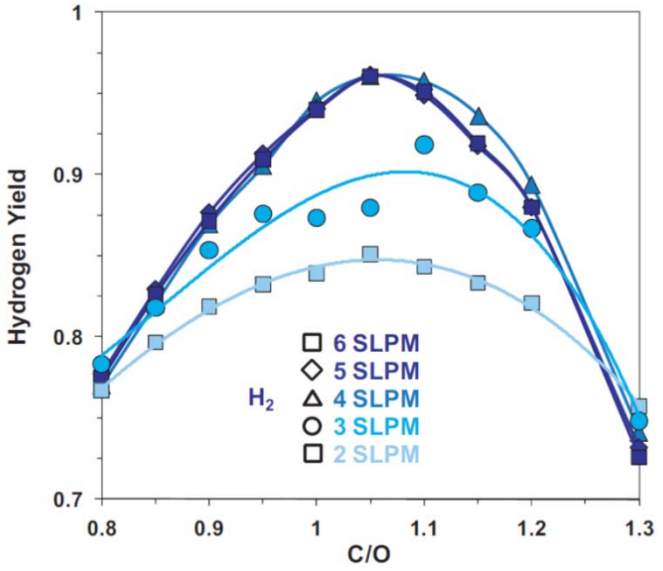
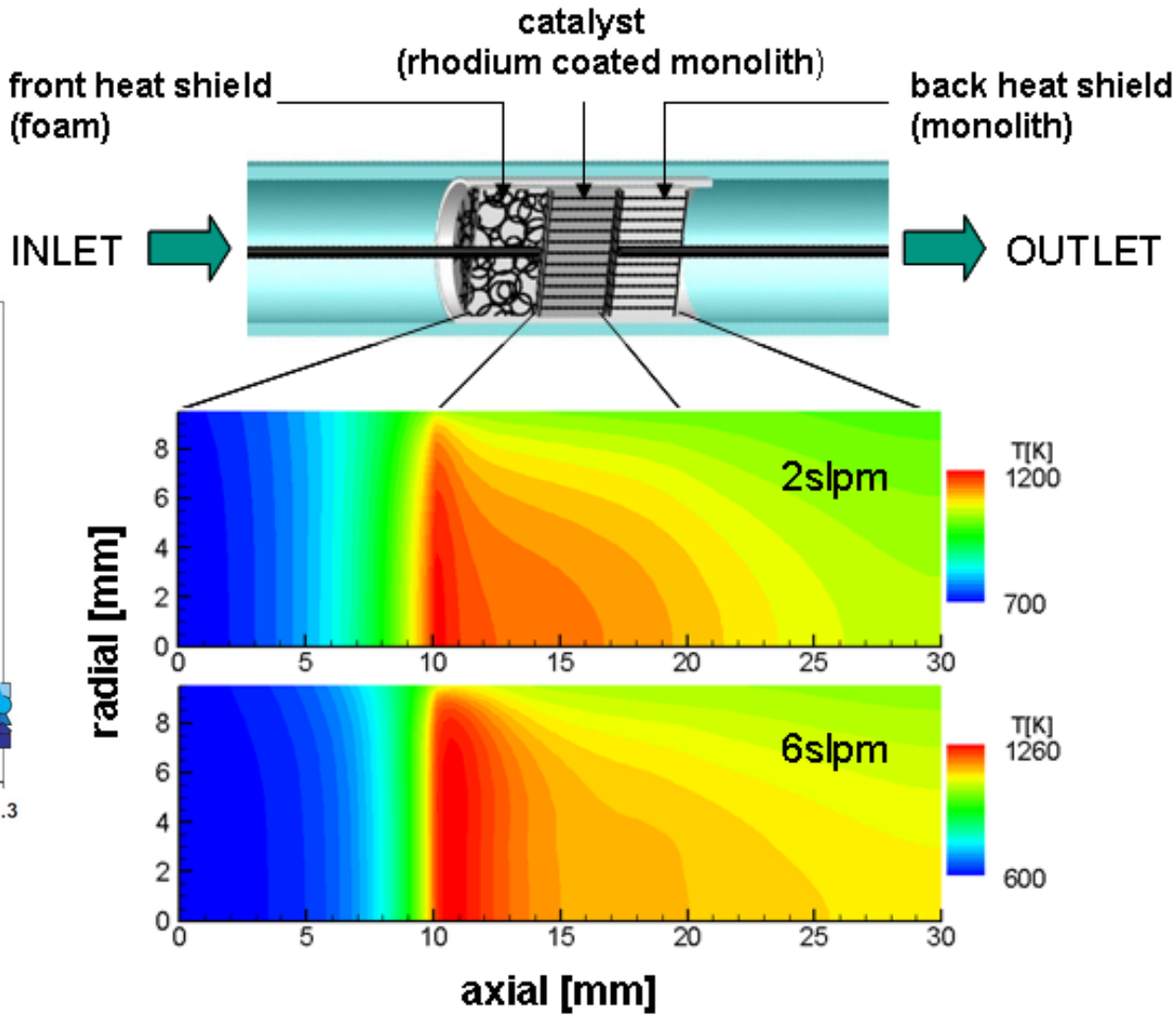
CPOX of i-octane: Impact of flow rate on hydrogen yield
Computed temperature distribution in the reactor



M. Hartmann, L. Maier, O. Deutschmann. Appl. Catalysis A: General 391 (2011) 144.



L. Maier, M. Hartmann, O. Deutschmann, Combust. Flame 158 (2011) 796–808.

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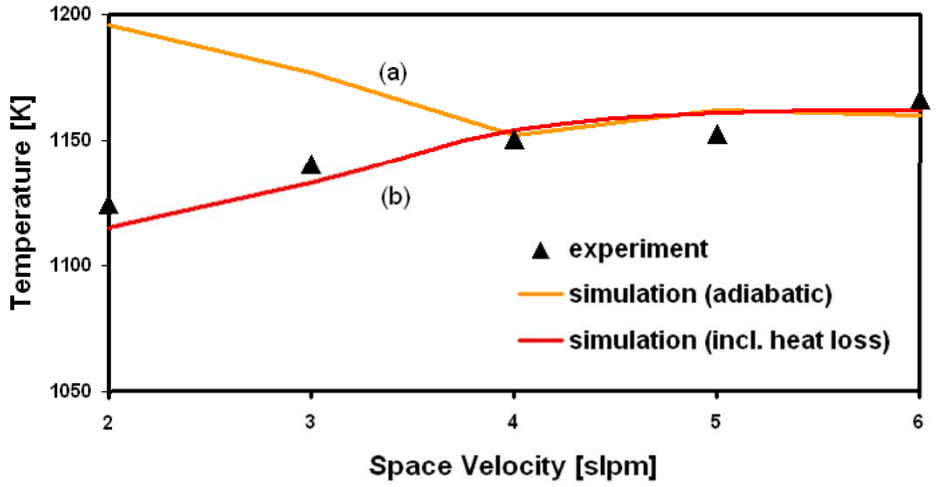
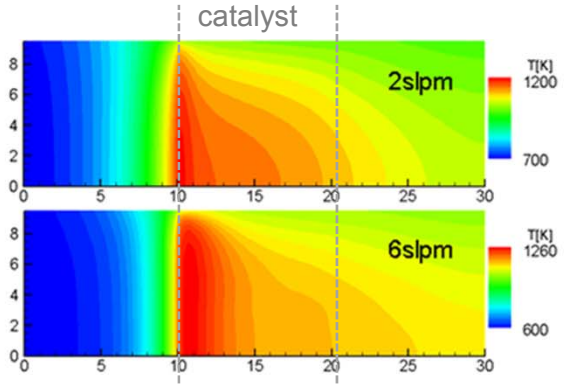
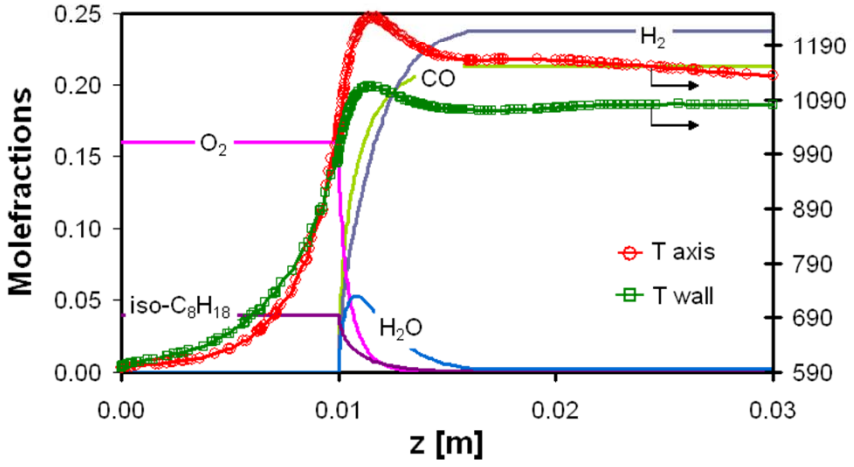
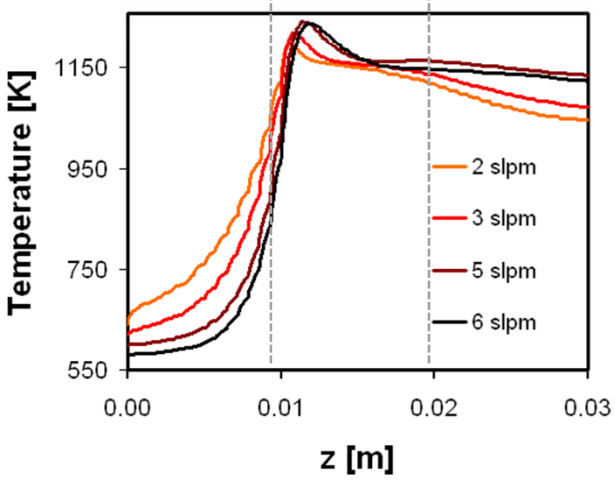
CPOX of HC: Counter-intuitive increase of yields with decreasing residence time understood





(a) (b)





L. Maier, M. Hartmann, O. Deutschmann, Combust. Flame 158 (2011) 796–808.

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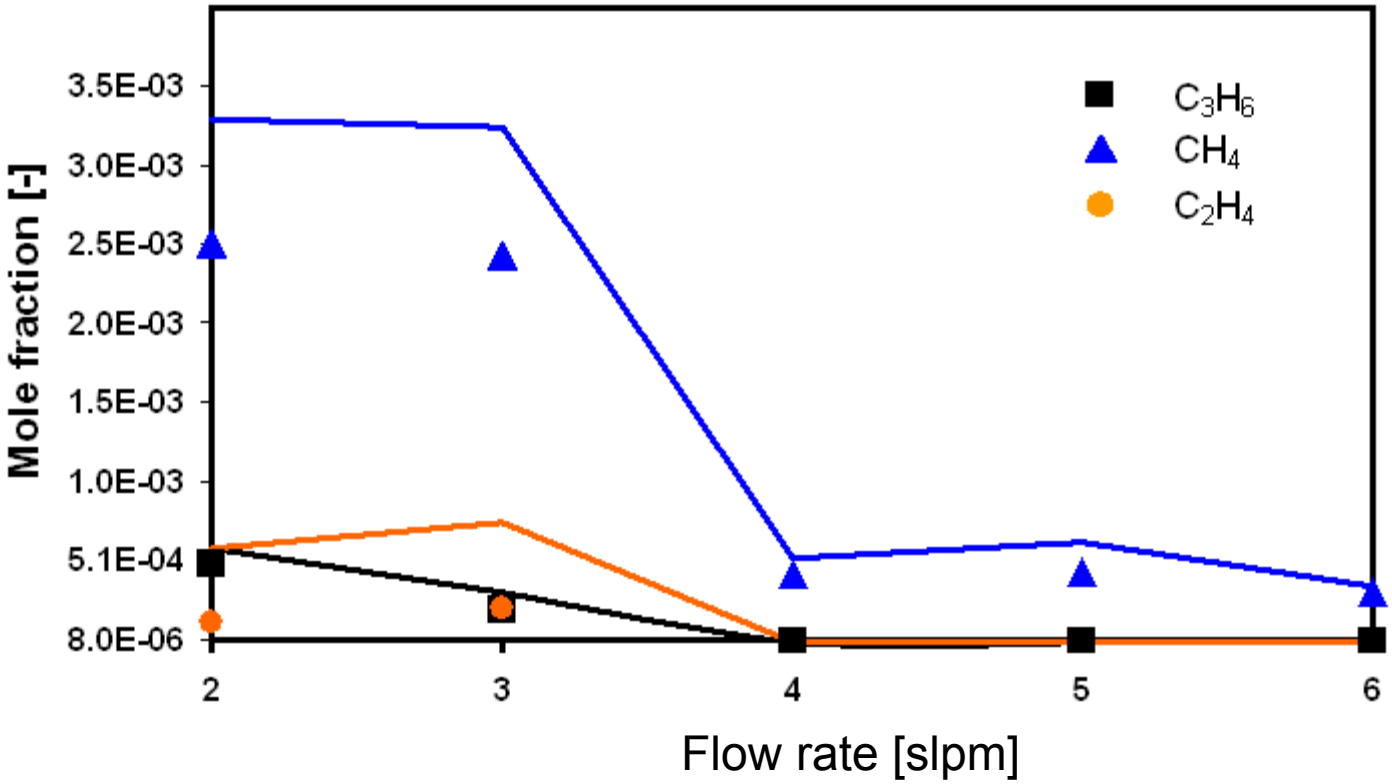
CPOX of iso-octane:
Coke precursor formation also depends on flow rate

Modeling (lines) versus experiment (symbols)



C/O = 1.0

L. Maier, M. Hartmann, O. Deutschmann, Combust. Flame 158 (2011) 796–808.

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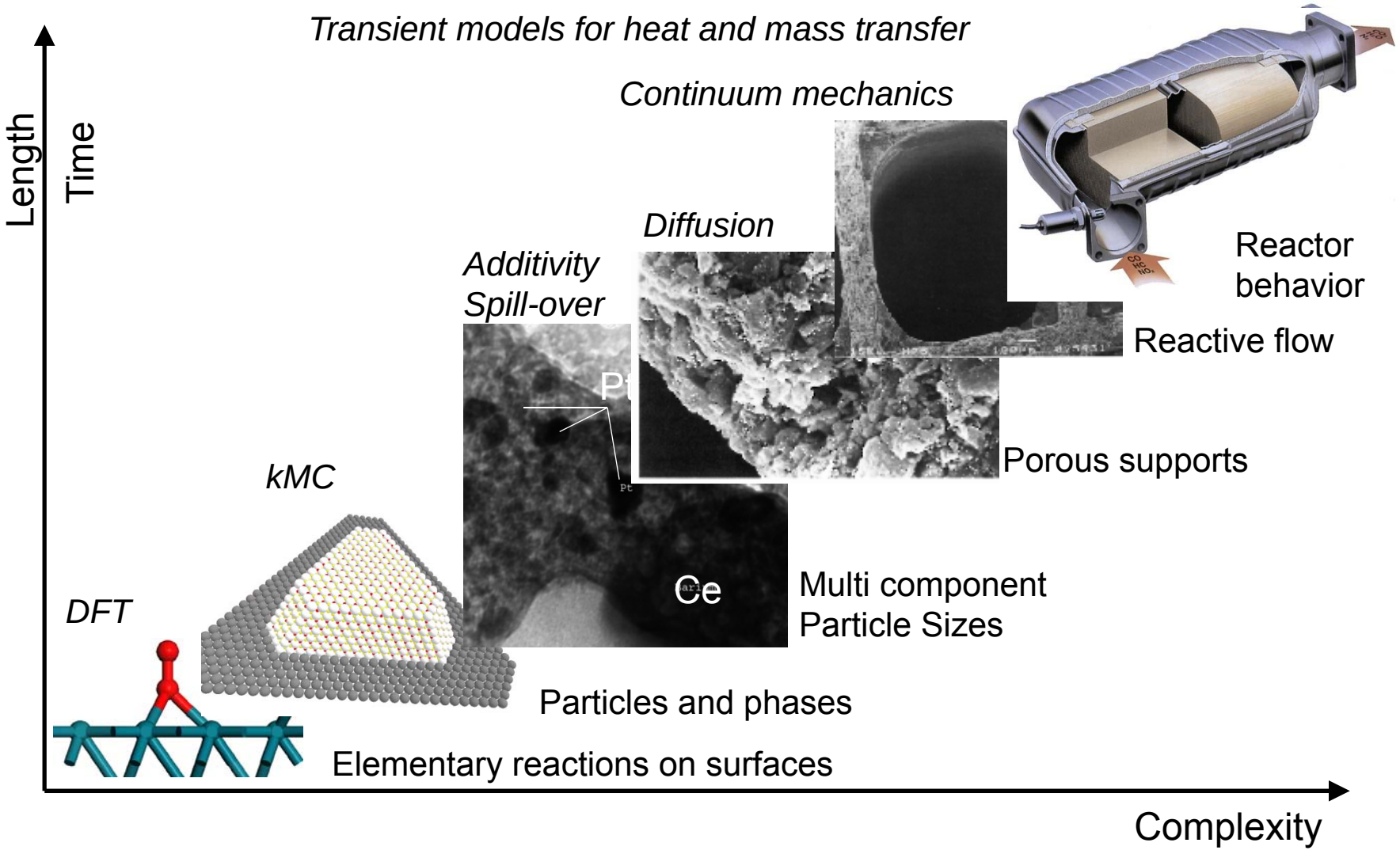
Simulation of catalytic reactors by multi-scale modeling: Information flux over the time and length scales



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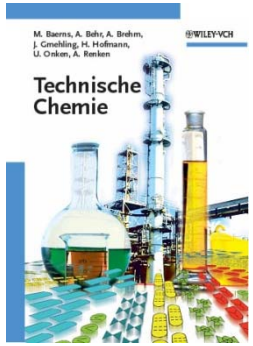

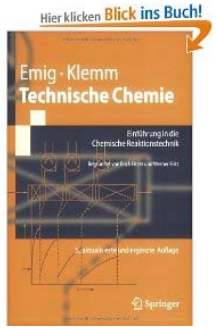

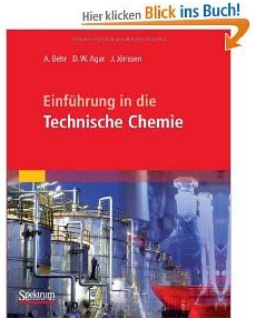

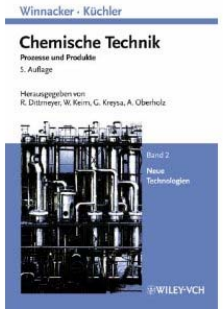

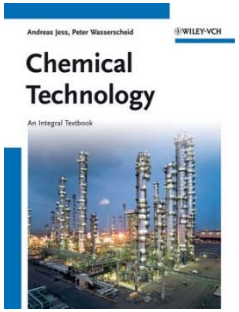

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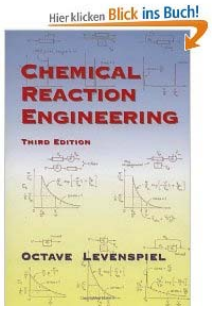

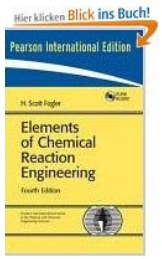

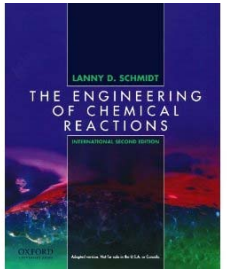

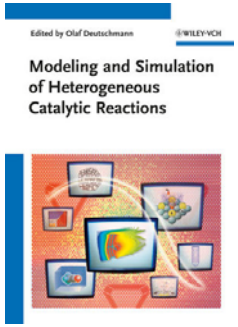

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